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Formation and Properties of Medium and High Molecular Weight Compounds of Elements of Groups 3, 4, and 5[**]

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The differences between compounds of carbon and of silicon are discussed, and the role of silicon as a fundamental structural component in inanimate nature is described. Starting with silicic acid and silicates, the structure and properties of the silicones and of compounds having Si–C–Si skeletons are described. The possibilities for the formation of high molecular-weight compounds between elements of Groups 3 and 5 of the periodic system are considered, with particular reference to boron nitride and to aluminum-phosphorus compounds.

1. Introduction

High molecular-weight substances have a special significance in nature. They are characterized by the linking together of numerous building components to form large composite structures. Their properties are very largely determined by the forces that hold the building units together. These forces may be purely electrostatic (as in ionic crystals) or metallic bonding forces (as in metal crystals and intermetallic compounds) or directional covalent bonds. It is necessary in many cases to assume that different types of bonds are involved, each type making a different contribution. These principles are found in the structural substances in inanimate nature, as well as in biologically important high molecular-weight substances such as proteins and polysaccharides. The structures of the latter are largely based on the ability of the carbon atom to form C–C bonds.

2. Differences Between Compounds of Carbon and of Silicon

A glance under the thin covering of the animate world shows that the earth's crust is built up from structural systems in which the element silicon, with its strong tendency to form the Si–O–Si grouping, plays a key part. Silicon is situated directly under carbon in the periodic table. In order to gain an insight into the diverse functions of these elements in nature, and so to establish general principles for the structure of inorganic high polymers, it seems advisable first to inquire into the reasons for the differences in the behavior of carbon and silicon atoms.

The ground state electronic configuration of carbon is $1s^2\,2s^2\,2p^2$, while that of silicon is $1s^2\,2s^2\,2p^6\,3s^2\,3p^2$. Unlike the C atom, the Si atom has a free 3d level, and is therefore capable of forming coordination compounds and of utilizing lone pairs of electrons of attached atoms to strengthen the bonding. While carbon can achieve stronger bonding by the formation of multiple bonds (π bonds), which at the same time satisfy the requirements for the polymerization and polyaddition reactions that are so important in carbon chemistry, silicon forms no corresponding multiple bond systems. The electronegativity of silicon is lower than that of carbon (Si 1.8; C 2.5), and the polar components in silicon compounds are consequently greater than in the corresponding carbon compounds. This and the ability of silicon to form coordination compounds largely determine the chemical behavior of this element. It is therefore understandable why CCl_4 is resistant to water, whereas $SiCl_4$ is very readily hydrolyzed with formation of the Si–O–Si grouping. Finally, the bond energies of compounds of silicon and of carbon differ appreciably in some cases (Si–Si 53, C–C 83, Si–O 108, C–O 85, Si–H 75, C–H 99 kcal/mole) [1].

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[**] Lecture at the Conference of the Gesellschaft Deutscher Naturforscher und Ärzte e.V. in Vienna on September 27th, 1966.

[1] *T. Cottrell*: The Strength of Chemical Bonds. Butterworths, London, 1958, 2nd. Edit., p. 270–280.

The differences between silicon and carbon are particularly obvious in their oxides. CO_2 is a molecular compound, and free CO_2 molecules exist in the gaseous state. SiO_2, on the other hand, is a high molecular-weight substance, the formula of which merely indicates its stoichiometric composition. The Si atom is situated at the center of a tetrahedron with the oxygen atoms at the corners, and the various tetrahedra are joined to one another by a common oxygen atom.

3. Structure of Silicic Acid and Silicates

The structure of the silicates is also based on SiO_4 tetrahedra. The simplest silicic acid (and that with the highest oxygen content) is orthosilicic acid $Si(OH)_4$, which tends to lose water with formation of the Si–O–Si grouping (Fig. 1).

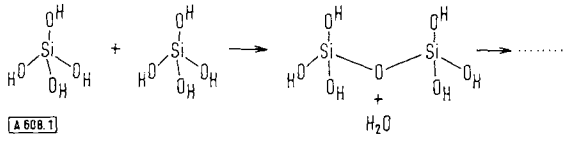


Fig. 1. Condensation of orthosilicic acid.

Isolated SiO_4^{4-} tetrahedra are found in the island structures, *e.g.* in olivine (Mg_2SiO_4). The nature of the linkage determines the type of silicate (Fig. 2).

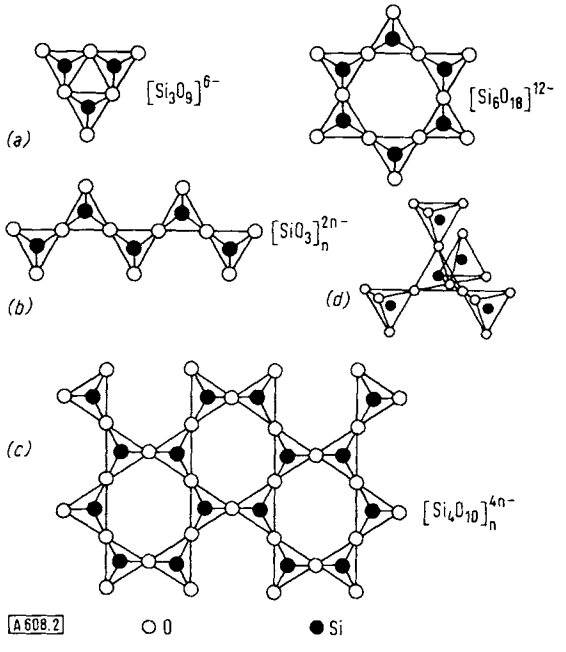


Fig. 2. Structures of the silicates:
(a) Ring structure $[Si_3O_9]^{6-}$; $[Si_6O_{18}]^{12-}$; (b) chain structure $[SiO_3]_n^{2n-}$; (c) layer structure $[Si_4O_{10}]_n^{4n-}$; (d) three-dimensional network structure. (Above each Si atom there is an O atom, which is not shown).

Nature gains an important variation in this structural principle by the replacement of the silicon ions by aluminum ions, since the radii of these two ions are very similar (Si^{4+} 0.41 Å; Al^{3+} 0.5 Å). The aluminum ion then assumes the 4-coordination of silicon. This results in an increase in the negative charge of the anionic skeleton by one unit per aluminum ion introduced. To compensate for these negative charges, cations are built into the open aluminosilicate anions, as is found *e.g.* in muscovite (Fig. 3).

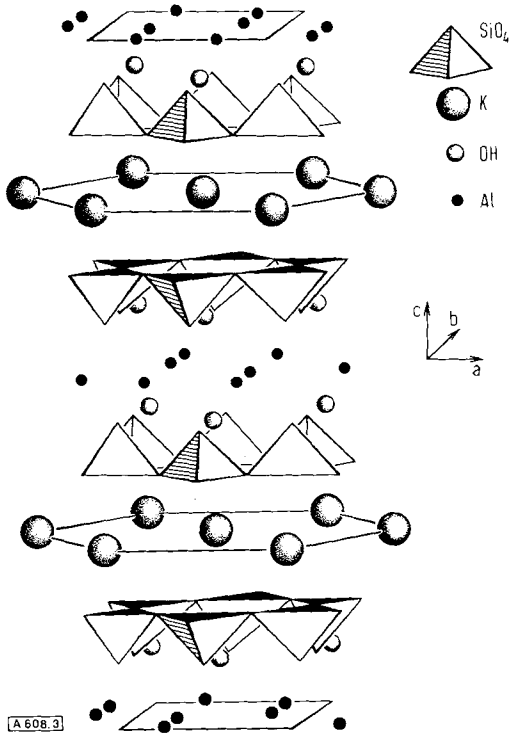


Fig. 3. Structure of muscovite ($KAl_2(OH)_2AlSi_3O_{10}$).

A particularly large group of natural aluminosilicates exists in three-dimensional lattice structures. This group includes the feldspars. A typical member is orthoclase $K(AlSi_3O_8)$.

The polymeric substances discussed so far are crystalline. The structure of the crystal is determined by the periodic arrangement of the structural units in the lattice. By breakdown of this regularity, it is possible to obtain glass-like substances. Figure 4 shows the arrangement of the SiO_4 tetrahedra in quartz glass (cf. the arrangement in crystalline quartz, Fig. 2c).

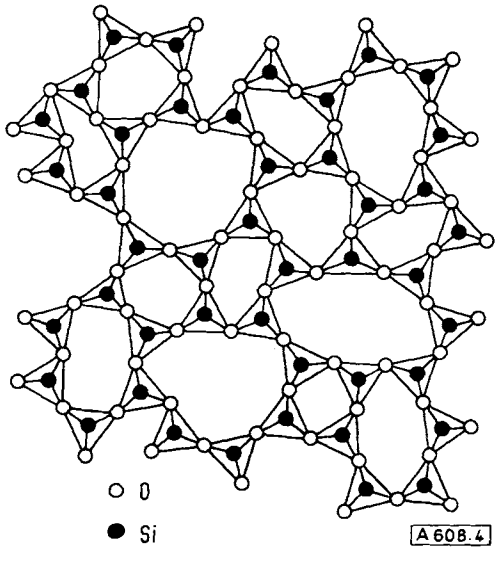


Fig. 4. Arrangement of the SiO_4 tetrahedra in quartz glass. (Above each Si atom there is an O atom, which is not shown.)

The vitreous state results from irregular linkages of the tetrahedra arising in the melt, which are retained on cooling because of its viscosity. Glasses are formed, not only by SiO_2, but also by B_2O_3, condensed phosphates, and oxides of arsenic, antimony, selenium *etc.*; many organic high polymers also occur as glasses. The vitreous state is unstable in relation to the crystalline state. In alkali metal and alkaline earth metal glasses, metal oxides are incorporated into the tetrahedral network (eq. (1)).

$$\text{Si–O–Si} + \text{CaO} \longrightarrow \text{Si–O Ca O–Si} \qquad (1)$$

This gives rise to points of fission, with the result that the softening temperature and the viscosity of the glass are lowered[2]. The more mobile the network becomes as a result of points of fission, the more readily do the components arrange themselves into the crystalline lattice. This process, which can be observed in all silicate glasses, is known as devitrification.

4. Structure of Silicones

The strength of the Si–O–Si linkage is responsible for the high stability of silicates and silicate glasses. However, the usefulness of these substances is limited by the fact that they are brittle and are fairly readily attacked by alkalis. If we imagine some of the oxygen atoms of the SiO_4 tetrahedra in a quartz glass of this type to be replaced by organic groups (*e.g.* CH_3), which can no longer link adjacent tetrahedra, certain units (*e.g.* long chains having an Si–O–Si skeleton) can be isolated from the SiO_2 glass. The resulting derivatives of the silicates still possess some of the characteristics of the silicate structure, but also have properties attributable to the $\equiv Si–CH_3$ groups. This relationship is illustrated in Figure 5.

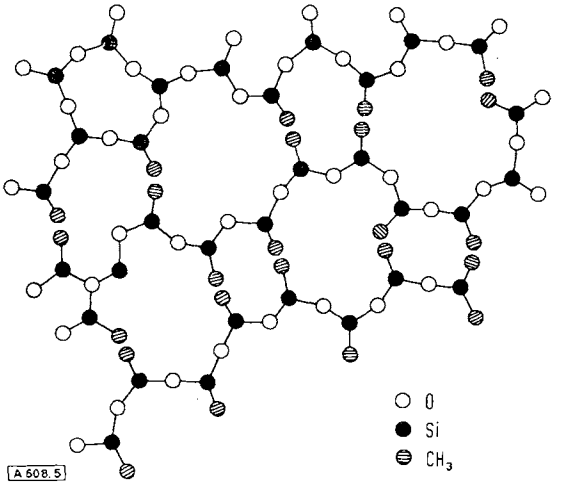


Fig. 5. Derivation of the structure of a silicone from the structure of a silica glass. (Above each Si atom there is an O atom, which is not shown.)

Compounds of this type are known as organosiloxanes or silicones[3,4]. This group of compounds cannot be obtained in the manner described, nor do they occur in nature. To obtain silicones, silicon must first be prepared by reduction of SiO_2 and then converted into alkylchlorosilanes. These can be prepared by reaction of $SiCl_4$ with methylmagnesium chloride, or preferably by "direct" synthesis. This involves the reaction of elementary silicon with methyl chloride, a reaction whose occurrence and course are strongly dependent on the catalyst. The reaction leads to the formation of a mixture of silicon halides, the most valuable of which is $(CH_3)_2SiCl_2$ (eq. (2)).

$$CH_3Cl + Si \xrightarrow[300\,^\circ C]{\text{cat.}} \begin{matrix}(CH_3)_2SiCl_2,\ CH_3SiCl_3,\ (CH_3)_3SiCl,\ SiCl_4\\ HSiCl_3,\ CH_3SiHCl_2,\ (CH_3)_2SiHCl,\ Si(CH_3)_4\end{matrix} \qquad (2)$$

This reaction, which is used on the industrial scale (Rochow synthesis), was observed independently and at about the same time[4] by *R. Müller* and *Rochow*.

As was previously mentioned, the SiCl grouping is readily hydrolyzed, the initial reaction products being silanols. Like orthosilicic acid, these compounds have a strong tendency to lose water with formation of the Si–O–Si grouping (eq. (3)), the resulting products, *e.g.* in the case of $(CH_3)_2SiCl_2$, being long chains.

$$\begin{matrix}CH_3\\ |\\ -O-Si-O-\\ |\\ CH_3\end{matrix}\left[\begin{matrix}CH_3\\ |\\ Si-O\\ |\\ CH_3\end{matrix}\right]_n\begin{matrix}CH_3\\ |\\ -Si-\\ |\\ CH_3\end{matrix} \qquad (3)$$

$(CH_3)_3SiCl$ can form only one such linkage, whereas CH_3SiCl_3 can form three. It is thus possible to obtain linear and crosslinked three-dimensional structures, and the physical properties of the condensation products can be widely varied in this way.

The linear silicones are oils or, where the chains are very long, rubbery substances. The highly crosslinked substances, *i.e.* the silicone resins, become increasingly like silica glass with increasing crosslinking. The silicones are now popular synthetic materials, since they combine the properties of the Si–O–Si bond of the silicates with typical characteristics of organic groups. The polar component of the Si–O–Si linkage is about 50%. The bonding is strengthened by π components as a result of interaction of the electrons from the oxygen with the 3d orbitals of the silicon. The Si–C bond in the $SiCH_3$ group is about 88% covalent and 12% polar. These facts explain the high thermal stability, the hydrophobic properties, and the solubility behavior of the silicones.

With silicone chemistry as a basis, it is possible to construct skeletons in which Si–O–Si groups are replaced *e.g.* by Si–O–Al, Si–O–Sn, Si–O–Ti, and Si–O–P[5].

5. Structure of Carbosilanes

The CH_2 group is isoelectronic with the O atom. Compounds in which the silicon atoms are linked by a single carbon atom (by a CH_2 group in chains or simple rings), which are known as carbosilanes, are mainly formed by free-radical reactions on thermal

[2] *A. Dietzl*, Naturwissenschaften *29*, 537 (1941); *31*, 22, 110 (1943); Z. Elektrochem. angew. physik. Chem. *48*, 9 (1942).

[3] *W. Noll*: Chemie und Technologie der Silicone. Verlag Chemie, Weinheim/Bergstr. 1960, p. 193.

[4] *E. G. Rochow*: Einführung in die Chemie der Silicone. Verlag Chemie, Weinheim/Bergstr. 1956.

[5] *K. A. Adrianov*: Metal Organic Polymers. Interscience, New York 1965.

cleavage of tetramethylsilane and the methylchlorosilanes [6]. The thermal decomposition of $Si(CH_3)_4$ and of the methylchlorosilanes in the gas phase yields mixtures of oily, tarry, and even crystalline compounds, whose molecular skeletons consist mainly of alternate silicon and carbon atoms. Cyclic products are formed preferentially [7]. Figure 6 shows some of the low molecular-weight compounds of this class.

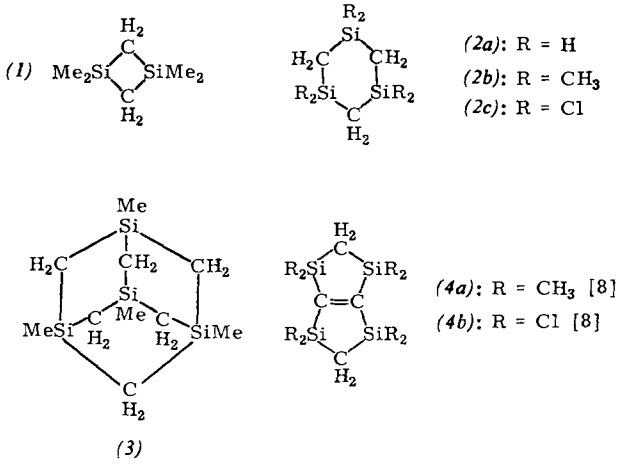


Fig. 6. Some low molecular-weight carbosilanes obtained by pyrolysis of $Si(CH_3)_4$ and the methylchlorosilanes. The compounds containing *SiH* groups were prepared from compounds containing SiCl groups by reduction with $LiAlH_4$. (Me = methyl.)

The formation of carbosilanes is due to the primary cleavage of the silicon-carbon bond in $Si(CH_3)_4$ at about 700 °C, which yields methyl and silyl radicals (eq. (4)). The methyl radicals react further in accordance with eq. (5). Combination of the radicals leads to the

$$(CH_3)_3Si{-}CH_3 \rightarrow (CH_3)_3Si^{\bullet} + CH_3^{\bullet} \quad (4)$$

$$(CH_3)_3Si{-}CH_3 + CH_3^{\bullet} \rightarrow (CH_3)_3Si{-}CH_2^{\bullet} + CH_4 \quad (5)$$

simplest member of the class $(CH_3)_3Si{-}CH_2{-}Si(CH_3)_3$. The structure of the medium and high molecular-weight substances, which have not yet been very extensively studied, is based on the same principle. These substances are particularly important since when heated they form compounds having still higher molecular weights, with no separation of silicon or carbon. An extremely wide variety of high molecular-weight compounds are formed, ranging from the simple $Si{-}CH_2{-}Si$ chain to silicon carbide.

The properties of the carbosilanes are very largely determined by the character of the Si–C bond. Accordingly, the fully methylated compounds are very inert, and are solvolyzed only under extreme conditions. The compounds containing SiCl bonds can enter into further reactions. Thus by hydrolysis of these SiCl groups, Si–C–Si skeletons can be linked by Si–O–Si groupings, or the SiCl groups may be converted into SiH groups, which can then be oxidized.

6. High Polymers with a Silicon Network

The tendency toward the formation of high molecular-weight compounds by free-radical reactions is very pronounced in the chemistry of silicon. This is seen in the formation of compounds whose skeletons consist of Si–Si bonds. Thus $(SiH)_x$ can be prepared from SiH_4 by heating [9]. $SiCl_4$ and H_2 react to form the higher silicon chlorides up to $(SiCl)_n$ [10]. $(SiCH_3)_x$ is obtained among other products from SiH_4 and ethylene [11]. In the high molecular-weight compounds $(SiH)_x$, $(SiCH_3)_x$, and $(SiCl)_x$, each silicon atom is directly bonded to three others.

The route to high molecular-weight compounds need not start with the small structural units (monomers) and lead by growth reactions (condensation, polymerization) to large structures. These can also be prepared with care from crystallographically definite structures of the desired basic skeleton. Thus $CaSi_2$ forms a layer structure (Fig. 7) [12].

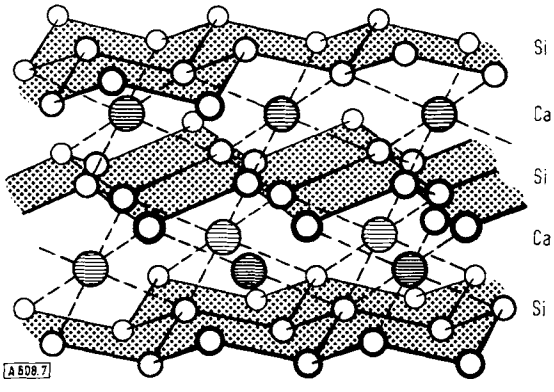


Fig. 7. Structure of $CaSi_2$.

To expose the silicon network, the calcium atoms connecting the layers must be dissolved out or replaced by monovalent atoms or by radicals. This is achieved by reaction of $CaSi_2$ with an $SbCl_3$ melt [13]. The silicon is first exposed in accordance with equation (6), but is unfornately chlorinated to a greater or lesser

$$3\,CaSi_2 + 2\,SbCl_3 \rightarrow 6\,Si + 2\,Sb + 3\,CaCl_2 \quad (6)$$

extent (eq. (7)), depending on the reaction conditions.

$$x\,Si + {}^1/_3\,x\,SbCl_3 \rightarrow (SiCl)_x + {}^1/_3\,x\,Sb \quad (7)$$

[6] *G. Fritz*, Fortschr. chem. Forsch. *4*, 460 (1964); *G. Fritz, J. Grobe*, and *D. Kummer*, Advances inorg. Chem. Radiochem. *7*, 349 (1965.

[7] *G. Fritz, H. J. Buhl*, and *D. Kummer*, Z. anorg. allg. Chem. *327*, 165 (1964).

[8] *G. Fritz, R. Haase, E. Krahé, H. Scheer, D. Kummer*, and *H. G. v. Schnering*, unpublished.

[9] *A. Stock, P. Stiebeler*, and *F. Zeidler*, Chem. Ber. *56*, 1695 (1923).

[10] *R. Schwarz* and *U. Gregor*, Z. anorg. allg. Chem. *241*, 395 (1939).

[11] *G. Fritz*, Z. Naturforsch. *5b*, 395 (1950).

[12] *J. Böhm* and *O. Hassel*, Z. anorg. allg. Chem. *160*, 152 (1927).

[13] *H. Kautsky* and *L. Haase*, Chem. Ber. *86*, 1226 (1953).

After conversion into SbI_3 with iodine, the liberated antimony can be removed from the reaction mixture with anhydrous organic solvent. As expected, the silicon left behind is extremely reactive; it reacts even with water, whereupon violent liberation of H_2 takes place. When heated, it changes into normal silicon. Direct reaction of $CaSi_2$ suspended in CCl_4 with chlorine or ICl also gives this form of silicon, as well as $(SiCl)_x$ formed by further chlorination [14, 15].

$$^1/_2\, x\, CaSi_2 + {}^1/_2\, x\, Cl_2 \xrightarrow[20-40\,^\circ C]{} (Si)_x + 1/2\, x\, CaCl_2 \qquad (8)$$

$$(Si)_x + 1/2\, x\, Cl_2 \xrightarrow[40\times 60\,^\circ C]{} (SiCl)_x \qquad (9)$$

The resulting $(SiCl)_x$ and its derivatives occur in the lepidoide form, *i.e.* ideally in a layer on which all the functional groups are situated on the surface of the insoluble substance, and are thus directly accessible to reactions.

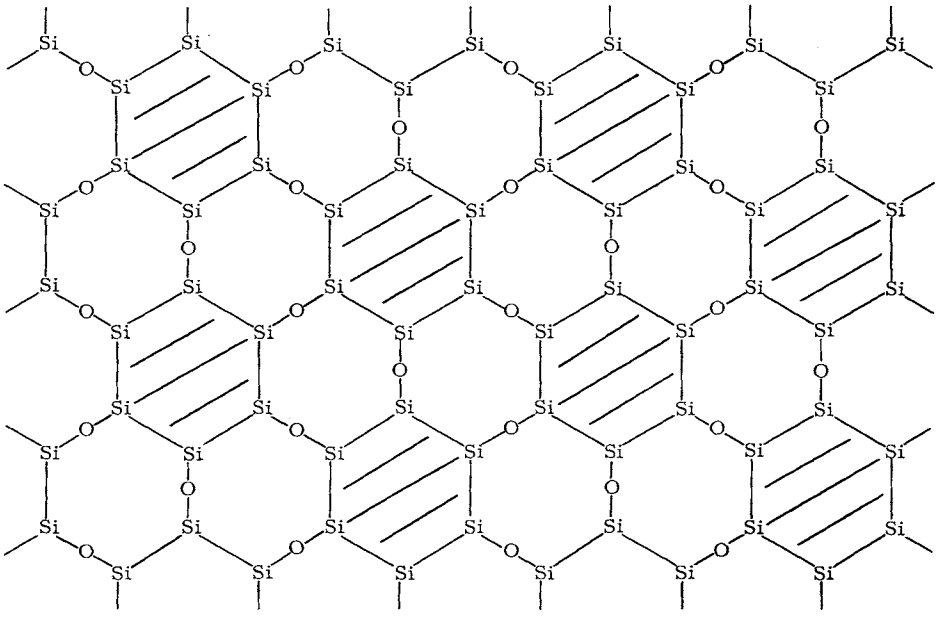
H. Kautsky [16] tried to dissolve the calcium out of the $CaSi_2$ layer lattice and to replace it by hydrogen atoms in order to separate the layers and so obtain the polymeric lepidoide $(SiH)_x$. However, this is not possible, since the anions of the acid and the oxygen of the solvent intervene in the replacement of calcium by hydrogen, so that a permutitic high polymer having the composition $(Si_6O_3H_6)_n$ is formed [16]. The silicon layer in this case consists of six-membered silicon rings joined by oxygen atoms. This substance reacts very rapidly and quantitatively with *e.g.* Br_2 to form surface compounds having a definite stoichiometric composition and having the same basic network structure. The reactions involve substitution of the SiH groups on the surface. The structure of the siloxene network is illustrated in Figure 8.

The layer therefore carries reactive groups, by means of which chemical reactions can be carried out on an ideal surface, offering the possibility of obtaining model substances. A second, very interesting characteristic of these compounds is their color and fluorescence [17]; for example, dibromosiloxene reacts with CH_3OH to form an orange derivative (two OCH_3 groups), while tetrabromosiloxene forms a red compound (four OCH_3 groups). The explanation of this phenomenon for the siloxene network and for the high molecular-weight silicon compounds should add considerably to our knowledge of color, fluorescence, and energy transfer on surfaces.

7. High Molecular-Weight Compounds between Elements of Groups 3 and 5

Graphite and boron nitride (Fig. 9) form very similar layer lattices.

The groups B–N and C–C are isosteric; unlike graphite, $(BN)_x$ is white and non-conducting. Its high thermal stability therefore makes it suitable for use as an insulator and lubricant at high temperatures. At 1400 °C and 7000 atm, boron nitride can be converted from the graphite-like structure to a diamond structure; in this form it burns only at 1900 °C and is as hard as diamond.



[A 608. 8]

Fig. 8. Structure of a siloxene network (the Si_6 rings are shaded). The fourth valence on the Si atom is occupied by H atoms, which can be replaced *e.g.* by halogens [16].

The chemistry of the low molecular-weight, boron-nitrogen compounds is similar in some respects to carbon chemistry. While the formation of molecular compounds between compounds of the group 4 ele-

[14] *E. Bonitz*, Chem. Ber. *94*, 220 (1961).

[15] *E. Hengge* and *G. Scheffler*, Mh. Chem. *95*, 1450 (1964).

[16] *H. Kautsky*, Z. Naturforsch. *7b*, 174 (1952).

[17] *H. Kautsky*, Kolloid-Z. *102*, 1 (1943); *E. Hengge*, Chem. Ber. *95*, 648 (1962).

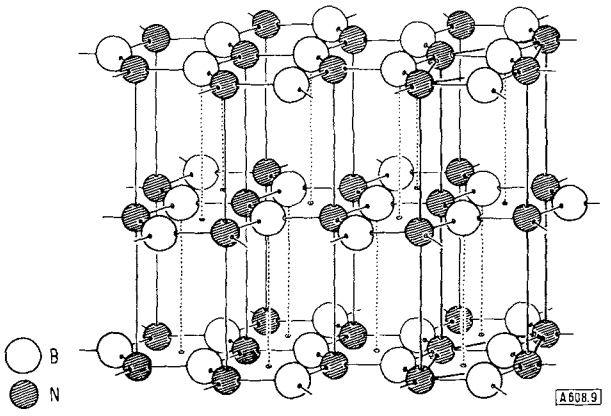


Fig. 9. Lattice of boron nitride.

ments is dominated by substitutions, condensations, and additions, the first reaction step in the case of compounds between elements of groups 3 and 5 is often adduct formation, owing to the electronic structure in these compounds. Interesting compounds can be formed from the adducts by removal of atoms and groups, as is illustrated by the formation of borazole [18] from B_2H_6 and NH_3 (eq. (10)).

$$3\ (BH_3)_2 + 6\ NH_3 \longrightarrow 2 \begin{array}{c} H \\ B \\ HN \quad NH \\ \| \quad \| \\ HB \quad BH \\ N \\ H \end{array} + 12\ H_2 \qquad (10)$$

This route is not satisfactory for the formation of compounds between aluminum and phosphorus, though the chemical behavior is still largely governed by the tendency toward adduct formation [19]. High molecular-weight compounds are obtained when the aluminum carries more than one group that is capable of coordination [20].

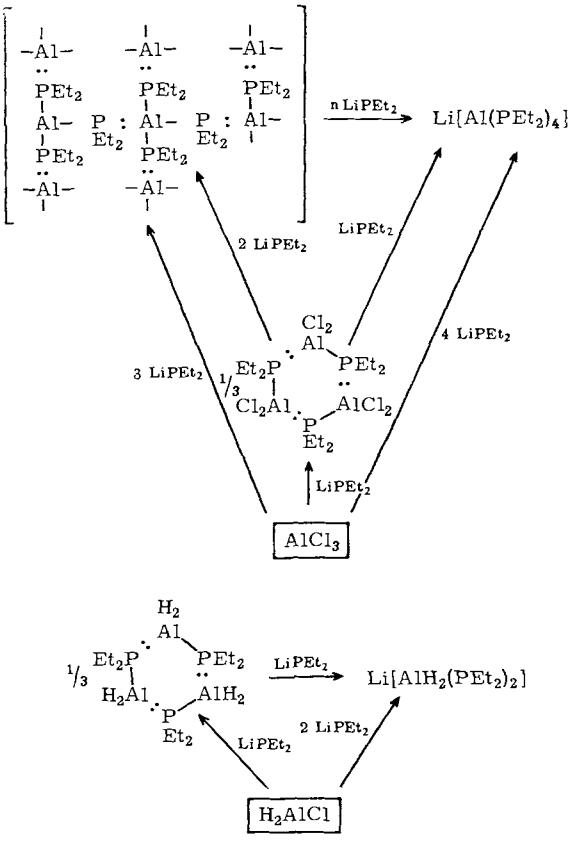
In these cases extensive crosslinking takes place, the degree of crosslinking being greatest when the aluminum carries three PR_2 groups.

In most of the classes of substances discussed, the bonding between the individual groups is predominantly homopolar, with a more or less pronounced polar component. This explains some of the properties,

[18] *A. Stock*: Hydrides of Boron and Silicon. Cornell University Press, Ithaca, and Oxford University Press, London 1933; *F. G. A. Stone*, Quart. Rev. (chem. Soc., London) *9*, 174 (1955).

[19] *R. Höltje* and *F. Meyer*, Z. anorg. allg. Chem. *197*, 93, 102 (1951); *N. Davidson* and *H. C. Brown*, J. Amer. chem. Soc. *64*, 316 (1942).

[20] *G. Fritz* and *G. Trenczek*, Z. anorg. allg. Chem. *331*, 206 (1964).



[A 608. 10]

Fig. 10. Reactions of $AlCl_3$ and of H_2AlCl with $LiPEt_2$ (Et = C_2H_5).

such as the solubility, and the possibility of solvolysis. The stability is largely determined by the tendency toward formation of the oxygen compounds. The optimum stability is reached in the naturally occurring silicate skeletons. At the other end of the scale we find the aluminum-phosphorus compounds, which are very readily oxidizable, and most of which ignite spontaneously.

We started by comparing silicon and carbon as building elements in the skeletal substances of animate and inanimate nature. The modification of these natural structural systems offers the chemist a multitude of possibilities for the synthesis of high molecular-weight substances that are nowadays indispensable. These possibilities are still far from exhausted both theoretically and in their applications. We may therefore look forward to many interesting developments in the future.

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Directed Aldol Condensations

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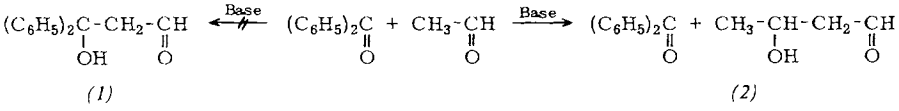
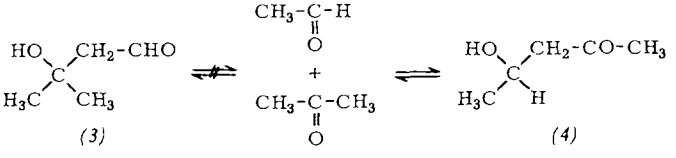
The present article describes the discovery of a new procedure for aldol condensations for the preparation of α,β-unsaturated carbonyl compounds[***]. *The scope of this process is demonstrated by many examples, including some from the natural products sector; at the same time, however, these examples also mark its limitations. The metalated Schiff's bases may be classified as ambident anions; this also explains acylations on the nitrogen. A comparison of the new directed aldol condensation with the formation of unsaturated carbonyl compounds through olefination via phosphorylids shows that the latter method fails when a ketone is used as the substrate. This is where the described procedure using metalated Schiff's bases proves its value.*

1. Introduction

Until a few years ago, the aldol addition could not be directed in such a way that an aldehyde having a hydrogen atom in the α position added to the carbonyl group of a ketone, since the preferred reaction is the self-addition of the aldehyde. For example, the reaction of acetaldehyde with benzophenone in the presence of the usual basic catalysts does not lead to the desired aldol adduct *(1)*, but to acetaldol *(2)* which loses water to form crotonaldehyde.



(1) *(2)*



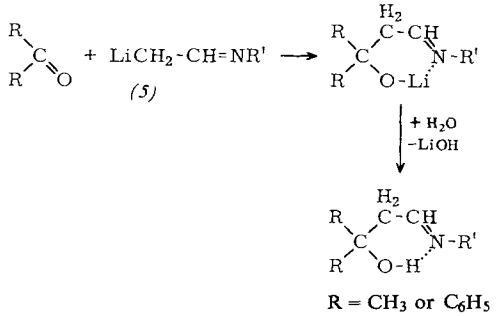
(3) *(4)*

Even condensation with more reactive ketones such as acetone fails to yield the adduct *(3)*, but leads instead to compound *(4)* [1], since acetaldehyde has the more reactive carbonyl group and acetone has a more nucleophilic carbon atom after anionization.

It is not possible to remove first a proton from the acetaldehyde and then add the electrophile *e.g.* in the form of acetone. Generally the two components must be placed together in the reaction vessel, the base then being added dropwise. Moreover, the base cannot be chosen arbitrarily, since it must be such that it does not add to the carbonyl group.

These difficulties can be avoided by conversion of the carbonyl group of the aldehyde into the azomethine group, metalation of the resulting "protected" acetaldehyde (*e.g.* with lithium diisopropylamide) to obtain *(5)*, and reaction of *(5)* with acetone or benzophenone [2, 3].

Since the protective group can be readily removed after the aldol addition, this method opens new routes to aldol condensations by way of organometallic compounds.



(5)

R = CH_3 or C_6H_5

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[**] The articles in this series have been published in five volumes by Verlag Chemie, Weinheim/Bergstr. An English edition has also been published. This article will appear, with added procedures, in Volume VI of the series.

[***] *G. Wittig, H. Pommer,* and *W. Stilz,* German Patent 1199252 (April 5, 1963), BASF; Chem. Abstr. *63*, P 1739c (1965).

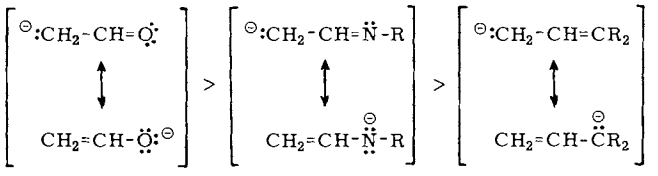
[1] Methoden der organischen Chemie (Houben-Weyl). 4th Edit., Georg Thieme Verlag, Stuttgart, 1954, Vol. VII/1, p. 76ff.

[2] *G. Wittig* and *H. D. Frommeld,* Chem. Ber. *97*, 3541 (1964).

[3] *G. Wittig, H. D. Frommeld,* and *P. Suchanek,* Angew. Chem. *75*, 978 (1963); Angew. Chem. internat. Edit. *2*, 683 (1963).

2. Theoretical Considerations

The new method of aldol addition *via* Schiff's bases seems plausible in retrospect, since the metalated Schiff's bases should have been expected to be intermediate in their reactivity between the allyl anions and the anionized carbonyl compounds.



Both the allyl and the enolate anions react readily with carbonyl compounds. It was therefore considered very probable that the anionized Schiff's bases would react in a similar manner. The feasibility of directed aldol condensations depended on whether the metalated Schiff's bases would add rapidly to the unmetalated species (as is the case with the anionized carbonyl compounds) or whether they would behave more like the allyl anions, which do not enter into additions of this nature.

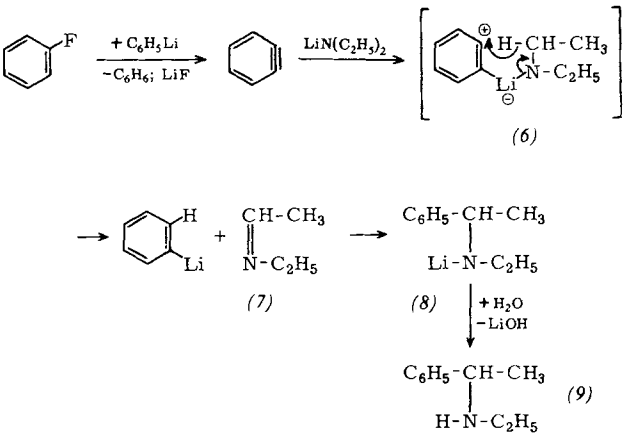
In fact, the electrophilicity of the azomethine group is so low that the self-addition can be suppressed by the procedure described in Section 4. The metalated Schiff's base, on the other hand, is sufficiently nucleophilic to attack even inert carbonyl groups, such as those of ketones. This effect contributes to the success of the new method.

3. Discovery of the Principle of the Directed Aldol Condensation

The foregoing theoretical considerations did not, however, precede the actual experiments. On the contrary, attention was directed toward the metalated Schiff's bases by unexpected experimental results.

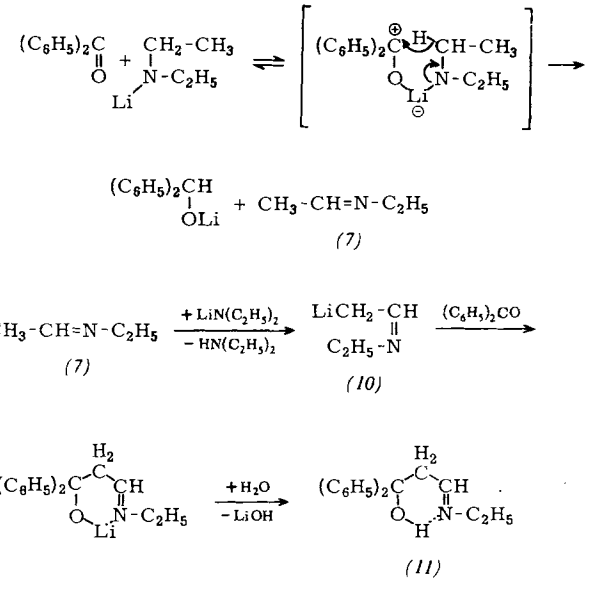
In the course of investigations on dehydrobenzene, phenyllithium was allowed to react with fluorobenzene in the presence of lithium diethylamide. In addition to the expected diethylaniline, the products also included α-phenyldiethylamine. Closer investigation [4] showed that the lithium diethylamide evidently adds to dehydrobenzene, formed as an intermediate, to give the ate-complex *(6)*, which has not been isolated. The anionic loosening of the ligand adjacent to the nitrogen leads to a hydride transfer, which results in the formation of phenyllithium and the Schiff's base *(7)*. These two compounds combine irreversibly by addition of the organolithium compound to the C=N group to form the lithium amide *(8)*, hydrolysis of which yields α-phenyldiethylamine *(9)*.

This ability of lithium diethylamide to act as a hydride donor led to further experiments. To verify that lithium diethylamide does in fact occur as the reducing



agent, it was allowed to act on benzophenone. We expected reduction to benzohydrol *via* the ate-complex, coupled with oxidation of the amine to form the Schiff's base *(7)*. Up to 35% of benzohydrol was actually isolated; however, a more complicated compound was obtained instead of ethylideneethylamine *(7)*. Careful determination of its structure [4], followed by synthesis, showed that this product was the Schiff's base *(11)*, *i.e.* an aldimine adduct.

Thus part of the benzophenone is evidently reduced to benzohydrol in a redox reaction, in which a corresponding quantity of the Schiff's base *(7)* is formed. After metalation of *(7)* by lithium diethylamide that is still present, the metalated Schiff's base reacts with unreduced benzophenone to form the aldimine adduct *(11)*. The surprising thing is that all these reactions proceed to completion within a minute at 0 °C.



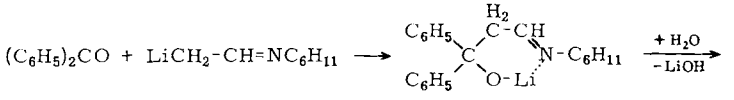
Since the end product *(11)* can be readily converted into β-phenylcinnamaldehyde by mineral acid, the overall reaction is an aldol condensation in which the methyl group of the acetaldehyde is specifically condensed with the carbonyl group of the ketone. This possibility of a directed aldol condensation was pursued further, particularly since it was soon found that the method can be generalized within wide limits and generally gives good results.

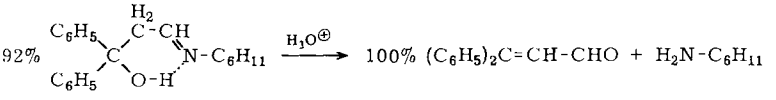
[4] *G. Wittig, H.-J. Schmidt*, and *H. Renner*, Chem. Ber. *95*, 2377 (1962).

4. Directed Aldol Condensations

The optimum conditions ("standard method") for the metalation or anionization of Schiff's bases on the one hand and the subsequent reaction with carbonyl compounds to form aldimine adducts on the other are described below. Cyclohexylamine was found to be suitable as the amine component of the Schiff's bases, since Schiff's bases having branched alkyl substituents on the nitrogen have less tendency toward self-addition than those with unbranched ligands[5]. For obvious steric reasons lithium diisopropylamide proved to be a particularly suitable metalating agent instead of lithium diethylamide.

Thus on reaction of ethylidenecyclohexylamine with lithium diisopropylamide in ether at 0 °C and, after





(12a)

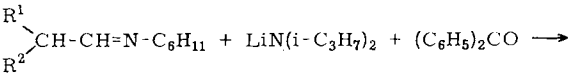
10 min, addition of benzophenone at −70 °C, hydrolysis gave the Schiff's base *(12a)* in 92% yield[2].

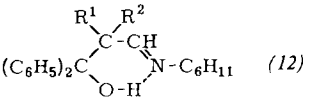
The favorable results are also due to the fact that the resulting lithium salts of the aldol adducts, as formulated above, exist as chelates. The IR spectrum in every case confirmed that the nitrogen of the aldimine group in the hydrolysis products is linked to the hydroxyl group by an intramolecular hydrogen bond. Broad absorption bands were observed at 3200 to 3100 cm^{-1} for KBr disks and at 3300 to 3200 cm^{-1} in $CHCl_3$ or benzene, no change being found in the solution spectra even at high dilutions.

It is interesting to note that methyllithium, which was used to convert the diisopropylamine into its lithium derivative, preferentially metalated ethylidenecyclohexylamine on the methyl group at −70 °C, and added only to a small extent to the C=N group. After the addition of benzophenone followed by hydrolysis, the aldimine adduct *(12a)* was isolated in 71% yield. Since the aldimine adduct could be converted almost quantitatively into β-phenylcinnamaldehyde, the problem of carrying out a directed aldol condensation on aromatic ketones was solved.

However, the directed aldol condensation, though proceeding particularly smoothly with aromatic ketones, is limited in its applicability. To determine the influence of the inductive and steric effects on the new procedure, the Schiff's bases of α-substituted acetaldehydes were metalated under the standard conditions with lithium diisopropylamide, and the aldimine adducts obtained with benzophenone were isolated[6]. The yields are given in Table 1.

Table 1. Directed aldol condensation: influence of inductive and steric effects on the formation of aldimine adducts.



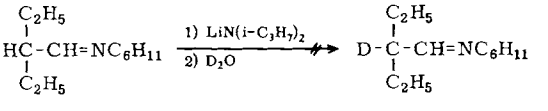


(12)

	R^1	R^2	*(12)* Yield (%)	M.p. (°C)
(12a)	H	H	92	127–128
(12b)	CH_3	H	91	82– 83
(12c)	C_2H_5	H	71	104–105
(12d)	CH_3	CH_3	29	107–108
(12e)	C_2H_5	C_2H_5	0	–

It can be seen that the yield decreases with increasing branching on the α-carbon of the Schiff's base. 2-Ethylbutylidenecyclohexylamine *(12c)* does not react.

The reason for this was shown by the following observations. When the Schiff's base *(13)* was treated for 2 hours with lithium diisopropylamide in ether (the Schiff's base of the unsubstituted acetaldehyde is immediately metalated in ether) and the product hydrolyzed with D_2O, *(13)* was recovered in 95% yield[6]. The IR and in particular the NMR spectra showed that the compound contained no deuterium, and so had not been metalated. *(13)* could not be metalated even by tritylsodium in ether or by tritylpotassium in ethylene glycol dimethyl ether; the solutions were still deep red after four weeks, and back-titration showed that they still contained 80 and 96%, respectively, of unreacted base[6].



(13)

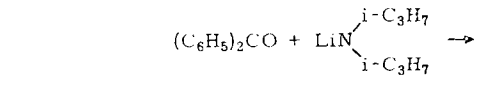
This also explains the fact that almost 50% of benzohydrol was detected on reaction of *(13)* with lithium diisopropylamide in the presence of benzophenone. The lithium diisopropylamide reacts with benzophenone instead of with *(13)*, hydride transfer taking place as formulated earlier to give benzohydrolate and the new Schiff's base *(14)*. *(14)* is metalated by lithium diisopropylamide and then enters into aldimine addition with unreacted benzophenone to give *(15)*.

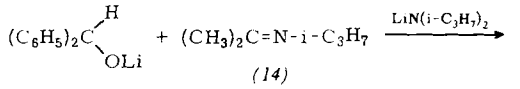
On subsequent hydrolysis and distillation *(15)* decomposed into benzophenone and *(14)*.

The decrease in metalation with increasing alkylation of the aldimine is probably due to the combined effects of the increasing steric hindrance and the hyperconjugation which decreases the mobility of the α-protons.

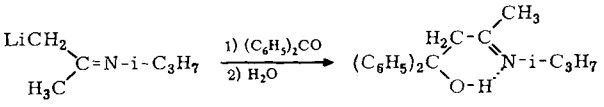
[5] *R. Tiollais*, Bull. Soc. chim. France *14*, 716 (1947).

[6] *H. Reiff*, Dissertation, Heidelberg University, 1966.



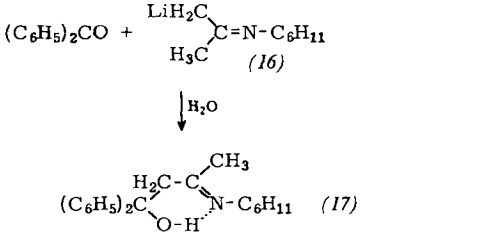


(14)

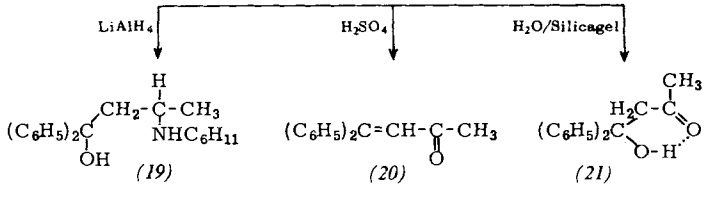


(15)

In this connection the reaction of *(14)* with the metalating agent and benzophenone was studied more closely. It corresponds to an aldol addition of acetone to benzophenone, which *A. Klages* and *E. Fanto* [7] had already unsuccessfully tried to achieve. Isopropylidenecyclohexylamine was metalated under the usual conditions to give *(16)*, which was then brought into contact with benzophenone. The aldimine adduct *(17)* could be isolated in 64% yield [8].



(16) (17)



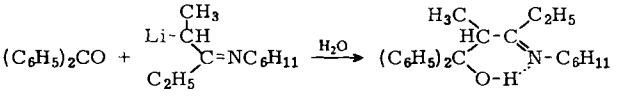
(19) (20) (21)

Reduction of *(17)* with $LiAlH_4$ (which at the same time established its constitution) gave the amino alcohol *(19)* in 81% yield. The IR spectrum of *(19)* no longer contained an azomethine band.

Decomposition of *(17)* with dilute sulfuric acid led to the unsaturated ketone *(20)* (78% yield), which was found to be identical with a comparison product prepared by a more laborious route. Even the nitrogen-free aldol adduct *(21)* could be obtained in 68% yield [8]. Thin-layer chromatography of *(17)* on silica gel gave two products; the compound having the higher R_f value was identified as benzophenone, while the other compound ($C_{16}H_{16}O_2$, m.p. 85 °C) was found, from the position of the NMR signals and the proton ratio ($CH_{arom.}:OH:CH_2:CH_3 = 10:1:2:3$), to be the previously unknown ketol *(21)*.

In the reaction of the Schiff's base of the homologous diethyl ketone with benzophenone, the ketimine adduct *(22)* could be isolated but the corresponding ketol could not be obtained by thin-layer chromatography [8].

The acidic decomposition of *(22)* also failed to yield the unsaturated ketone; both operations gave only benzophenone, the branching on the α-carbon atom in this case evidently again opposing the stability of the aldol adduct.

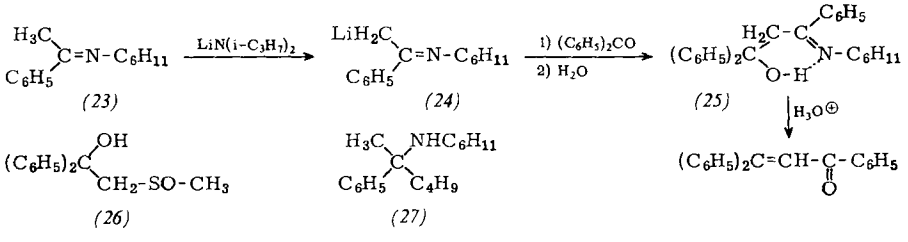


(22)

The Schiff's base *(23)* of acetophenone, on anionization with lithium diisopropylamide to give the deep yellow *(24)* and combination with benzophenone, gave the adduct *(25)* (55% yield), which was converted, on treatment with dilute mineral acid, into 1,1-diphenyl-2-benzoylethylene in 95% yield [6].

Variation of the metalation conditions in this case gave rise to a number of secondary reactions, of which we shall select only a few [6]. Potassium *tert*-butoxide in ether or tetrahydrofuran, instead of metalating *(23)*, cleaved the benzophenone present into benzoic acid in a Haller-Bauer reaction [9]. When the reaction was carried out in dimethyl sulfoxide, which, according to *D. J. Cram* [10], particularly favors anionization, the addition product *(26)* of the methylsulfinyl carbanion was obtained in 89% yield [11].

When *(23)* was treated with ethereal butyllithium in the absence of a ketone, 22% of *(23)* and 67% of *(27)* could be isolated after hydrolysis; this indicates that the organolithium compound had added preferentially to the C=N bond. A further insight into the reaction was afforded by hydrolysis with D_2O after the reaction of *(23)* with butyllithium [6].



(23) (24) (25) (26) (27)

The NMR spectrum of the recovered Schiff's base *(29)* showed that one hydrogen on the acidic methyl group and one in the ortho position of the benzene nucleus

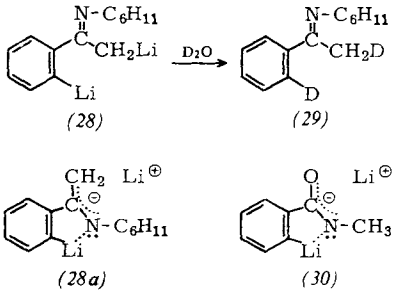
[7] *A. Klages* and *E. Fanto*, Ber. dtsch. chem. Ges. *32*, 1433 (1899).

[8] *G. Wittig* and *P. Suchanek*, Tetrahedron *22*, 347 (1966).

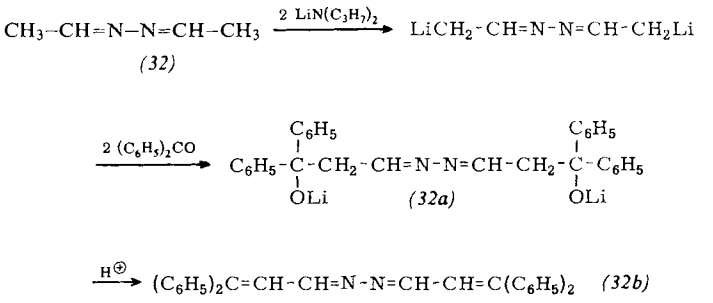
[9] *K. E. Hamlin* and *A. W. Eston*, Org. Reactions *9*, 2 (1957).

[10] *D. J. Cram et al.*, J. Amer. chem. Soc. *83*, 3678 (1961); *84*, 4358 (1962).

[11] Cf. *E. J. Corey* and *M. Chaykowsky*, J. Amer. chem. Soc. *84*, 864 (1962).



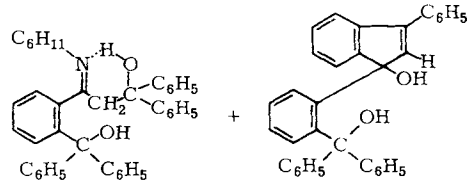
(28) (29) (28a) (30)



(32) (32a) (32b)

had been replaced by deuterium. Thus apart from a C=N addition, *(23)* was converted by butyllithium into the double metalation product *(28)*. In analogy with the formation of the dilithium derivative *(30)* on metalation of *N*-methylbenzamide with butyllithium, as observed recently by *C. R. Hauser* [12], we formulate our product as indicated in *(28a)* [6] to express the fact that the formation of a five-membered chelate ring has a decisive influence on the *o*-metalation.

Whereas metalation of *(23)* with lithium diisopropylamide followed by addition of benzophenone yielded the normal ketimine adduct *(25)* as described above, metalation of *(23)* with 2 moles of butyllithium in ether followed by reaction with benzophenone led to the expected bis-adduct *(31)* (16%), the main product,



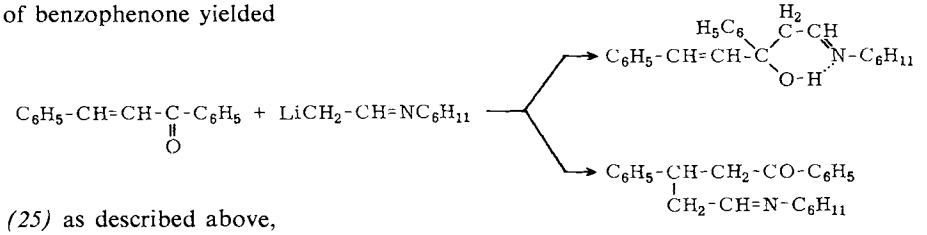
(31) (31a)

however, being the diol *(31a)* (48% yield). The determination of the structures and the interesting reactions of the two compounds on treatment with acids will not be discussed here [6].

On the other hand, an interesting question in connection with the dimetalation of *(23)* is whether the directed aldol condensation can also be extended to azines.

Preliminary experiments (metalation followed by hydrolysis) with the readily obtainable acetaldazine *(32)* showed that the α,ω-dimetalated compound is relatively stable at −70 °C. When two moles of benzophenone were added to the doubly metalated acetaldazine in ether at −70 °C, the bis-adduct *(32a)* of benzophenone could be isolated in 30% yield [6]. The crystalline compound *(32a)* (m.p. 182–183 °C) could be readily and quantitatively converted into β-phenylcinnamaldehydazine *(32b)*.

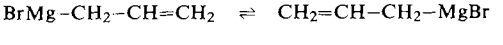
The dependence of the aldimine addition on the external conditions is shown by the behavior of metalated ethylidenecyclohexylamine toward unsaturated ketones such as benzylideneacetophenone. When the two components were brought together in ether at −70 °C, the 1,2-adduct *(33)* could be isolated in 51% yield, whereas reaction at room temperature gave only 32% of this adduct and 6% of the Michael adduct *(34)* [8].



(33) (34)

5. Metalated Schiff's Bases as Ambident Anions

Before discussing the particularly interesting aldimine additions that lead to natural products, we must first consider the question of structure and the mechanistic processes occurring in reactions with metalated Schiff's bases. NMR-spectroscopic studies by *J. D. Roberts* [13] show that the two methylene groups in the allyl Grignard compounds are indistinguishable. The simple AX_4 spectrum obtained can be reconciled only with a fast equilibrium.



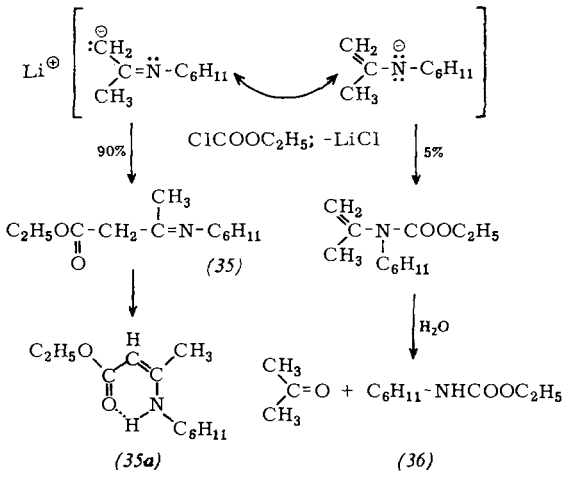
Electrophilic reagents can therefore attack at both ends of the resonance-stabilized allyl system. By analogy with this, it must be expected that the anionized Schiff's bases can also react in the resonance form having the negative charge on the nitrogen.

The reaction of the anionized Schiff's base of acetone with ethyl chloroformate yields 90% of *(35)*, the IR and NMR spectra of which indicate that it exists in its chelate form *(35a)* as ethyl β-cyclohexylaminocrotonate; 5% of *N*-cyclohexylurethane *(36)* is also obtained [6].

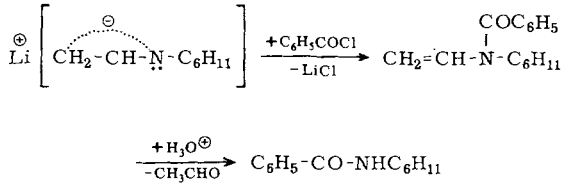
The ethoxycarbonyl group has therefore been introduced onto carbon and onto nitrogen, the ratio of the

[12] *W. H. Puterbaugh* and *C. R. Hauser*, J. org. Chemistry *29*, 853 (1964); *R. L. Vaulx*, *W. H. Puterbaugh*, and *C. R. Hauser*, *ibid. 29*, 3514 (1964).

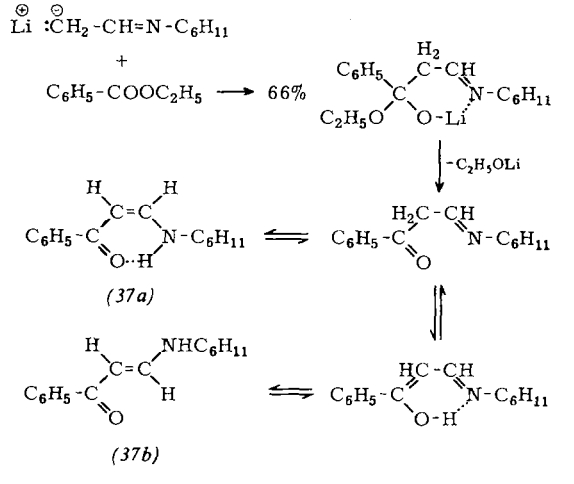
[13] *J. D. Roberts* and *J. E. Nordlander*, J. Amer. chem. Soc. *81*, 1769 (1959).



products being determined by the electrophilicity of the other reactant. The action of benzoyl chloride on lithium ethylidenecyclohexylamine gave 35% benzoylation on the nitrogen, together with oils and resins that were not examined further [6].



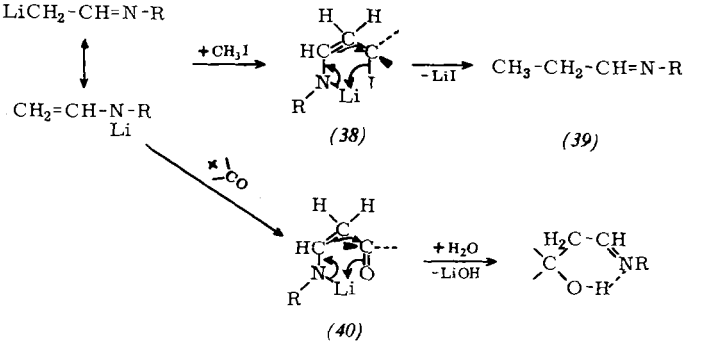
The analogous reactions with ethyl benzoate and with *N,N*-dimethylbenzamide, on the other hand, led to mixtures of *cis*- and *trans*-β-cyclohexylaminovinyl phenyl ketones *(37a)* and *(37b)* in 66 and 84% yields, respectively, *i.e.* to *C*-benzoylation products [8].



The configurations were assigned on the basis of IR and NMR spectra, which will not be discussed here.

Why should the reactions of metalated Schiff's bases with aldehydes or ketones (or even with alkyl halides) yield *C*-substituted products, whereas with reagents such as ethyl chloroformate or benzoyl chloride they undergo appreciable or predominant *N*-substitution? Metalated Schiff's bases may be regarded as ambident anions or, in other words, as bifunctional nucleophiles. As a rough simplification it may be said that halides such as methyl iodide that react in substitutions by an S_N2 mechanism, attack anions of this type [14] at the atom of the mesomeric system that has the lower electron density according to the electronegativity scale, *i.e.* at the carbon atom in this case, as we have found in a series of examples. On the other hand, halides that are solvolyzed by an S_N1 mechanism (*e.g. tert*-butyl iodide) are preferentially attacked by the atom of the ambident system that carries the greater electron density, *i.e.* the nitrogen.

This situation has been plausibly interpreted by *A. Brändström* [15]. In the metalated Schiff's base, the metal cation (*i.e.* the lithium in our case) preferentially resides on the most electronegative part of the molecule (*i.e.* on the nitrogen). Unionized reagents such as methyl iodide then approach in such a way as to give the six-membered ring transition state *(38)*, from which the product *(39)* can be formed by elimination of lithium halide.



The reaction with ketones, *i.e.* the directed aldol condensation itself, also appears to be readily explained as proceeding by this mechanism *via (40)*. The role played by the solvation of the electropositive metal cation in this reaction should not be overlooked.

On the other hand, with compounds that ionize relatively readily, the first step is rapid formation of lithium halide. The remaining cation then seeks out the point in the anion at which the electron density is greatest. Thus, as has already been mentioned, the reaction of lithium ethylidenecyclohexylamine with benzoyl chloride proceeds *via* the unstable enamine (*N*-vinylcyclohexylbenzamide) to give *N*-cyclohexylbenzamide as the main product.

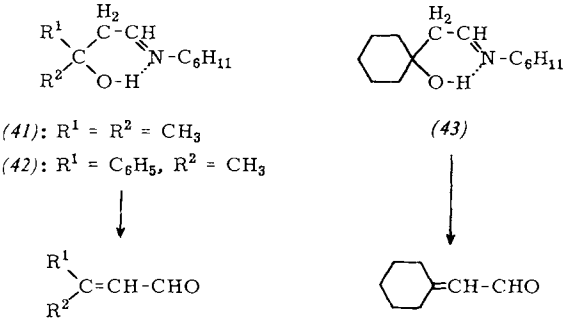
6. Conversion of the Aldol Adducts into the α,β-Unsaturated Carbonyl Compounds

It appeared at first that problems might arise in the use of the new procedure for the synthesis of natural products, since it was possible that with methyl ketones such as β-ionone, the $CO-CH_3$ system might

[14] Cf. *R. Gompper*, Angew. Chem. *76*, 412 (1964); Angew. Chem. internat. Edit. *3*, 560 (1964).

[15] *A. Brändström*, Ark. Kemi *6*, 155 (1954).

undergo transmetalation with the metalated Schiff's base. Model experiments with acetone, acetophenone, and cyclohexanone showed that the transmetalation could be substantially suppressed by operating under the standard conditions (see Section 4), *i.e.* the Schiff's base was metalated in ether at 0 °C and brought into contact with the ketone or aldehyde at −70 °C. After hydrolysis and recrystallization (preferably from petroleum ether), the new, well-crystalline Schiff's bases are always obtained in yields of between 50 and 90%.



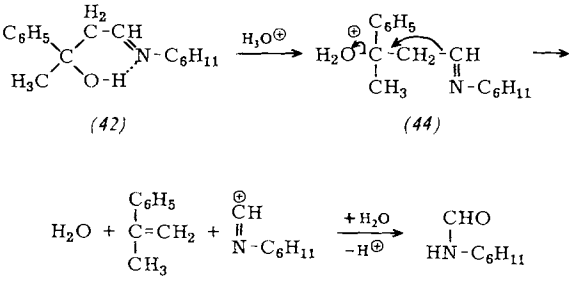
(41): $R^1 = R^2 = CH_3$

(42): $R^1 = C_6H_5$, $R^2 = CH_3$

(43)

These aldimine adducts can generally be converted into the α,β-unsaturated aldehydes or ketones in a single operation by steam distillation in the presence of oxalic acid; the final products distil over. Under the conditions described, the thermodynamically more stable product, *i.e.* the *trans*-olefin, is usually formed. Thus *(41)* gave 51% of β-methylcrotonaldehyde, *(42)* gave 71% of β-methylcinnamaldehyde, and *(43)* gave 60% of cyclohexylideneacetaldehyde.

Acid hydrolysis did not always lead to only one product. Thus the aldol adduct of lithium ethylidenecyclohexylamide and acetophenone gave 71% of β-methylcinnamaldehyde (identified as its semicarbazone) and 19% of α-methylstyrene, which was probably formed by fragmentation *via* compound *(44)*.



(42) *(44)*

7. Preparation of Natural Products

The procedure for the directed aldol condensation was finally used for the synthesis of α,β-unsaturated carbonyl functions in natural products and in compounds that are important intermediates in the preparation of natural products. The compounds listed in Table 2 can be prepared relatively easily by the new process [3,8].

The first crystalline sample of β-cyclocitrylideneacetaldehyde was obtained after synthesis by this method.

Table 2. Preparation of natural products by directed aldol condensation in accordance with the scheme.

$$R{-}CO{-}R' + LiCH_2{-}CH{=}NR + H_2O \rightarrow R{-}CR'{=}CH{-}CHO + LiOH + H_2NR$$

(R' = Alkyl, Aryl, H)

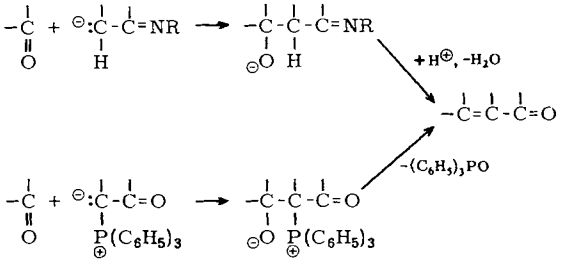
Carbonyl-component	Aldimine adduct M.p. (°C)	Yield (%) [a]	α,β-Unsaturated aldehyde B.p. (°C/torr)	Yield (%) [a]
Butyraldehyde	not isolated		2-Hexen-1-al 42—48/15	65
β-Cyclocitral	92—93	58	β-Cyclocitrylidene-aldehyde 72.5—75/0.1	50
6-Methyl-5-hepten-2-one	32—33.5	76	Citral (*cis-trans*-mixture) 68—74/0.5	64
β-Ionone	46—47	80	β-Ionylideneacet-aldehyde 115—120/0.001	42

[a] Yield based on carbonyl component used.

When precipitated from petroleum ether by cooling, it melts between −2 and +2 °C. The two aldehydes citral and β-ionylideneacetaldehyde are particularly important, in that they are intermediates in the synthesis of vitamin A and other carotenoids.

It may be asked whether these chain-lengthening processes with formation of α,β-unsaturated aldehydes or ketones could not be better carried out through olefination *via* phosphorylids. Though this method has found a wide range of applications and has been used by *S. Trippett* [16] for the preparation of α,β-unsaturated aldehydes, it is in this very application that its disadvantages become obvious. The scopes of the two methods are shown in Table 3.

Table 3. Preparation of α,β-unsaturated carbonyl compounds by directed aldol condensation and *via* phosphorylids; comparison of yields.



Unsaturated carbonyl compound	Preparation by directed aldol condensation Yield (%) [a]	Preparation *via* phosphorylids Yield (%) [a]
$CH_3{-}CH_2{-}CH_2{-}CH{=}CH{-}CHO$	65	81
$C_6H_5{-}CH{=}CH{-}CHO$	72	60
$(CH_3)_2C{=}CH{-}CHO$	40	0
$C_6H_5{-}C(CH_3){=}CH{-}CHO$	71	0
$(C_6H_5)_2C{=}CH{-}CHO$	78	0
$(C_6H_5)_2C{=}C(CH_3){-}CHO$	81	0
$(C_6H_5)_2C{=}CH{-}C(CH_3){=}O$	50	0

[a] Yields based on carbonyl component used.

[16] *S. Trippett* and *D. M. Walker*, J. chem. Soc. (London) *1961*, 1266.

According to Table 3, the olefination of aldehydes *via* phosphorylids also gives good results; however, this method is totally unsuccessful with ketones. This is where the new directed aldol condensation becomes really valuable.

It would be interesting in this connection to ex-amine the question of whether the imine derivatives of β-carbonylmethylenephosphoranes $(C_6H_5)_3P{=}CH{-}CH{=}NR$, like the metalated Schiff's bases, react with ketones in the desired manner.

The authors are grateful to the Stiftung Volkswagenwerk, the Deutsche Forschungsgemeinschaft, and the Badische Anilin- & Soda-Fabrik AG. for their support of the investigations.

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Translated by Express Translation Service, London.

Circular Dichroism and Optical Rotatory Dispersion – Principles and Application to the Investigation of the Stereochemistry of Natural Products [1]

BY G. SNATZKE [*]

The principles of circular dichroism and of optical rotatory dispersion are described. Examples are given to illustrate the use of these methods for the determination of the configurations and conformations of natural and synthetic products. Some limitations of the octant rule are mentioned.

1. History

The phenomenon of optical activity was discovered by *Arago* [2] in 1811 whilst experimenting with quartz, and was subsequently studied in some depth by *Biot*. In 1815, *Biot* [3] found that this property is not peculiar to crystals, but is also exhibited by liquids such as oil of turpentine or a solution of camphor in alcohol. Two years later [4] he reported that the angle of rotation becomes greater when the measurement is carried out at shorter wavelengths; this observation laid the foundation for spectropolarimetry. Though a few prominent chemists and physicists later used this method, it remained largely unknown to those not specialized in it until about 1953.

Lowry [5] attributes the long period of stagnation to the invention of the Bunsen burner (1866), which made it extremely easy to produce (practically) monochromatic light, *i.e.* that of the sodium D-line (589 nm). Instead of using a monochromator, which had been particularly troublesome in the previous century, one had only to hold a piece of rock salt into the flame if one wanted to measure the optical rotation of a substance. Owing to the simplicity of this method, nearly all the earlier workers ignored the much more valuable information of a complete rotatory dispersion curve, and it is quite surprising that so many stereochemical problems were solved by $[\alpha]_D$ measurements alone [6].

The Bunsen burner was thus responsible for the delayed development of spectropolarimetry, and it was left to *Carl Djerassi* in the USA to bring it back to life in 1953. Within a few years, he and his co-workers carried out measurements on more substances [7] than had been investigated in all the preceding 140 years. This was partly made possible by the first commercial spectral polarimeter [8], which had two important characteristics: firstly, it allowed measurements to be extended into the UV range, so that the optical rotatory dispersion (ORD) could be measured even within the absorption bands of many chromophores, and secondly, the instrument was extremely simple to operate. A number of automatic recording spectropolarimeters are now commercially available [9], and such instruments are an essential part of the equipment of any natural products institute.

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[1] Based on a lecture delivered at several universities and research institutes, as well as at the Conference of the „Analytische Chemie" Group of the Gesellschaft Deutscher Chemiker in Berlin (Sept. 1967).

[2] *M. Arago*, Mém. Classe Sci. Math. Phys. Inst. Impér. France *12 I*, 93 (1811).

[3] *J. B. Biot*, Bull. Soc. philomath. Paris *1815*, 190.

[4] *J. B. Biot*, Mém. Acad. Roy. Sci. Inst. France *2* [2], 41 (1817).

[5] *T. M. Lowry*: Optical Rotatory Power. Republication, Dover Publications New York 1964, p. 105.

[6] A corresponding situation in UV spectroscopy would arise if conclusions about constitution were to be drawn from the molar absorption coefficient ε at a single wavelength, *e.g.* at 350 nm.

[7] *C. Djerassi*: Optical Rotatory Dispersion. McGraw-Hill, New York 1960.

[8] *H. Rudolph*, J. opt. Soc. America *45*, 50 (1955).

[9] For a review of commercial instruments see [10, 11]. Since the publication of these articles, a new version of the spectropolarimeter whose spectral range is extended toward shorter wavelengths has been placed on the market by Perkin-Elmer (Bodenseewerk, Überlingen).

[10] *G. Snatzke*, Z. Instrumentenkunde *75*, 111 (1967).

[11] *G. Snatzke*: Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry. Heyden & Son, London 1967. See the contribution by *F. Woldbye*, p. 85.

Circular dichroism (CD) was first observed in amethyst by *Haidinger*[12] in 1847. Circular dichroism in solutions was studied in particular by *Cotton*[13], who also found the phenomenological connection between CD and ORD. Owing to the more sophisticated equipment needed, however, CD measurements were even less used than ORD measurements, and they became common only after the introduction, about six years ago, of the first commercial instrument. This was the Dichrographe, which made use of the electro-optical (Pockels) effect[14]. Various instruments are now also available for the measurement of CD[9].

2. Fresnel Theory and Measured Quantities

2.1. Fresnel Theory

Linearly polarized light is characterized in that its electric vector is propagated in the form of a planar cosine vibration (Fig. 1)[15]. According to *Fresnel*[16, 17], a beam of linearly polarized light may be thought of as resulting from the superposition of two circularly polarized rays with opposite directions of rotation, but having the same wavelength and intensity. A beam of circularly polarized light is characterized in that the tip of the electric vector describes a helix (Fig. 2). Thus

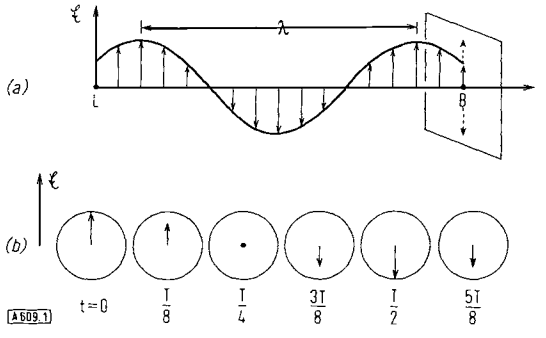


Fig. 1. Electric vector $\mathfrak{E}$ of a linearly polarized light beam. L is the ligh source, B the observer looking toward the light source. The straight line LB and its continuation beyond B is called the light path. (a) Dependence of the electric field strength $\mathfrak{E}$ on the distance at a given time t. (b) Dependence on time (at the observer's position B); T is the period of the vibration (defined by $T = \lambda/c$, c = velocity of light in vacuum).

an observer looking against a beam of linearly polarized light sees the vector varying its length in accordance with a cosine function, but vibrating always in the same

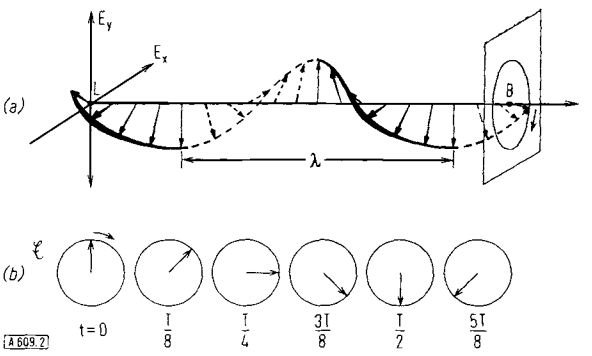


Fig. 2. Electric vector $\mathfrak{E}$ of a right-handed circularly polarized light beam. (a) Dependence of the field vector $\mathfrak{E}$, as well as its components E_x and E_y, on the distance at a given time t. (b) Dependence on time (at the observer's position B).

direction, whereas in the case of circularly polarized light the vector $\mathfrak{E}$ of constant length changes its direction proportional to time. For right-handed circularly polarized light, the tip of the vector runs clockwise, while for left-handed circularly polarized light it runs anticlockwise[18]. If the light source emits simultaneously in one direction coherent beams of left-handed and right-handed circularly polarized light of the same wavelength and intensity the superposition of the two produces a linearly polarized vibration. This can be shown easily either by calculation or by a vector diagram (Fig. 3).

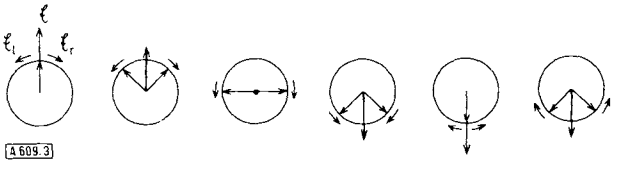


Fig. 3. Superposition of right-handed and left-handed circularly polarized light beams of same wavelengths and intensities emitted in phase by a light source. The sum of $\mathfrak{E}_l$ and $\mathfrak{E}_r$ gives a vector having the properties of a linearly polarized light beam.

If, on the other hand, the two beams propagate with different velocities (*i.e.* different wavelengths) through the medium under investigation, the resultant vector will not have a constant direction, but will make an angle with the original direction of vibration that increases with increasing distance traversed (Fig. 4).

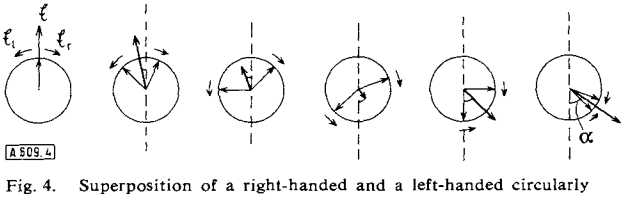


Fig. 4. Superposition of a right-handed and a left-handed circularly polarized light beam having different propagation velocities. As in Figure 3, these are all "snapshots" taken at the same time but at increasing distances from the light source. The right-handed circularly polarized beam is faster than the left-handed in this case.

Thus according to *Fresnel*, optical rotation is simply due to the difference in the velocities of right-handed and left-handed circularly polarized light in an "op-

[12] *W. Haidinger*, Poggendorfs Ann. *70*, 531 (1847).

[13] *A. M. Cotton*, Ann. Chim. Physique *8* [7], 347 (1896) and later publications.

[14] *M. Grosjean* and *M. Legrand*, C. R. hebd. Séances Acad. Sci. *251*, 2150 (1960).

[15] The plane in which the electric vector is propagated is generally known as the "vibration plane" of linearly polarized light. The corresponding magnetic vector is perpendicular to this plane.

[16] *A. Fresnel*, Memoirs No. XXVIII (1822), No. XXX (1823). However, most of this author's work was not published until the middle of the last century. See also [17].

[17] *P. Drude*: Lehrbuch der Optik. Hirzel, Leipzig 1900, p. 379.

[18] It can be seen from Figure 2 that the "screw" moves forward from L to B without turning, *i.e.* it is not screwed like a mechanical screw into its thread.

tically active medium", and the angle of rotation α (in radians) is given by the Fresnel equation

$$\alpha(\text{rad}) = \pi(n_l - n_r)l/\lambda_{vac}$$

(l: length of the tube, λ_{vac}: wavelength in vacuum, n_l and n_r: refractive indices for left-handed and right-handed circularly polarized light). The proportionality factor in this equation is called the "specific rotation", and conversion into degrees (which is more familiar to the chemist), taking into account the dependence on concentration in the case of solutions, gives

$$[\alpha]_\lambda^T = \alpha/(lc')$$

(l in dm, concentration c' in g/ml). λ and T are the wavelength and the temperature at which the measurement is carried out. In spectral polarimetry, however, it is customary to use the "molecular rotation" to

$$[\Phi] = ([\alpha] \times \text{molecular weight})/100$$

facilitate comparison *e.g.* of homologs.

2.2. Optical Rotatory Dispersion

If the angle of rotation α (or $[\alpha]$ or $[\Phi]$) is measured as a function of the wavelength, greater absolute values are obtained at shorter wavelengths (Fig. 5) – a behavior already found by *Biot*. This behavior is described as "plain curve" (normal ORD), and in spectral regions that are remote from the absorption bands, it can be expressed by a Drude equation

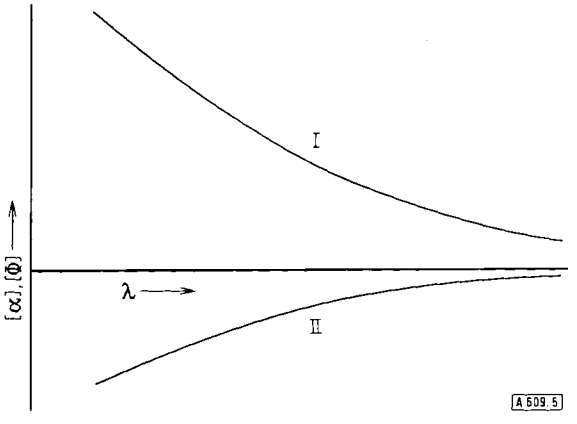


Fig. 5. Plain ORD curves of two optically active substances (I: dextrorotatory, II: levorotatory) in a spectral range in which no absorption takes place (schematic).

$$[\Phi] = \sum_i A_i/(\lambda^2 - \lambda_i^2)$$

(A_i and λ_i are constants).

2.3. Circular Dichroism and the Cotton Effect

In the region of an absorption band, left-handed and right-handed circularly polarized light are not only propagated with different velocities, but they are also absorbed to different extents. This behavior, which is known as "circular dichroism", is most simply described by the difference of the molar decadic absorption coefficients

$$\Delta\varepsilon = \varepsilon_l - \varepsilon_r$$

Calculations or a vector diagram similar to Figure 4 shows that as a result of circular dichroism, an S-shaped component is superimposed on the plain ORD curve in the region of the absorption band. A curve of this type is described as "anomalous ORD", and both effects, CD and anomalous ORD, are known as the "Cotton effect". If one of the two curves is known over the entire spectral range, the other can be calculated with the aid of the Kronig-Kramers transform [19].

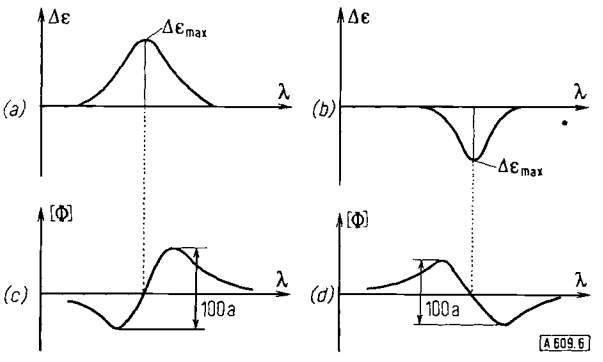


Fig. 6. Positive (a) and negative (b) CD with corresponding ORD partial curves (c) and (d).

Figure 6 shows that the maximum of a CD curve coincides with the point of inflection of the S-shaped part of the ORD curve; moreover, by going from long toward short wavelengths, in the case of positive CD the ORD curve first reaches a peak and then a trough, while for negative CD the trough appears before the peak [20] (*Natanson* [21] and *Bruhat* [22] rule).

Figure 7 shows the four possible types of Cotton effect ORD curves.

The CD is characterized by four quantities, *i.e.* $\Delta\varepsilon$ at the maximum ($\Delta\varepsilon_{max}$), λ_{max}, the sign, and the shape of the curve (*e.g.* fine structure). The same is true of an ORD curve, the magnitude in this case being described by the "amplitude", which is defined by

$$a = ([\Phi]_1 - [\Phi]_2)/100.$$

$[\Phi]_1$ in this expression refers to the extremum at longer wavelengths, $[\Phi]_2$ to that at shorter wavelengths of an anomalous curve. In the case of Gaussian-type CD curves, the approximation

$$a \approx 40\ \Delta\varepsilon_{max}$$

is valid.

[19] a) Cf., *e.g.*, *W. Moffit* and *A. Moscowitz*, J. chem. Physics *30*, 648 (1959); b) *C. A. Emeis, L. J. Oosterhoff*, and *G. de Vries*, Proc. Roy. Soc. (London) *A 297*, 54 (1967).

[20] To avoid confusion with UV curves, the terms peak and trough are used for ORD curves, and positive (or negative) maximum for CD curves.

[21] *L. Natanson*, Bull. Acad. Sci. (Kraków) *1908*, 764; J. Physique *8* [4], 321 (1909).

[22] *G. Bruhat*, Ann. Physique *3* [9], 232, 417 (1915); *13* [9], 25 (1920).

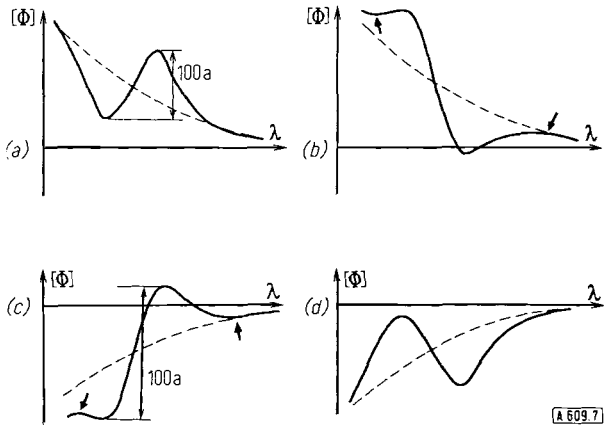


Fig. 7. The four possible types of actual ORD curve. (a) Positive and (b) negative Cotton effect with positive background rotation (plain ORD), (c) positive and (d) negative Cotton effect with negative background rotation. Arrows indicate "pseudo-extremes".

It can be seen by comparison of Figure 7 with Figure 6 that the distance from the peak to the trough of a real ORD curve does not exactly correspond to 100*a* (defined as shown in Figure 6); the difference in the background rotations at λ_1 and λ_2 should be introduced as a correction, but this is seldom done.

When a light beam that was originally linearly polarized leaves a medium that exhibits a Cotton effect in the range under investigation, it is elliptically polarized. This can be seen from the vector diagram (Fig. 8). Owing to the difference

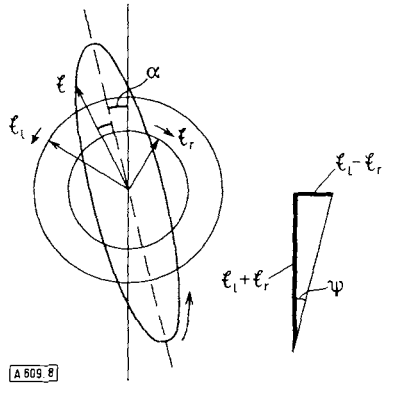


Fig. 8. Ellipticity. On emerging from a substance exhibiting circular dichroism, $\mathfrak{E}_l$ is different from $\mathfrak{E}_r$; the tip of the resultant vector consequently describes an ellipse (which is very narrow in practice). This representation shows the behavior of the resultant vector at a given point as a function of time. The principal axis of the ellipse forms the angle of rotation α with the original direction.

in the absorptions of left-handed and right-handed circularly polarized light, the vectors $\mathfrak{E}_l$ and $\mathfrak{E}_r$ now have different magnitudes (the intensity of a light beam is given by the square of its amplitude), and the tip of the resultant vector consequently follows an elliptical path. Its shape is decribed by the ellipticity ψ where *a* is the major axis and *b* the minor

$$\psi = \arctan(b/a)$$

axis of the ellipse. In analogy with the quantities related to rotation, one can define a specific ellipticity

$$[\psi] = \psi/lc'$$

and a molecular ellipticity

$$[\theta] = ([\psi] \times \text{molecular weight})/100$$

the latter being related to $\Delta\varepsilon$ by the equation

$$[\theta] \approx 3300\ \Delta\varepsilon_{max}.$$

Finally, mention must also be made of the rotatory (or rotational) strength, which is useful in quantitative calculations. It is defined [19] on the basis of the dipole strength [23] by

$$R = \frac{3\,hc\,10^3 ln\,10}{32\,\pi^3 N} \int \frac{\Delta\varepsilon}{\nu}\,d\nu$$

Thus a Cotton effect can be characterized either by measurement of an angle (determination of $[\Phi]_{peak}$ and $[\Phi]_{trough}$) or by a differential absorption measurement ($\Delta\varepsilon_{max}$). In all cases in which it is possible to make measurements in the region of absorption bands the interpretation of the CD is easier, since its half-band width is smaller than that of an anomalous ORD curve. In the investigation of chromophores that absorb in an inaccessible region, on the other hand, the ORD measurement must be used. The advantages and disadvantages of the two methods have been compared by several authors [24]; for details of equipment, the reader is referred to other reviews [11, 12, 25].

3. Relationship Between the Cotton Effect and Stereochemistry

3.1. Conditions for the Occurrence of a Cotton Effect

Pasteur [26] had already recognized that the condition for the occurrence of optical activity in solution is "molecular dissymmetry", *i.e.* that a molecule cannot be converted into its mirror image by mere rotation. A compound of this type is now described as "chiral" [27], the geometric condition for this being that the molecule (on time average in the case of a conformational equilibrium) should not have a rotation-reflection axis [28] S_p.

A Cotton effect is associated with the presence of a chromophore, and according to *Moscowitz* [29], it is possible to differentiate between two types of chromophores, *i.e.* "inherently (or intrinsically) dissymmetric" chromophores and chromophores having local symmetry, but being dissymmetrically perturbed. When light is absorbed, one electron is excited from a (doubly) occupied orbital into an unoccupied antibonding orbital, and if these two orbitals (owing to a suitable skeleton) are chiral, a strong Cotton effect is

[23] *R. S. Mulliken*, J. chem. Physics *7*, 14 (1939).

[24] Cf., *e.g.*, *P. Crabbé*, Tetrahedron *20*, 1211 (1964); Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry. Holden-Day, San Francisco, 1965; *P. Crabbé* [11], p. 126.

[25] *W. Heller* in *A. Weissberger*: Physical Methods of Organic Chemistry. Interscience, New York 1960, Vol. 1/3, p. 2147.

[26] *L. Pasteur*, Ann. Chim. Physique *24*, [3], 443 (1848).

[27] *R. S. Cahn, C. K. Ingold*, and *V. Prelog*, Angew. Chem. *78*, 413 (1966); Angew. Chem. internat. Edit. *5*, 385 (1966).

[28] This condition implies that the molecule must not contain either a reflection plane ($\equiv S_1$) or center of inversion ($\equiv S_2$).

[29] *A. Moscowitz*, Tetrahedron *13*, 48 (1961).

to be expected on interaction with the light beam. The rotatory strength of such inherently dissymmetric chromophores can assume a value of 10^{-38} cgs units. Some examples are shown in Figure 9.

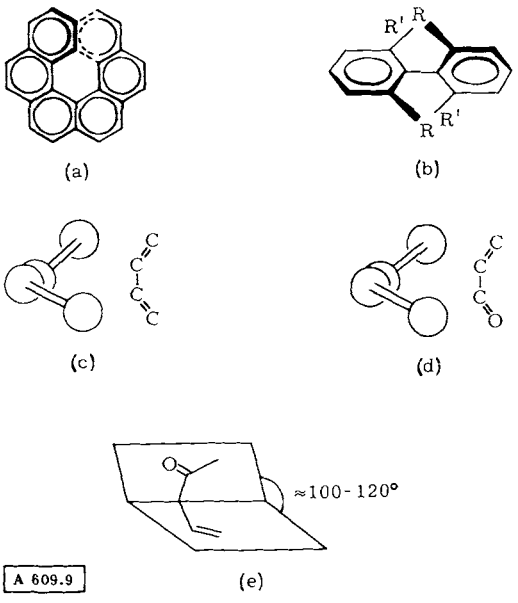


Fig. 9. Examples of inherently dissymmetric chromophores. (a) Hexahelicene, (b) biphenyl derivatives (conjugation band), (c) nonplanar conjugated dienes, (d) conjugated nonplanar enones (K-band), (e) β,γ-unsaturated ketones of suitable geometry (R-band).

For example, hexahelicene cannot have a planar structure, but must be helical. This means that the π system is also chiral, resulting in a $\Delta\varepsilon_{max}$ of over 100[30]. Biphenyls exhibit several bands, some of which correspond to local excitations (within the π system of one of the two rings), while others are due to the entire 12 π system. When the biphenyl skeleton is nonplanar, the compounds are also inherently dissymmetric[31]. A special case is that of β,γ-unsaturated ketones in which the π orbital of the C=C bond can overlap simultaneously and chirally with the p orbital and the π* orbital of the C=O group. These compounds have long been known to give enhanced extinction in the UV region[32], and the Cotton effect can again assume very high values[33].

However, most chromophores possess local symmetry (plane of symmetry). Their electron system is thus achiral, and should interfere equally with a beam of left-handed and right-handed circularly polarized light. If chromophores of this type (cf. Fig. 10) are incorporated into a chiral environment, however, as is *e.g.* the keto group in camphor, there is still at least some dissymmetric perturbance of the otherwise symmetric orbitals, which again gives rise to a Cotton effect. Chromophores of this type, some of which are shown in Figure 10, are known as "inherently symmetric but dissymmetrically perturbed" chromophores. Their rotatory strength does not generally exceed about 10^{-40} cgs units.

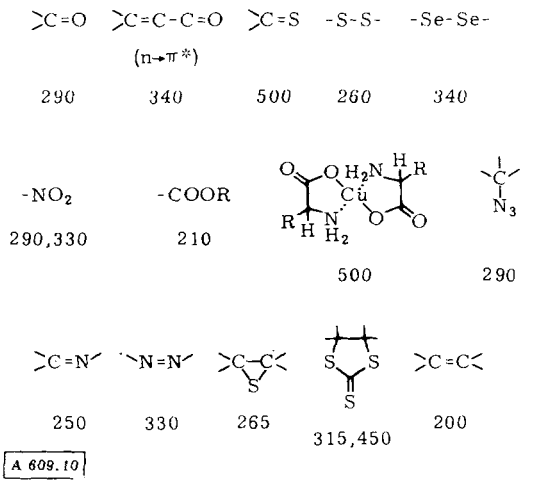


Fig. 10. Examples of inherently symmetrical but dissymmetrically perturbed chromophores. The numbers under the formulas indicate the absorption regions.

Finally, compounds having no chromophore (in the usual sense) can be successfully studied by conversion into derivatives that give a Cotton effect ("Cottonogenic derivatives"). Some of these are shown in Figure 11.

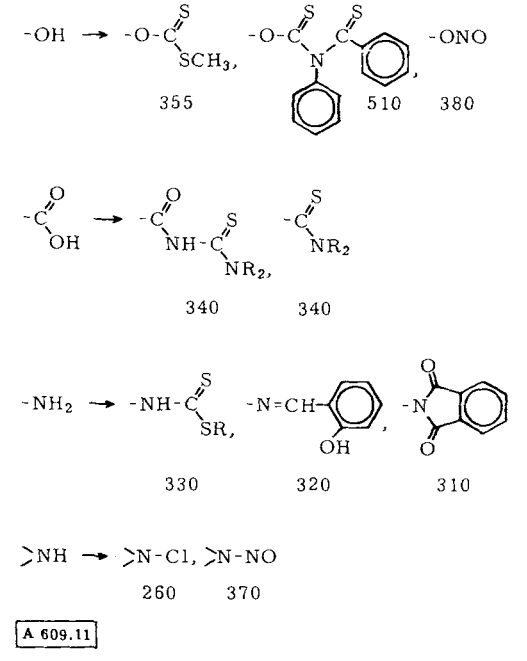


Fig. 11. Some "cottonogenic derivatives" of alcohols, acids, and amines. The numbers under the formulas indicate the absorption regions.

3.2. Sign of the Cotton Effect and Geometry of the Molecule

To find a relationship between the sign (and possibly the magnitude) of the Cotton effect and the geometry of the molecule, it is possible to proceed by one of three paths, one empirical, one semiempirical, and the third theoretical. Two examples will be given to illustrate the empirical procedure. We have found[34] that the salicylidene derivatives of 3-amino steroids

[30] *A. Moscowitz*, Dissertation, Harvard University 1957.

[31] Cf., *e.g.*, *J. Cymerman Craig* and *S. K. Roy*, Tetrahedron *21*, 395 (1965).

[32] *H. Labhart* and *G. Wagnière*, Helv. chim. Acta *42*, 2219 (1959).

[33] *A. Moscowitz*, *A. E. Hansen*, *L. S. Foster*, and *K. Rosenheck*, Biopolymers Symposia *1*, 75 (1964); *A. Moscowitz*, Proc. Roy. Soc. (London) *A 297*, 40 (1967).

[34] *H. Ripperger*, *K. Schreiber*, *G. Snatzke*, and *K. Heller*, Z. Chem. *5*, 62 (1965).

give a positive CD around 320 nm when the NH_2 group is in the β position [*(1)*, *(2)*] and a negative CD when the NH_2 is in the α position [*(3)*, *(4)*], irrespective of whether the linkage of rings A and B is *cis* or *trans* (Fig. 12). Similarly, the stereochemistry of an OH group on C-20 of pregnan-20-ol derivatives can be established from the sign of the Cotton effect of the *O*-nitroso derivative at about 370 nm [35] (Fig. 13).

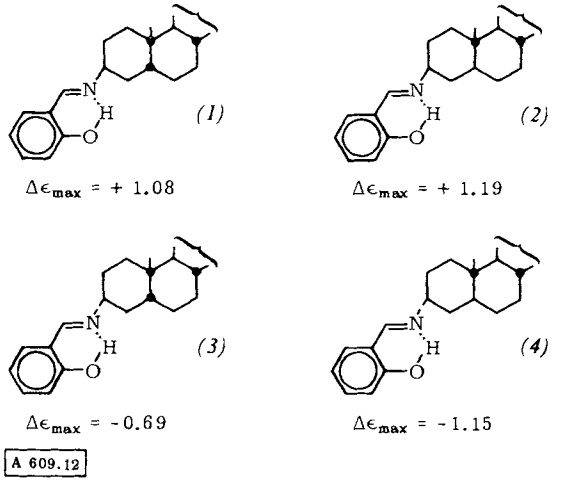


Fig. 12. $\Delta\varepsilon_{max}$ values for the 3-(salicylidenamino) steroids *(1)*–*(4)*.

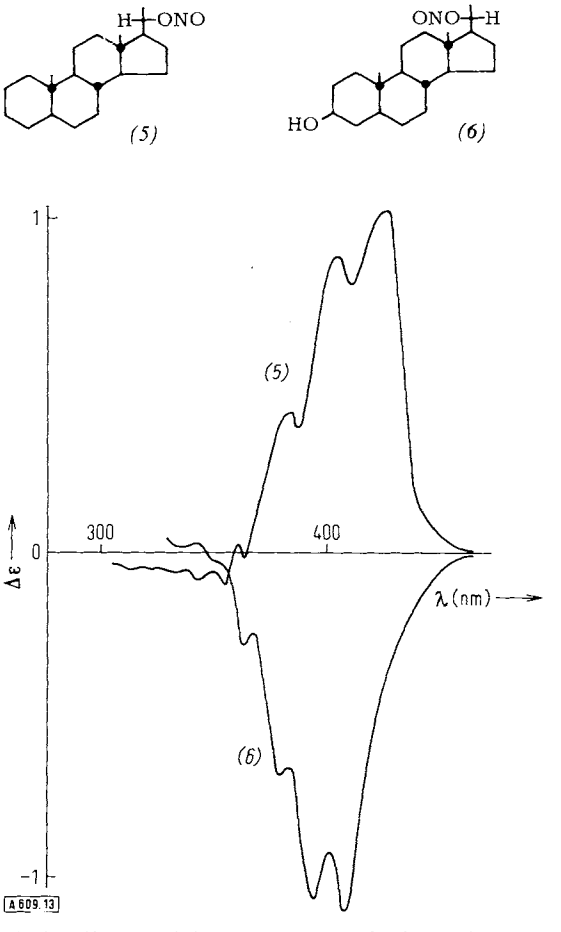


Fig. 13. CD of the nitrites of a 5α-pregnan-20α-ol *(5)* and a 5α-pregnan-20β-ol *(6)*.

[35] *M. Legrand* and *R. Viennet*, C. R. hebd. Séances Acad. Sci. *255*, 2985 (1962); *C. Djerassi, H. Wolf*, and *E. Bunnenberg*, J. Amer. chem. Soc. *85*, 2835 (1963).

The principle of the theoretical route can just be touched upon in this review. According to the theory of optical activity [36], the rotatory strength of a band is given by the equation

$$R = \mu_e \mu_m \cos\gamma$$

where μ_e is the electric and μ_m the magnetic transition moment vector during the excitation of the electron, and γ is the angle between these two moments. If these quantities can be calculated *ab initio*, it is possible to predict at least the sign of the Cotton effect for a given geometry, since it follows from the cosine function that parallel moments lead to a positive CD and antiparallel moments to a negative CD.

This calculation will be illustrated qualitatively for the α-helix of polypeptides or proteins [37]. Each turn of the α-helix contains 3.6 amide groups, and the direction of the transition moment vectors is known for the K-band of these amide groups (Fig. 14a).

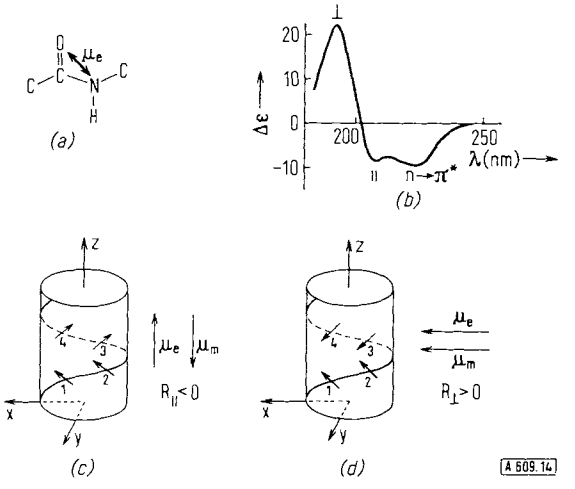


Fig. 14. Determination of the sign of the Cotton effect of the amide bands in an α-helix. (a) Direction of μ_e of the amide group [38], (b) observed CD of poly-L-glutamic acid at pH = 4.3 [39], (c) direction of the transition moment vectors for the band polarized parallel to the axis, (d) direction of the transition moment vectors for one of the two bands polarized perpendicular to the axis. (For details see text.)

According to exciton theory, the amide groups cannot be excited independently of one another, and coupling takes place over the entire chain. Only three coupled vibrations are possible: either all the transitions are in phase or the transitions of each adjacent pair are in phase opposition. This is indicated in Figures 14c and 14d by the direction of the arrows, each of which represents an amide unit. In 14d there are two possibilities, *i.e.* "1" and "2" upward and "3" and "4" downward, or else "2" and "3" upward and "4" and "1" downward. Only one case is shown in the diagram.

The electric transition moment vectors add up in 14c to give a resultant vector in the *z* direction, whereas in 14d they give a total moment perpendicular to the axis (*e.g.* in the *x* direction in this case). This displacement of electronic charges is associated with a magnetic transition moment vector. If one looks along the axis in 14c (in the positive *z* direction), the arrows are arranged anticlockwise; according to the right-hand rule, this corresponds to a magnetic moment vector

[36] *L. Rosenfeld*, Z. Physik *52*, 161 (1928); *E. Condon, W. Altar*, and *H. Eyring*, J. chem. Physics *5*, 753 (1937); *E. Hückel*, Z. Elektrochem. angew. physik. Chem. *50*, 13 (1944).

[37] This simplified description follows a rigorous derivation, which is given in a review by *A. D. McLachlan*, Proc. Roy. Soc. (London) *A 297*, 131 (1967). Further original literature is also cited in this review.

[38] *D. L. Peterson* and *W. T. Simpson*, J. Amer. chem. Soc. *77*, 3929 (1955).

[39] *L. Velluz* and *M. Legrand*, Angew. Chem. *77*, 842 (1965); Angew. Chem. internat. Edit. *4*, 838 (1965).

that opposes μ_e. Thus in the case of a right-handed helix, as in Figure 14c, the above formula shows that the band, which is polarized parallel to the axis of the helix (since the total moment μ_e is parallel to this axis) must give a negative Cotton effect. A similar argumentation applied to 14d shows that in this case the two moments are parallel to each other, so that the two bands, which are polarized perpendicular to the axis, must have a positive sign.

The exciton theory also states that the bands polarized perpendicular to the axis must lie at shorter wavelengths than those polarized parallel to the axis, so that the CD curve of poly-L-glutamic acid, which is shown in Figure 14b[39], must correspond to a right-handed helix[40]. At a time when CD measurements were still difficult, *Moffitt*[41] deduced an equation for the ORD curve from these relationships:

$$[\Phi]_{pu}\frac{3}{n^2+2} = a_0\frac{\lambda_0^2}{\lambda^2-\lambda_0^2} + b_0\frac{\lambda_0^2}{(\lambda^2-\lambda_0^2)^2}$$

($[\Phi]_{pn}$: molecular rotation per amino acid unit, n: refractive index of the solvent; a_0, b_0, and λ_0 are constants), in which b_0 assumes a value of about -600 when the polypeptide is entirely in the form of a right-handed α-helix[42].

Great success has been achieved in the establishment of semiempirical rules that predict, on the basis of theoretical considerations, the change in the sign of the contribution of a substituent to the Cotton effect when the position of this group in relation to the chromophore is varied, and in which the sign itself is found from experimental data. This may be illustrated by the octant rule[43], although several *ab initio* calculations now exist for this rule.

Saturated ketones exhibit a weak band at about 300 nm due to an n → π* transition. The n orbital has a nodal plane, which is identical with the (x,z) plane. For the π* orbital, the (y,z) plane and another surface perpendicular to this, intersecting the O=C bond roughly in the middle, are nodal surfaces (Fig. 15). For the sake of simplicity, this third nodal surface is also drawn as a plane. These three surfaces divide the space around the ketone (in our example a cyclohexanone) into eight octants, the four more important rear octants of which are shown in Figure 15d in an "octant projection". The viewing direction is from the O toward the C of the carbonyl group. If the dissymmetric perturbance of the carbonyl chromophore, which is by itself symmetric, is due to Coulomb interactions of the incompletely screened nuclei of the molecule, the contributions to the Cotton effect of two substituents in adjacent octants must according to the theory[19a,44] have opposite signs.

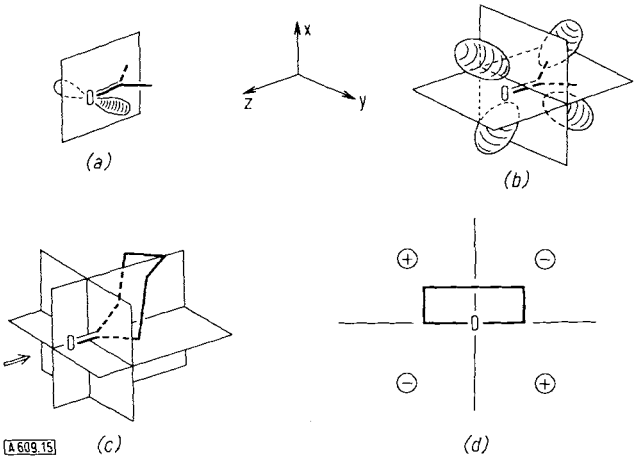


Fig. 15. Octant rule for saturated cyclohexanones (with c_s symmetry). (a) Nodal plane of the n orbital, (b) nodal surfaces of the π* orbital, (c) the eight octants formed by the three nodal surfaces, (d) signs for the four rear octants by projecting from O toward C of the carbonyl group.

The large volume of data available, which was obtained in particular in the laboratories of *Djerassi*, *Klyne*, and *Ourisson*, made it possible to establish the signs as shown in Figure 15d. These have also been deduced theoretically[19a,44]. Nevertheless, the octant rule is mentioned here as a semiempirical method, since other theoretical calculations lead only to a quadrant rule[45]. On the basis of the extensive material available, however, there can be no doubt about the change in sign on passage to the front octants.

Pao and *Santry*[46] very recently carried out another calculation that leads to division into twelve sectors. A further nodal surface is added to those already mentioned. Figure 16 shows a projection from above onto the (y,z) surface (*i.e.* not the usual octant representation), according to which the contribution of

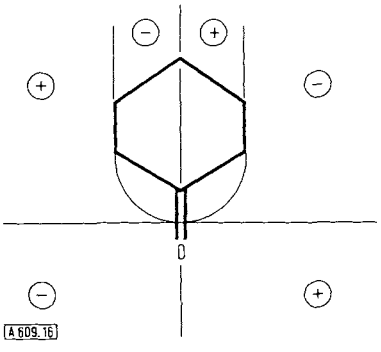


Fig. 16. Upper sectors for ketones according to *Pao* and *Santry* [46].

an axial substituent β to the carbonyl group should give a sign opposite to that found by the octant rule. Our investigations on optically active adamantanone derivatives[47] have now shown that a COOR group chlorine, bromine, or iodine in this position actually gives the "wrong" contribution. It is not yet known whether this means that the octant rule will have to be modified, or whether this "antioctant behavior" has to be attributed to the strong polarity of these groups.

[40] The band at 224 nm is due to a n→π* excitation of the amide group.

[41] *W. Moffit*, J. chem. Physics *25*, 467 (1956); Proc. nat. Acad. Sci. USA *42*, 736 (1956); *W. Moffit* and *J. T. Yang*, *ibid. 42*, 596 (1956).

[42] For a detailed treatment of the determination of "% helix content" of a polypeptide, cf. *e.g. E. R. Blout*, *J. P. Carver*, and *E. Schechter* in [11], p. 224.

[43] *W. Moffitt*, *R. B. Woodward*, *A. Moscowitz*, *W. Klyne*, and *C. Djerassi*, J. Amer. chem. Soc. *83*, 4013 (1961).

[44] *A. Moscowitz*, Advances chem. Physics *4*, 67 (1962).

[45] *G. Wagnière*, J. Amer. chem. Soc. *88*, 3937 (1966). A more recent theoretical treatment based on a model of dynamic coupling also gives an octant rule with the correct signs: *O. E. Weigang jr.*, and *E. G. Höhn*, *ibid. 88*, 3673 (1966).

[46] *Y.-H. Pao* and *D. P. Santry*, J. Amer. chem. Soc. *88*, 4157 (1966).

[47] *G. Snatzke*, *G. Eckhardt*, and *B. Ehrig*, unpublished.

4. Examples from the Natural Products Field

The success of the octant rule will now be illustrated by a classical example[43] (Fig. 17). 5α-Cholestan-2-one *(7)* and 5α-cholestan-3-one *(8)* exhibit a positive Cotton effect, which is roughly twice as large for *(7)* as for *(8)*. This can be readily explained by the octant rule. In the 3-oxo compound *(8)*, the contributions of the atoms of rings A and C cancel out on grounds of symmetry, and the two methyl groups lie in the (*x*,*z*) nodal surface, so that only the methylene groups C-6 and C-7 (and the groups C-15 and C-16, which are very remote from the chromophore) contribute to the Cotton effect. According to Figure 15d, these contributions should be positive. In the 2-oxo compound *(7)*, on the other hand, all the C atoms except those of ring A (which are disregarded on symmetry grounds) and C-6 lie in the rear upper left octant, and so give rise to the high positive Cotton effect.

The Cotton effect is not always sufficiently large to permit a definite interpretation. Thus tetrahydroionone *(9)*[48] gives practically no effect at room temperature, since the side chain containing the chromophore can assume different conformations, which differ only slightly in their energy content, with the result that the contributions to the Cotton effect are

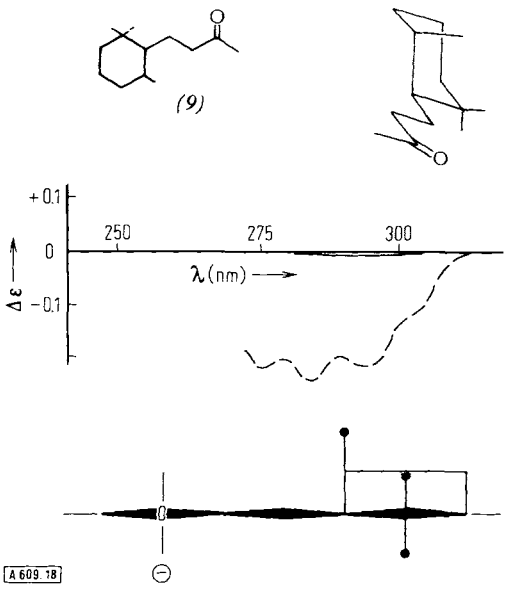


Fig. 18. Most stable conformation of tetrahydroionone *(9)* and its octant projection, as well as the observed CD at 20 °C (—) and −179 °C (– – –).

such as solvation complexes. Practically all our results for the variation of the CD with temperature support this assumption.

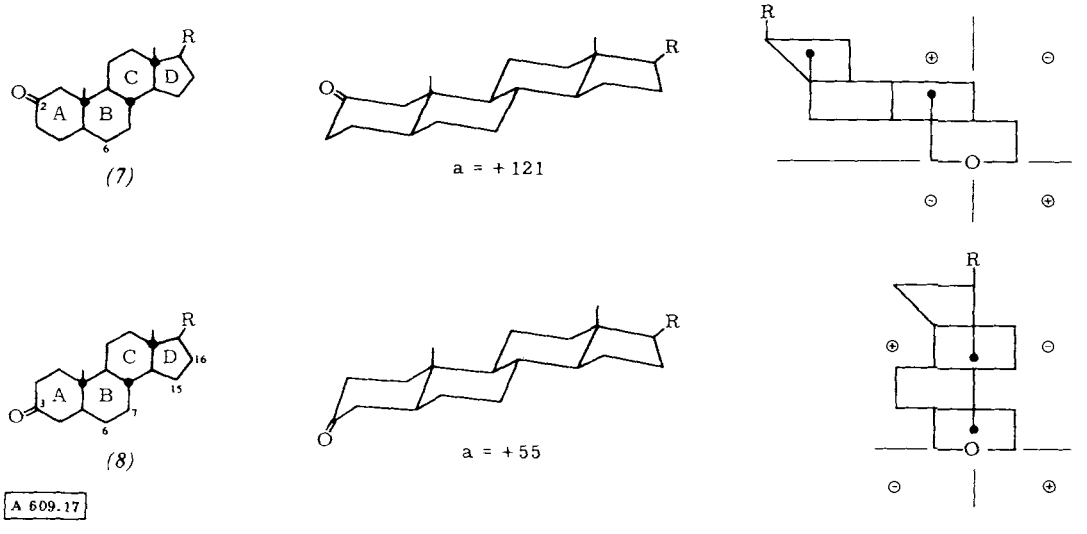


Fig. 17. Stereoformulas and octant projections of the steroids *(7)* and *(8)*.

substantially compensated. However, if the solution is cooled to a sufficiently low temperature, the population of the conformation with the lowest free energy must steadily increase[49], and a distinctly measurable CD was in fact found at −179 °C (Fig. 18). If the chair form of the ring and the equatorial position and zigzag form of the side chain are assumed to be most stable, a negative CD would actually be predicted by the octant rule. However, this interpretation is based on the assumption that the change in the CD with temperature is due only to the displacement of the conformational equilibria, and is not connected with other factors

A limiting case for the application of the octant rule is found in the compounds *(10)* through *(12)* (Fig. 19). Tetrahydropyranone *(10)*[48] exhibits a weak negative CD at room temperature, which increases by a factor of more than two when the temperature is lowered.

If one again assumes a chair conformation for the heterocyclic ring, there are two possibilities, *i.e.* an equatorial vinyl group and an axial methyl group and *vice versa*. If the vinyl group (at least on the fully substituted C atom) is assumed to be bulkier than the methyl group, one obtains a projection as shown in Figure 19 (R = vinyl as the equatorial substituent). The only group that can contribute to the Cotton effect is one of the two geminal methyl groups, which lies in a negative octant, in agreement with the observed negative CD.

However, it is doubtful whether the replacement of CH_2 by O in the ring itself has no appreciable effect. The CD of the

[48] I am grateful to Dr. *G. Ohloff*, Firmenich & Cie, Geneva, for supplying this substance. The sign of the Cotton effect of compound *(10)* has already been described by *M. Mousseron-Canet* and *C. Levallois*, Bull. Soc. chim. France *1965*, 1339.

[49] In an equilibrium between two conformers whose free energies differ *e.g.* by 0.65 kcal/mole (with $\Delta S = 0$), 25% of the less stable isomer are present at 25 °C, but only 1.9% at −190 °C, *i.e.* at this temperature the more stable isomer is present practically alone in the solution.

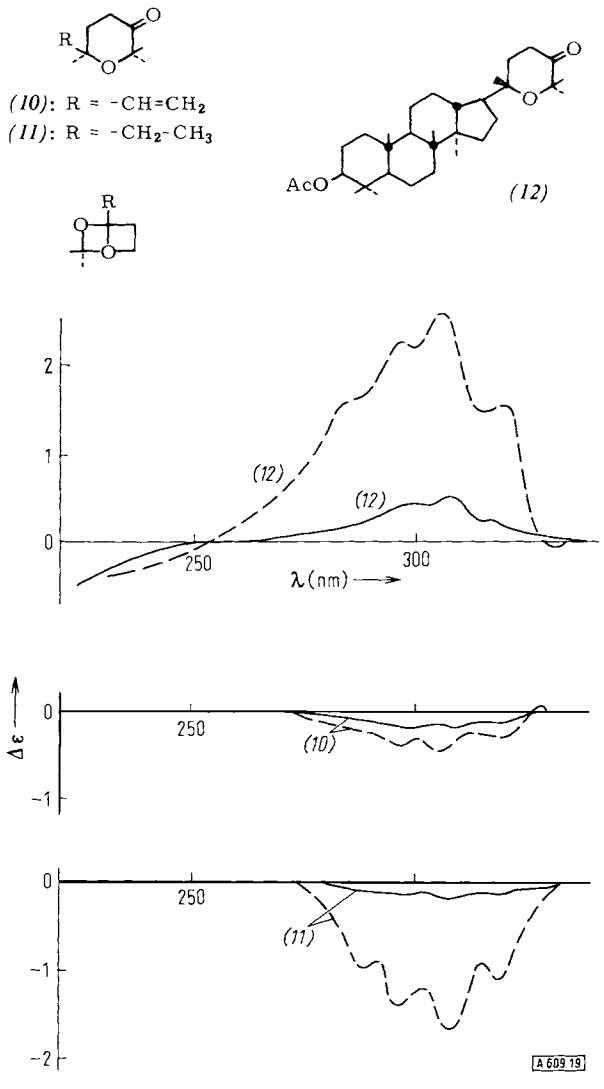


Fig. 19. CD of *(10)* through *(12)* at 20 °C (—) and −180 °C(— — —) and octant projection of *(10)* and *(11)*.

saturated compound *(11)* seems to support this, as the ethyl group now definitely occupies the equatorial position, and according to its greater size, the CD is greater in *(11)*. Even without the use of the octant rule, which is problematic in this case, it is possible to deduce from the positive CD of the degradation product *(12)* of dipterocarpol [50] that the configuration of the latter at the quaternary carbon adjacent to the ring oxygen is opposite to that of *(10)* and *(11)*; this supports the configuration assigned [50] to C-20.

A good insight into conformational equilibria was also provided by the perhydroazulene derivative *(13)* [51], which is closely related to the sesquiterpenes. It had been shown by X-ray analysis [52] that this molecule occurs in the crystal in a conformation having an equatorial bromine. According to the octant projection (Fig. 20), one should expect a positive CD for this compound. However, a negative CD is actually found in solution [51], the maximum occurring at 315 nm (in methylcyclohexane/isopentane 1:3 v/v), which indi-

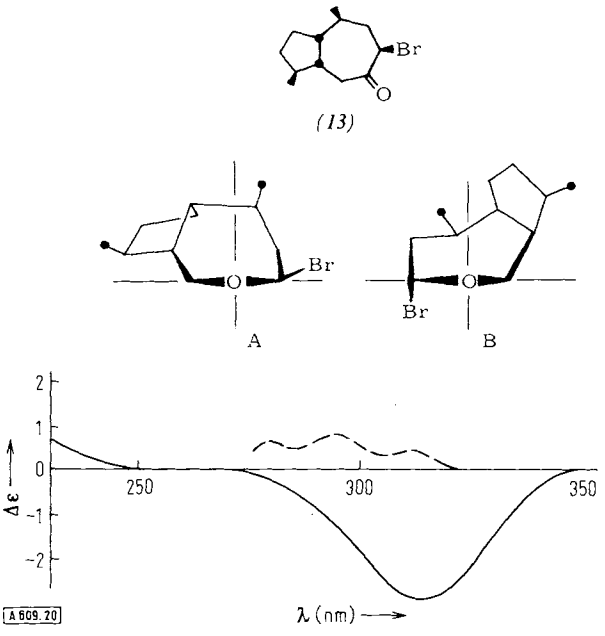


Fig. 20. CD of the bromo ketone *(13)* at +20 °C (—) and −180 °C (— — —) and octant projection of two conformers A and B.

cates that the bromine is axial [53]. According to the "axial α-haloketone rule" [54], this points to a conformation such as B (Fig. 20). The question now was whether the conformation A (Fig. 20) occurring in the crystal was really the most stable, or whether it was a somewhat less favorable arrangement stabilized *e.g.* by lattice forces. Measurement at −180 °C led to reversal of the sign of the CD with a simultaneous shift of λ_{max} to 294 nm, which is characteristic of equatorial bromine [53]. This CD, which is in agreement with the projection A, shows that A actually has the lower energy content; however, conformation B cannot be much less stable. The same conclusion could be reached from CD measurements in various solvents [51].

Though most of the investigations described so far have been concerned with ketones, the Cotton effect can also be used to determine the configurations or conformations of other chromophores. While the Cotton effect of saturated lactones cannot always be unequivocally deduced from the structure [55], the situation is much more favorable for unsaturated and epoxy lactones, since the findings for the corresponding ketones [56] are also applicable to these compounds [57]. It must be remembered, however, that the −C−CO−O- grouping is coplanar, as is shown by X-ray studies (in

[50] *J.-F. Biellmann*, Tetrahedron Letters *1966*, 4803. I wish to thank Dr. *Biellmann*, Strasbourg, for a sample of this substance.

[51] *K. Kuriyama, T. Iwata, M. Moriyama, M. Ishikawa, H. Minato*, and *K. Takeda*, J. chem. Soc. (London) (C) *1967*, 420.

[52] *T. Sato, H. Minato, M. Shiro*, and *H. Koyama*, Chem. Commun. *1966*, 363.

[53] *R. C. Cookson*, J. chem. Soc. (London) *1954*, 282; *R. C. Cookson* and *S. H. Dandegaonker, ibid. 1955*, 352.

[54] *C. Djerassi* and *W. Klyne*, J. Amer. chem. Soc. *79*, 1506 (1957).

[55] *J. P. Jennings, W. Klyne*, and *P. M. Scopes*, J. chem. Soc. (London) *1965*, 7211, 7229; *H. Wolf*, Tetrahedron Letters *1966*, 5151; *G. Snatzke, H. Ripperger, C. Horstmann*, and *K. Schreiber*, Tetrahedron *22*, 3103 (1966); *K. Kuriyama* in [11], p. 366; *M. Legrand* and *R. Boucourt*, Bull. Soc. chim. France *1967*, 2241.

[56] *G. Snatzke*, Tetrahedron *21*, 413, 421, 439 (1965).

[57] *G. Snatzke, H. Schwang*, and *P. Welzel* in *R. Bonnett* and *J. G. Davis*; Some Newer Physical Methods in Structural Chemistry. United Trade Press, London 1967, p. 159.

the solid state)[58]. This may be illustrated by the case of parasorbic acid *(14)*, in which the methyl group is known from NMR measurements to be equatorial[59]. Figure 21 shows the projection of parasorbic acid;

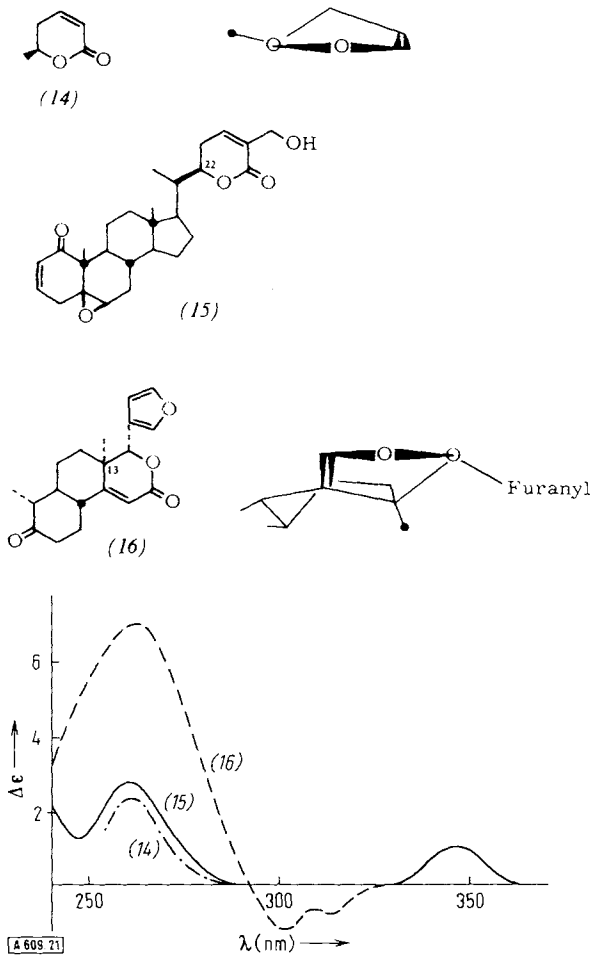


Fig. 21. Projection and CD (at 20 °C) of parasorbic acid *(14)* (—·—·—), CD of jaborosolactone A *(15)* (—), and projection and CD of odoratin *(16)* (— — —).

according to the corresponding rules for ketones[56], the chirality of the nonplanar enone systems gives a positive Cotton effect. A positive CD was also found[60] for jaborosolactone A *(15)*, in which the "steroid substituent" of the enelactone must again be equatorial; this fixes the stereochemistry at C-22 in the side chain[61]. Finally, the positive CD at 264 nm in odoratin *(16)* helped to establish the stereochemistry at C-13 (13α), which had already been deduced from biogenetic considerations[62].

Cyclopentenones show opposite signs for the CD of the n→π* band[56] to that of cyclohexenones of identical chirality of the enone system. This rule is again applicable to the corresponding enelactones[57], and was used to determine the absolute configuration of loliolide (digiprolactone) *(17)*[63] (Fig. 22)[57]. No sign could be predicted according to the octant rule from the CD of its oxidation product *(18)*, since the contribution of a methyl group had to be balanced against that of a lactone group.

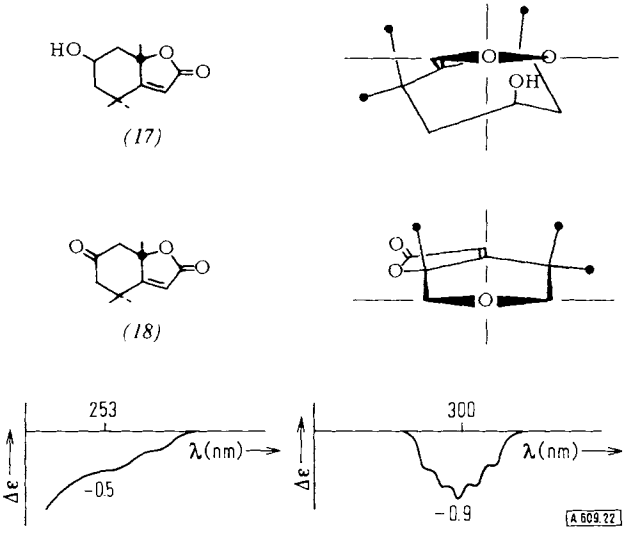
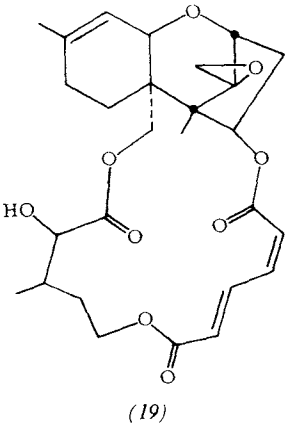


Fig. 22. Projection of loliolide (digiprolactone) *(17)* and its oxidation product *(18)*; CD of *(17)* (left) and of *(18)* (right).

In the above lactone examples, the conformation was known and the configuration was determined from the CD. The reverse was true in the case of verrucarin A *(19)*[64], in which the only detectable chromophore is a muconic acid unit. Molecular models indicate that the mobility of the large lactone ring is very restricted, and two bands are in fact found for *(19)* at 288 and 255 nm (Fig. 23)[65]. The first of these corresponds to the n→π* band of the muconic acid chromophore, which is not clearly recognizable in the UV spectrum, and the two ester groups may, to a first approximation,



[58] *A. McL. Mathieson* and *J. C. Taylor*, Tetrahedron Letters *1961*, 590; *J. F. McConnell*, *A. McL. Mathieson*, and *B. P. Schoenborn*, *ibid. 1962*, 445; *A. McL. Mathieson*, *ibid. 1963*, 81; *K. K. Cheung*, *K. H. Overton*, and *G. A. Sim*, Chem. Commun. *1965*, 634; cf., however, *G. A. Jeffrey* and *S. H. Kim*, *ibid. 1966*, 211.

[59] *J. A. Elvidge* and *P. D. Ralph*, J. chem. Soc. (London) (B) *1966*, 243.

[60] *R. Tschesche*, *H. Schwang*, *H.-W. Fehlhaber*, and *G. Snatzke*, Tetrahedron *22*, 1129 (1966).

[61] The hydroxyl group does not interfere, as can be seen from the fact that the CD of a deoxy derivative that is hydrogenated except in the side chain is completely analogous [57, 60].

[62] *W. R. Chan*, *D. R. Taylor*, and *R. T. Aplin*, Chem. Commun. *1966*, 576.

[63] *T. Wada*, Chem. pharmac. Bull. (Tokyo) *12*, 1117 (1964); *R. Hodges* and *A. L. Porte*, Tetrahedron *20*, 1463 (1964).

[64] *J. Gutzwiller* and *Ch. Tamm*, Helv. chim. Acta *48*, 157 (1965).

[65] *G. Snatzke* and *Ch. Tamm*, Helv. chim. Acta *50*, 1618 (1967).

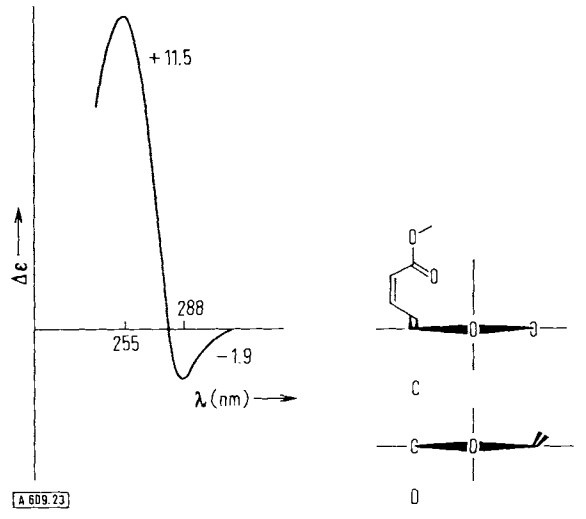


Fig. 23. Projection of the transoid (C) and the cisoid (D) enelactone group of the muconic acid part of verrucarin A *(19)* and CD of *(19)*. The deviation from coplanarity is exaggerated in C to facilitate drawing.

be regarded as separate partial chromophores. According to X-ray analysis [66], one of the enester groups is in the cisoid conformation (strongly angular), while the other is in the transoid conformation (almost planar). If we again apply the rules for the corresponding enones, we would expect a negative CD for both conformations, as is in fact found (Fig. 23). Conversely, it must be concluded from this value that the large ring in verrucarin A *(19)* (at least in the muconic acid region) has the same conformation in solution as in the crystalline state.

A chromophore that has been extensively studied both experimentally [67] and theoretically [68] is the nonplanar cisoid diene system. If this is arranged as a right-handed helix, it gives a positive Cotton effect, while a left-handed helix gives a negative Cotton effect. α-Phellandrene *(20)* seemed at first sight to be an exception to this rule, since it gives a negative Cotton effect [69], which would mean that the isopropyl group occupies a quasi-axial and not a quasi-equatorial conformation. It was therefore assumed that owing to the small difference in the energies of the two conformers, the less favorable conformation already had a higher population at room temperature; this assumption was supported by the temperature-dependence of the ORD amplitude between 10 and 90 °C [70]. It was therefore expected that the sign of the Cotton effect would be reversed at lower temperatures, as was in fact found below about −150 °C [71] (Fig. 24).

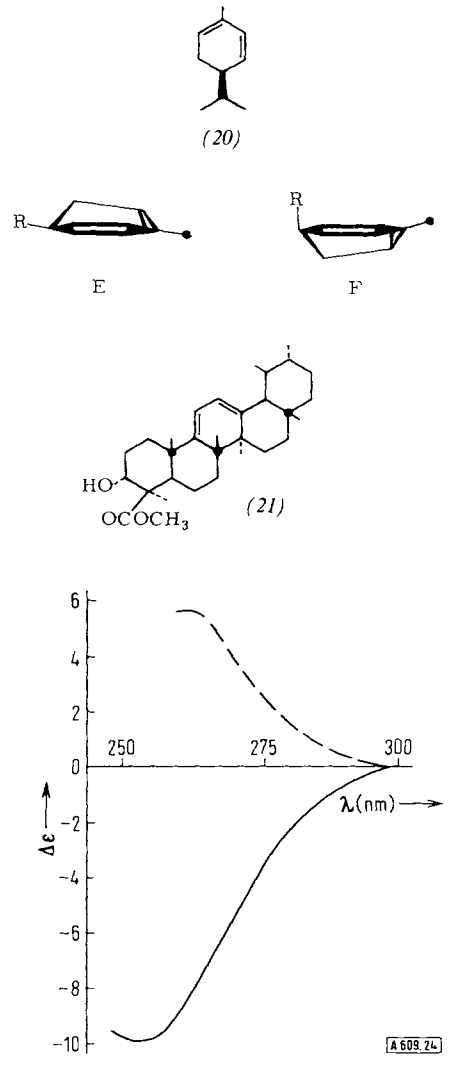


Fig. 24. Conformational equilibrium of α-phellandrene *(20)* and CD at 20 ° (—) and −177 °C (— — —). E gives a positive and F a negative Cotton effect. Formula of the rigid diene *(21)* shown for comparison.

This directly proves the postulated conformational equilibrium between the conformers E and F (Fig. 24). Since we had found an experimental $\Delta\varepsilon_{max}$ of +33 for the rigid diene *(21)* [72], it can be estimated to a rough approximation that 65 % of the less stable conformer F is present at room temperature, and only 42 % at −177 °C. The displacement of the equilibrium is thus not very great, despite a temperature difference of about 200 °C and the reversal of the sign of the CD.

The examples described show that configurations and conformations can be determined on an empirical or semiempirical basis with the aid of circular dichroism or optical rotatory dispersion, even without a rigorous theory. It has been necessary to omit any mention of applications in inorganic coordination chemistry [73], but it should be pointed out that these methods can be successfully used to locate bands that are often impossible to recognize in the UV spectrum, as was the case

[66] *A. T. McPhail* and *G. A. Sim*, Chem. Commun. *1965*, 350; J. chem. Soc. (London) (C) *1966*, 1394.

[67] a) *A. Moscowitz*, *E. Charney*, *U. Weiss*, and *H. Ziffer*, J. Amer. chem. Soc. *83*, 4661 (1961); b) *U. Weiss*, *H. Ziffer*, and *E. Charney*, Tetrahedron *21*, 3105 (1965).

[68] *E. Charney*, Tetrahedron *21*, 3127 (1965).

[69] *A. W. Burgstahler*, *H. Ziffer*, and *U. Weiss*, J. Amer. chem. Soc. *83*, 4660 (1962).

[70] *H. Ziffer*, *E. Charney*, and *U. Weiss*, J. Amer. chem. Soc. *84*, 2961 (1962).

[71] *G. Snatzke*, *E. sz. Kováts*, and *G. Ohloff*, Tetrahedron Letters *1966*, 4551. The temperature given in this article refers to the cell body; the temperature in the solution was −177 °C.

[72] *G. Snatzke* and *L. Vértesy*, Mh. Chem. *98*, 121 (1967).

[73] See, *e.g.*, *F. Woldbye* in *H. B. Jonassen* and *A. Weissberger*: Technique of Inorganic Chemistry. Interscience, New York 1965, IV, p. 249; *F. Woldbye* in [11], p. 101; *S. F. Mason*, *ibid.* p. 116.

e.g. in nitro compounds [74] or conjugated acids [67a]. Finally the phenomenon of optical activity induced by a magnetic field has presented the spectroscopist with a new aid for the determination of energy levels, particularly in inorganic compounds [75], whereas magneto-CD and magneto-ORD have not yet shown much promise in organic stereochemistry. However, we must await with interest the development of more sensitive instruments and those which can be used further into the UV range.

I am grateful to the Deutsche Forschungsgemeinschaft for their financial support. Furthermore, these investigations would have been impossible without the conscientious work of our technical assistants and the supply of interesting samples by many colleagues at the Institute and throughout the world. I should like to express my sincere thanks to all of them.

[74] *C. Djerassi, H. Wolf,* and *E. Bunnenberg,* J. Amer. chem. Soc. *85,* 2835 (1963); *G. Snatzke,* J. chem. Soc. (London) *1965,* 5002.

[75] *A. D. Buckingham* and *P. J. Stephens,* Annu. Rev. physic. Chem. *17,* 399 (1966); *P. Badoz* in [11], p. 389.

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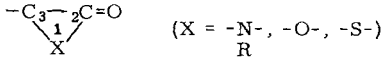
α-Lactams (Aziridinones)

BY I. LENGYEL AND J. C. SHEEHAN [*]

α-Lactams have often been postulated as intermediates in numerous processes. The isolation of the first α-lactam, N-tert-butyl-3-phenylaziridinone, was accomplished in 1962. Since then, further N- and C-3-substituted α-lactams have been synthesized. Most of these very reactive compounds undergo easy thermal decomposition; remarkable is the relative stability of 1,3-di-tert-butylaziridinone, which does not start to decompose below 140 °C. The α-lactam ring is opened by nucleophilic reagents. – The correlation of stability and substituents is discussed in the last section. An acyclic, planar or almost planar, charge-delocalized intermediate is suggested to explain the observed effects.

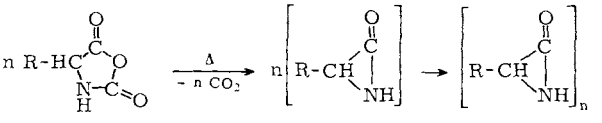
I. α-Lactams as Possible Intermediates; Unsuccessful Attempts at Preparation

α-Lactams [aziridinones] are the first and, to date, only representatives of the three-membered ring carbonyl compounds of general structure *(1)* to have been synthesized (see Section II).



(1)

It was *Leuchs* [1] who first proposed α-lactams as reactive intermediates. He observed that α-amino acid *N*-carboxy-anhydrides ("Leuchs-Anhydride") *(2)* rapidly lose carbon dioxide on heating to form polypeptides *(4)*. *Leuchs* postulated an α-lactam *(3)* as intermediate but it could not be isolated [2].



(2) *(3)* *(4)*

An α-lactam (*N*-phenylaziridinone) as a possible intermediate was also mentioned by *Sheehan* and *Izzo* [3], who isolated the β-lactam 1-phenyl-2-azetidinone during the reaction of phenyl isocyanate with diazomethane.

The possibility that certain α-haloamides may cyclize to α-lactams on dehydrohalogenation with bases has been investigated for two aromatic precursors of this class by two groups of workers [4]. In no case could an α-lactam be isolated or detected as intermediate.

The reaction of α-chloro-α,α-diphenylacetanilide *(5)* with sodium hydride [4b, 4c, 4f, 4g] gave 2-(3,3-diphenyl-2-indolinon-1-yl)-2,2-diphenylacetanilide *(6)* as the major product, together with smaller amounts of 3,3-diphenyl-2-indolinone *(7)* and 1,3-diphenyl-2-indolinone *(8)*. The formation of all three products can be explained through a common α-lactam intermediate *(9)* [4c, 4f].

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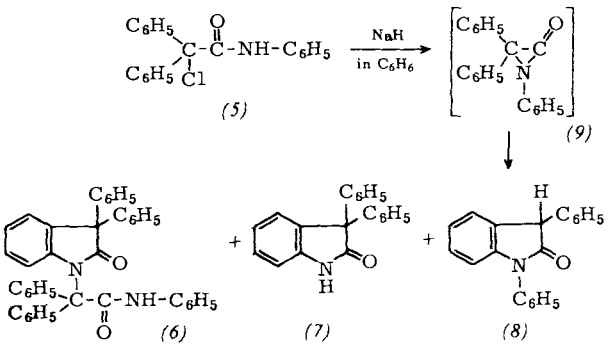
[1] *H. Leuchs* and *W. Geiger,* Ber. dtsch. chem. Ges. *41,* 1721 (1908).

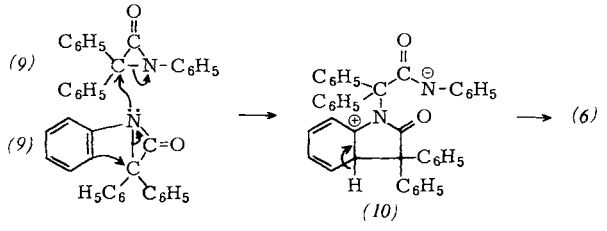
[2] *Leuchs'* assumption that the decarboxylation of α-amino acid *N*-carboxy anhydrides leads to cyclic polymers, proved erroneous later: it was recognized (*R. B. Woodward* and *C. H. Schramm,* J. Amer. chem. Soc. *69,* 1551 (1947)) that the products are linear polypeptides and not cyclic α-lactam polymers.

[3] *J. C. Sheehan* and *P. T. Izzo,* J. Amer. chem. Soc. *79,* 1985 (1948); *ibid. 71,* 4059 (1949).

[4] a) *S. Sarel* and *A. Greenberger,* J. org. Chemistry *23,* 330 (1958); b) *S. Sarel* and *H. Leader,* J. Amer. chem. Soc. *82,* 4752 (1960); c) *J. C. Sheehan* and *J. W. Frankenfeld,* J. Amer. chem. Soc. *83,* 4792 (1961); d) *S. Sarel* and *J. T. Klug,* Israel J. Chem. *2,* 143 (1964); e) *S. Sarel, F. D'Angeli, J. T. Klug,* and *A. Taube,* Israel J. Chem. *2,* 167 (1964); f) *S. Sarel, J. T. Klug, E. Breuer,* and *F. D'Angeli,* Tetrahedron Letters *1964,* 1553; g) *J. C. Sheehan* and *J. H. Beeson,* J. org. Chemistry *31,* 1637 (1966).

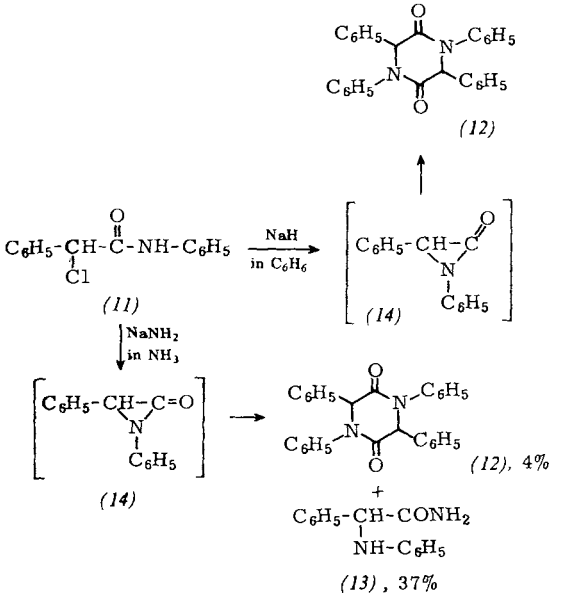


To explain the formation of the main product *(6)*, it has been suggested[4f] that *(9)* undergoes an unusual dimerization *via (10)*. The fact that the postulated α-lactam intermediate does not dimerize to the simpler symmetrical dimer, hexaphenylpiperazine-2,5-dione, is explained by *Sarel* and co-workers[4f] on steric grounds.

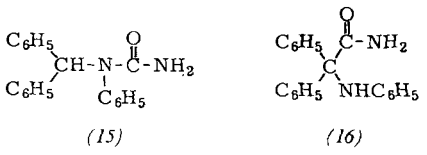


The analogous reaction of α-chloro-α-phenylacetanilide *(11)* with sodium hydride yields 1,3,4,6-tetraphenylpiperazine-2,5-dione *(12)* and a solid of uncertain structure. Here too, an α-lactam *(14)* has been suggested as an intermediate[4a,4b].

If sodium hydride is replaced by sodium amide, the rearrangement of *(11)* mainly into α-anilino-α-phenylacetamide *(13)* is observed[4a].

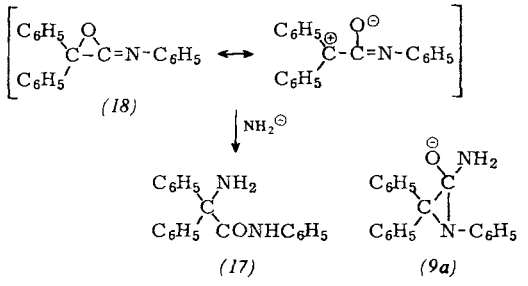


Interestingly, the course of the analogous reaction of *(5)* is fundamentally different: When α-chloro-α,α-diphenylacetanilide *(5)* is treated with sodium amide in liquid ammonia, *N*-benzhydryl-*N*-phenylurea *(15)*, α-anilino-α,α-diphenylacetamide *(16)*, and α-amino-α,α-diphenylacetanilide *(17)*, are formed in the ratio 5:1:1[4e]. (The reaction of *(5)* with NaH leads to *(6)*, *(7)*, and *(8)*.) It has been assumed[4e] that compounds *(15)* and *(16)* arise from the α-lactam intermediate *(9)* by reaction with $NH_2^{\ominus}$.



According to *Sarel et al.*[4a], product *(17)* may be formed either from the iminooxirane isomer *(18)* of the α-lactam[5] or by direct substitution of the α-chlorine atom in *(5)* by NH_2. The two phenyl substituents at the α-carbon facilitate the formation of a carbanion, derivable from the primary adduct *(9a)* of the α-lactam and $NH_2^{\ominus}$ through C–C fission, leading to benzhydrylurea *(15)* – the observed major product. C–N scission affords *(16)*. The α-lactam *(9)* could not be isolated or detected.

In 1962, *Sheehan* and *Lengyel* attempted to synthesize 1,3,3-triphenyl-2-aziridinone *(9)* *via* a photochemical route. The addition of diphenyl carbene to the CN double bond of phenyl isocyanate would, in principle, be the simplest synthesis of this α-lactam. Diphenyldiazomethane was selected as the source of diphenyl carbene. Since *Staudinger*[6] had already observed that diphenyldiazomethane does not react with phenyl isocyanate on simple mixing, *Sheehan* and *Lengyel* generated the diphenyl carbene photochemically and observed a smooth reaction with phenyl isocyanate[7]. This is the first example of the addition of a carbene to an isocyanate and the first photochemically initiated reaction of an isocyanate. However, no α-lactam could be isolated, but one of the products proved to be identical with the major product *(6)* of the reaction of α-chlorodiphenylacetanilide with sodium hydride. This product *(6)* possibly arises from an α-lactam intermediate *(9)* in the same way as was proposed for the formation of *(6)* from α-chlorodiphenylacetanilide[4f].



No authentic synthesis of 1,3-diphenylaziridinone *(14)* or 1,3,3-triphenylaziridinone *(9)* has been reported to date.

II. Preparation and Structure of α-Lactams

1. Dehydrohalogenation of *N*-Chloro- and α-Chloroamides

In 1961, *Baumgarten* and co-workers detected for the first time an α-lactam as an intermediate by a spectroscopic technique[8]. Studying the Favorskii-type rearrangement of *N-tert*-butyl-*N*-chloroamides by treatment with potassium-*tert*.-butoxide, they observed an

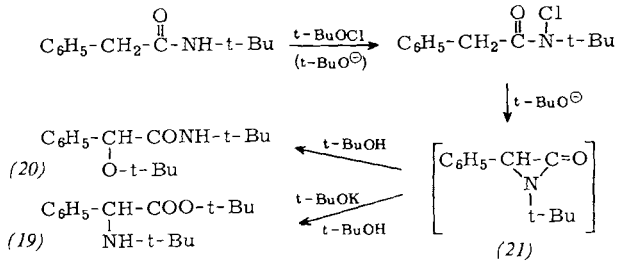
[5] Such an iminolactone intermediate was first suggested by *Sheehan* and *Lengyel* (see reference [25]).

[6] *H. Staudinger, E. Anthes*, and *F. Pfenninger*, Ber. dtsch. chem. Ges. *49*, 1928 (1916).

[7] *J. C. Sheehan* and *I. Lengyel*, J. org. Chemistry *28*, 3252 (1963).

[8] *H. E. Baumgarten, R. L. Zey*, and *U. Krolls*, J. Amer. chem. Soc. *83*, 4469 (1961).

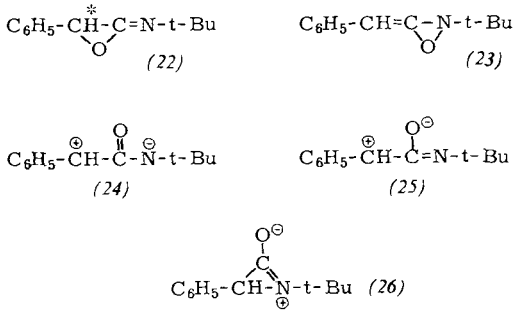
intermediate (which they could not isolate) that exhibited a carbonyl band at 1847 cm^{-1}. This wavelength is in full accord with theoretical expectations for an α-lactam [9].



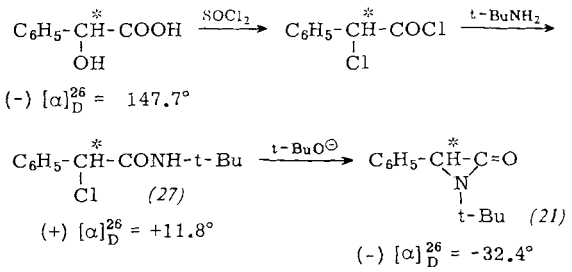
Furthermore, two different ring openings could be demonstrated through isolation of the end products, ester *(19)* and amide *(20)*. In 1962, *Baumgarten* starting with *N-tert*-butyl-*N*-chlorophenylacetamide (ν_{CO} = 1670 cm^{-1}) succeeded in isolating the α-lactam *(21)* (m.p. 32–33 °C) from the same reaction [10].

One year later, *Baumgarten* and co-workers reported [11] the synthesis of the same α-lactam, starting from *N-tert*-butyl-α-chlorophenylacetamide. The spectroscopic and analytical data were in agreement with the proposed structure.

Since, however, the reaction conditions, as well as the rearrangement observed by *Baumgarten*, strongly resembled those of the Favorskii-reaction of α-haloketones, the question arose whether the product may possibly have another structure. *Baumgarten* considered structures *(22)–(26)*. Structures *(24)–(26)* are analogous to those discussed by *House* [12]

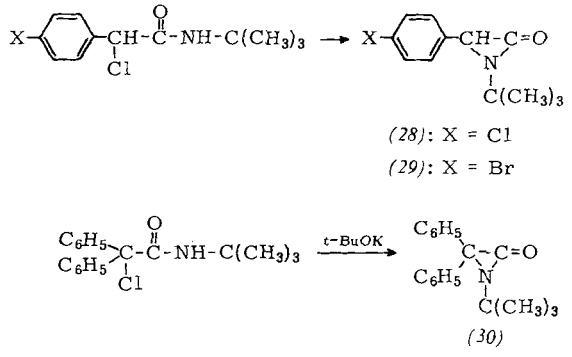


and *Fort* [13] for the "Favorskii intermediate". To elucidate the structure, *Baumgarten* and co-workers undertook the synthesis of an optically active form of *(21)* [11]. Since the precursor, the optically active (+)-*N-tert*-butyl-α-chlorophenylacetamide *(27)* easily racemizes, it was not possible to determine the optical purity of (–)-*(21)*. All mesomeric dipole structures [*e.g. (24)*, *(25)*, and *(26)*] with substantial charge separation require the α-carbon atom to be in sp^2 configuration, *i.e.* to be planar. The fact that the synthesis yields an optically active α-lactam, excludes both the dipole structures *(24)–(26)* and any charge-delocalized precursor. For the same reason, one could exclude another possibility,



the optically symmetrical oxazirane structure *(23)* simultaneously. To distinguish between the α-lactam and the iminolactone structure *(22)*, *Baumgarten* and co-workers have repeated the original synthesis [8] with *ca.* 50% ^{18}O-containing *N-tert*-butyl-*N*-chlorophenylacetamide and thus obtained an ^{18}O-labeled α-lactam. The IR spectrum of the starting material showed a carbonyl doublet at 1668 and 1645 cm^{-1} and that of the product at 1848 and 1827 cm^{-1}. The similarity of the two doublets was taken as evidence for the presence of an amide C=O group in both compounds. The three-membered ring amide structure received further corroboration from NMR measurements. The coupling constant for the α-^{13}C–H in the α-lactam *(21)* was 168.5 ± 0.5 Hz. This value is in excellent agreement with the $J^{13}CH$ values of other aziridine systems and corresponds to a 34% s character of the α-carbon atom.

By means of the same reaction, *i.e.* treatment of *N*-chloro- and α-chloroamides, respectively, with potassium *tert*-butoxide, the same workers later prepared three additional α-lactams in pure form [14], namely 1-*tert*-butyl-3-*p*-chlorophenylaziridinone *(28)*, (m.p. 35–36 °C) 1-*tert*-butyl-3-*p*-bromophenylaziridinone *(29)* (m.p. 56–57 °C), and 1-*tert*-butyl-3,3-diphenylaziridinone *(30)* (m.p.77–79 °C).These compounds are, in analogy to the other α-lactams known to date, low melting, highly reactive solids, exhibiting a carbonyl band in their IR spectra at about 1850 cm^{-1} [14].



Simultaneously and independently, *Sheehan* and coworkers (see [4c]) prepared a number of aliphatic *N*-alkyl-α-haloamides and studied their reaction with non-aqueous bases. α-Haloamides appeared better suited to the preparation of α-lactams than the corresponding *N*-haloamides, for two reasons: 1) Because of the greater solubility difference, it is easier to separate the α-lactam formed from an α-haloamide than from an *N*-haloamide; 2) the formation of an anion is more favored when the charge is situated on the nitrogen than when it is on the α-carbon; the reaction pathway (b) leading to the formation of an α-lactam appears to be more plausible starting with an α-haloamide. The

[9] Based on theoretical considerations one would expect α-lactams to show a carbonyl band between 1760 and 1840 cm^{-1}; γ-lactams absorb at 1700–1750 and β-lactams at 1730–1760 cm^{-1}. See, *e.g., L. J. Bellamy*: The Infrared Spectra of Complex Molecules. J. Wiley and Sons, Inc., New York 1958, p. 214.

[10] *H. E. Baumgarten*, J. Amer. chem. Soc. *84*, 4975 (1962).

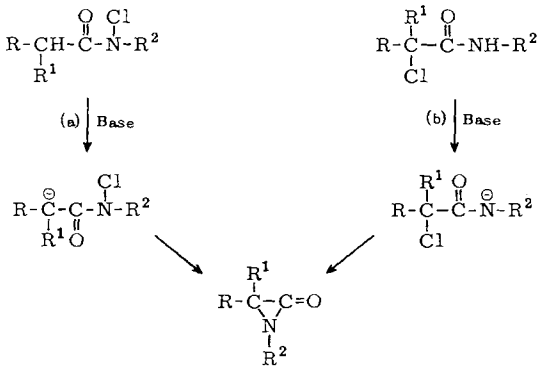
[11] *H. E. Baumgarten, J. J. Fuerholzer, R. D. Clark*, and *R.D. Thompson*, J. Amer. chem. Soc. *85*, 3303 (1963).

[12] *H. O. House* and *W. F. Gilmore*, J. Amer. chem. Soc. *83*, 3972, 3980 (1961).

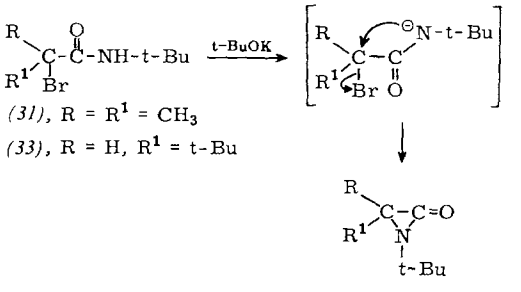
[13] *A. W. Fort*, J. Amer. chem. Soc. *84*, 2620 (1962); b) *ibid. 84*, 4979 (1962).

[14] *J. J. Fuerholzer*, Ph. D. Thesis, University of Nebraska, 1965.

choice of the precursor was further influenced by the known stabilizing effect of geminal alkyl substituents in the β-lactam [15] and β-thiolactone [16] series.



Starting from these considerations, *Sheehan* and *Lengyel* have dehydrohalogenated 2-bromo-2-methyl-*N*-*tert*-butylpropionamide *(31)* with potassium *tert*-butoxide or potassium metal at low temperature. The reaction yielded the desired α-lactam *(32)* [17,18], (m.p. 22–24 °C, carbonyl band at 1837 cm^{-1}, no NH-band at 3400 cm^{-1}) the first aliphatic representative of this class.



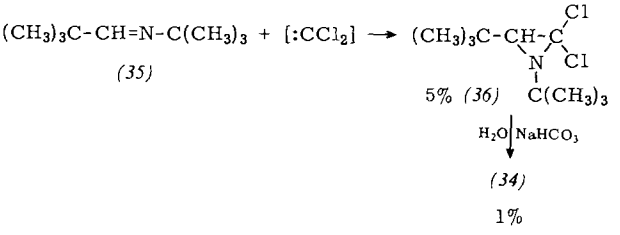
(31), R = R^1 = CH_3
(33), R = H, R^1 = t-Bu

(32), R = R^1 = CH_3
(34), R = H, R^1 = t-Bu

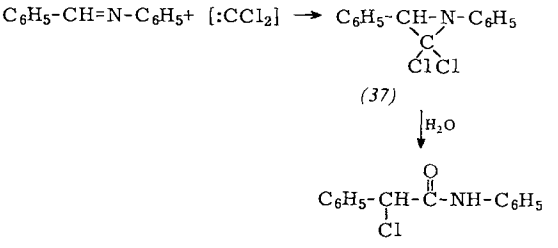
Using the same method, *Sheehan* and *Beeson* prepared in 1965 a new α-lactam, 1,3-di-*tert*-butylaziridinone *(34)* in almost quantitative yield [19,20]. This α-lactam has a far higher thermal stability and a much lower chemical reactivity than all other α-lactams known to date. It can be distilled at reduced pressure, survives gas chromatography under certain conditions, and can even be purified by column chromatography [19,20].

2. Preparation of an α-Lactam through Carbene Addition

1,3-Di-*tert*-butylaziridinone has also been prepared by *Sheehan* and *Beeson via* addition of dichlorocarbene to *N*-neopentylidene-*tert*-butylamine *(35)* and subsequent hydrolysis of the adduct *(36)*. This is the first successful conversion of a CCl_2 group in a three-membered heterocycle to a carbonyl group without ring opening [20]. The low yield of the addition is ascribed to the strong steric hindrance of the CN double bond of the imine.



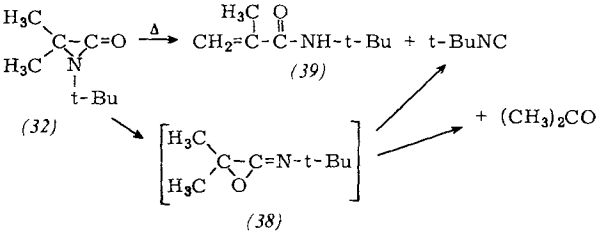
It was *Fields* and co-workers who first succeeded [21,22] in adding dichloro carbene to the CN double bond of Schiff's bases to form dichloroaziridines, which can be regarded as potential precursors of α-lactams. However, the 2,2-dichloro-3-phenylaziridine *(37)* prepared from benzalaniline yielded on hydrolysis no α-lactam but α-chlorophenylacetanilide. Similarly, the dichloroaziridines prepared from benzalanisidine and benzal-*p*-chloroaniline [22] gave on hydrolysis the corresponding α-chloroamides.



III. Reactions of α-Lactams

1. Thermal Decomposition

1-*tert*-Butyl-3,3-dimethylaziridinone *(32)* undergoes slow decomposition even at room temperature, and one hour's refluxing in ether effects complete destruction of the ring [18] to give the isomeric *N*-*tert*-butylmethacrylamide *(39)* as the major product [23]. Surprisingly, acetone and *tert*-butyl isocyanide are also produced [18]. It is assumed that the α-lactam *(32)*



(38)

[15] *J. C. Sheehan* and *E. J. Corey*: Org. Reactions *9*, 388 (1957).

[16] *J. C. Sheehan*, Ann. New York Acad. Sci. *88*, 665 (1960).

[17] *I. Lengyel*, Ph. D. Thesis, Massachusetts Institute of Technology, Sept. 1963.

[18] *J. C. Sheehan* and *I. Lengyel*, α-Lactams I, J. Amer. chem. Soc. *86*, 1356 (1964).

[19] *J. H. Beeson*, Ph. D. Thesis, Massachusetts Institute of Technology, June 1966.

[20] *J. C. Sheehan* and *J. H. Beeson*, α-Lactams IV, J. Amer. chem. Soc. *89*, 362 (1967).

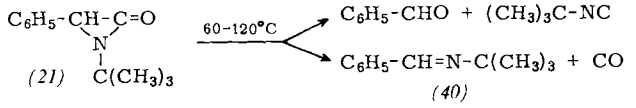
[21] *E. K. Fields* and *J. M. Sandri*, Chem. and Ind. *1959*, 1216.

[22] *A. G. Cook* and *E. K. Fields*, J. org. Chemistry *27*, 3686 (1962).

[23] The isomerization of α-lactam *(32)* to the α,β-unsaturated amide *(39)* seems to occur with particular ease because compound *(32)* possesses β-hydrogens for elimination. In α-lactams not having β-hydrogens (*e.g. (34)*) such isomerization cannot take place (see also summary).

partially rearranges on warming to the structurally isomeric iminolactone *(38)*, which fragments further to give a ketone and an isocyanide.

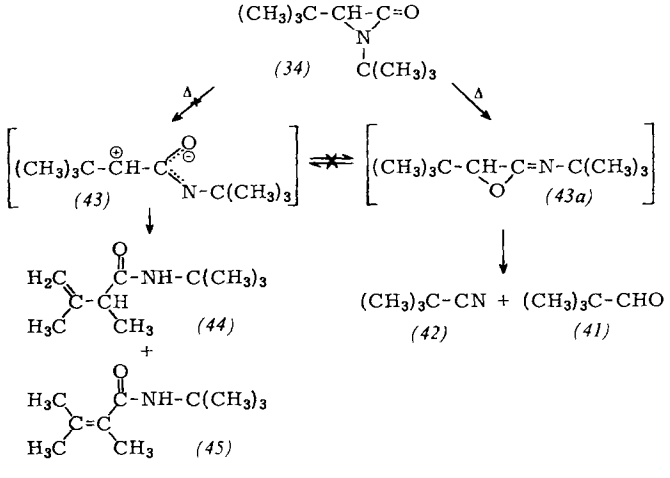
Nuclear magnetic resonance and mass spectrometric investigation of the pyrolysis products of 1-*tert*-butyl-3-phenylaziridinone (heated to 60–120 °C) showed [24] that the main path of decomposition leads to benzaldehyde and *tert*-butyl isocyanide. However, smaller amounts of *N*-benzylidene-*tert*-butylamine *(40)* and carbon monoxide were also detected, which indicates that the pyrolysis proceeds *via* at least two pathways.



(21) *(40)*

Whereas other α-lactams investigated to date decompose rapidly and completely at temperatures between 60 and 120 °C, decomposition of 1,3-di-*tert*-butylaziridinone *(34)* does not start below 140 °C [19,20]. Prolonged heating (12 h) of the compound at 175 °C in a sealed tube leads to a complex mixture, 60% of which is made up by pivalaldehyde *(41)* and *tert*-butyl cyanide *(42)*. It is assumed [19,20] that the *tert*-butyl cyanide arises from the originally formed *tert*-butyl isocyanide [18] by thermal isomerization. Gas-phase pyrolysis at 450 °C yields 93% of pivalaldehyde and *tert*-butyl cyanide.

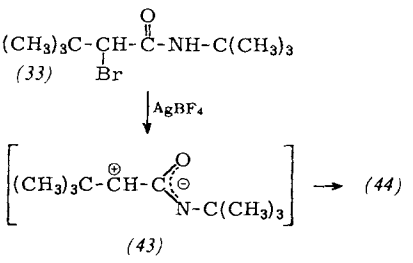
If this pyrolysis passed, at least in part, through a zwitterionic intermediate [*e.g. (43)*], one would expect to find in the pyrolysis mixture also products of a neopentyl rearrangement [*e.g. (44)* and *(45)*]. It has been



demonstrated by comparison with authentic substances [*(44)* and *(45)*] that such products are not formed in the pyrolysis.

The fact that treatment of 2-bromo-3,3-dimethyl-*N*-*tert*-butylbutyramide *(33)* with silver tetrafluoroborate does lead to a neopentyl rearrangement (most probably *via* the zwitterion *(43)* as intermediate) indicates that the iminolactone intermediate *(43a)* (postulated to explain the observed products) in the pyrolysis of α-lactam *(34)* does *not* arise *via (43)*,

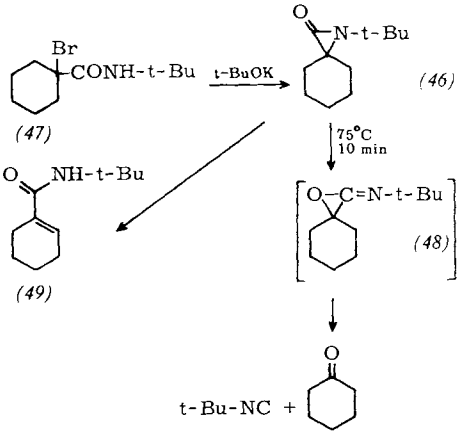
[24] Reference [14], p. 92.



or at least that *(43)* cannot have an appreciable lifetime.

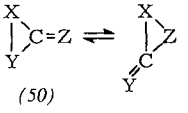
In 1964, *Sheehan* and *Lengyel* reported the thermal decomposition of spiro-α-lactam *(46)* [25]. This compound (isolated only in crude state from the reaction of 1-bromo-1-*N*-*tert*-butylcarboxamidocyclohexane *(47)* with potassium *tert*-butoxide) decomposed quantitatively within 10 min at 75 °C to give cyclohexanone and *tert*-butylisocyanide as major products, together with a smaller amount of *N*-*tert*-butyl-1-cyclohexanecarboxamide *(49)*.

This type of fragmentation [26] can best be explained again by assuming that, on heating, the spiro-α-lactam *(46)* rearranges



first to the isomeric iminolactone *(48)* which then fragments. Nevertheless, the experiment did not allow a decision to be made as to whether the by-product *(49)* was formed *via* an E_2 reaction directly from the starting material or, through a rearrangement, from the α-lactam. Similarly, the question of the mechanism of the rearrangement α-lactam *(46)* → iminolactone *(48)* has also remained unanswered.

As is well known, compounds of the general structure *(50)* are subject to thermal [27] X–Y bond rupture and/or isomerization [28]. An interesting example of



(50)

[25] *J. C. Sheehan* and *I. Lengyel*, α-Lactams II, J. Amer. chem. Soc. *86*, 746 (1964).

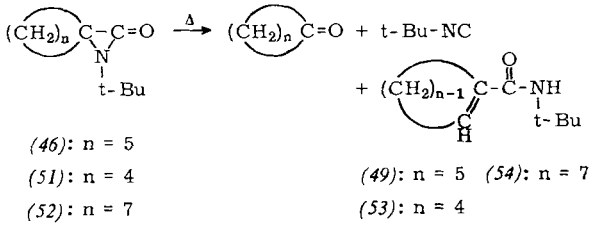
[26] While products of the ketone and isocyanide type are formed only in 12% yield in the pyrolysis of the α-lactam *(32)* [18], this type of fragmentation is the predominant one in the case of the spiro-α-lactam *(46)*: cyclohexanone and *tert*-butyl isocyanide are formed in 66% yield.

[27] *W. B. Hammond* and *N. J. Turro*, J. Amer. chem. Soc. *88*, 2880 (1966).

[28] *J. C. Shields, B. A. Shoulders, J. F. Krause, C. L. Osborn*, and *P. D. Gardner*, J. Amer. chem. Soc. *87*, 3026 (1965); *E. F. Ullman* and *W. J. Fanshawe*, J. Amer. chem. Soc. *83*, 2379 (1961).

this unusual rearrangement has been reported in the monochloroethyleneimine series by *Deyrup* and *Greenwald*[29].

The remarkable course of the "thermolysis" of *(46)*[25] awakened further interest in other spiro-α-lactams. *Sheehan* and *Beeson* investigated the thermal decomposition of 1-*tert*-butyl-tetramethylene- and heptamethylene-aziridinone *(51)* and *(52)*[19,30], prepared in the same manner. In these experiments, the two α-lactams were used as crude products.

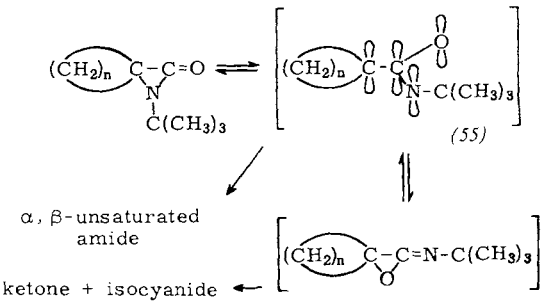


(46): n = 5
(51): n = 4
(52): n = 7

(49): n = 5 *(54)*: n = 7
(53): n = 4

Warming to 80–100 °C led, in analogy with the pentamethylene derivative *(46)*, to the formation of *tert*-butyl isocyanide, the corresponding cyclic ketone and an α,β-unsaturated amide [*(53)* and *(54)*, respectively]. The ratio of these products, however, was different in the four compounds investigated to date. From *(46)* ($n = 5$), amide and ketone are formed in the molar ratio 2.5:1; from *(51)* ($n = 4$) the ratio is 0.15:1[25]; and from *(52)* ($n = 7$) 14.0:1. On heating, the monocyclic α-lactam *(32)* affords amide and ketone type products in the molar ratio 5.4:1.

In the case of the tetramethylene and heptamethylene derivatives, it has been established that the unsaturated amides *(53)* and *(54)* do not arise during the α-lactam preparation from the bromoamides, but directly from the α-lactams on heating[30]. It is assumed[30] that the α-lactam pyrolysis



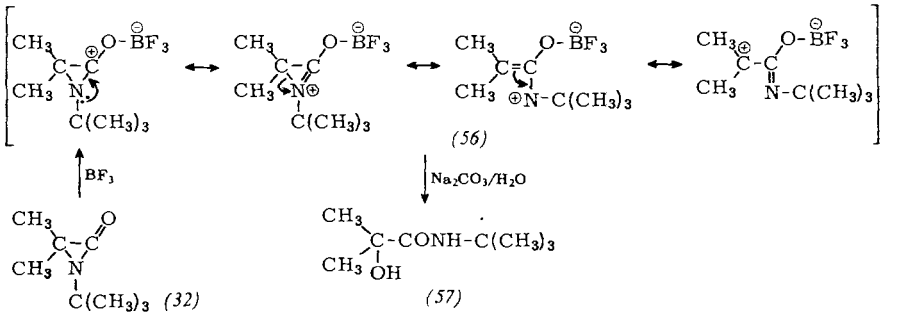
(55)

passes through a charge-delocalized transition state or "metastable intermediate" *(55)*, similar to that proposed for the Favorskii rearrangement of α-haloketones[12,13].

The results obtained hitherto for the α-lactam pyrolysis in the spiro series (such as the relative rates of formation of unsaturated amides *versus* ketones and *tert*-butyl isocyanide as a function of structure) are in qualitative agreement with this intermediate[30].

2. Salt- and Ylide-formation

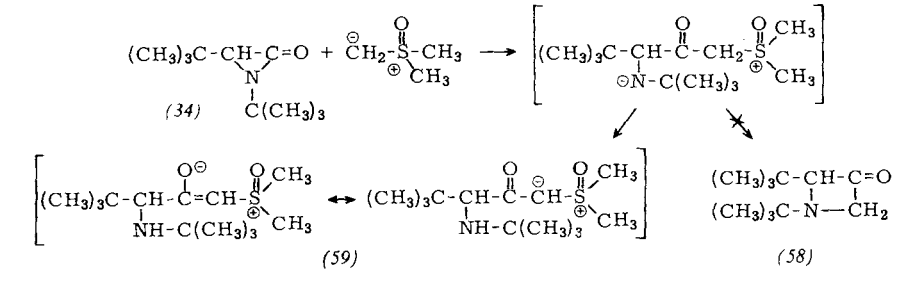
Treatment of 1-*tert*-butyl-3,3-dimethylaziridinone *(32)* with boron trifluoride yields a salt, $C_8H_{15}NO \cdot BF_3$[31]; polymerization is not observed. Sodium carbonate hydrolysis of the salt leads to *N*-*tert*-butyl-2-hydroxy-2-methylpropionamide *(57)* as the only product. The



(56) *(32)* *(57)*

salt may be formulated as a resonance hybrid of the dipolar structures *(56)*.

In the hope of obtaining a ring enlargement product *(58)*, *Sheehan* and *Beeson* treated α-lactam *(34)* with dimethyl sulfoxonium-methylide in DMSO at room



(34) *(59)* *(58)*

temperature. However, only a stable ylide *(59)* was formed[19,20].

Similar ylides are formed from ethyl propiolate, phenyl isocyanate, and diphenylketene with the same reagent[32].

[29] *J. A. Deyrup* and *R. B. Greenwald*, Tetrahedron Letters, *1966*, 5091.

[30] *J. C. Sheehan* and *J. H. Beeson*, α-Lactams V, J. Amer. chem. Soc. *89*, 366 (1967).

[31] *J. C. Sheehan* and *I. Lengyel*, unpublished results.

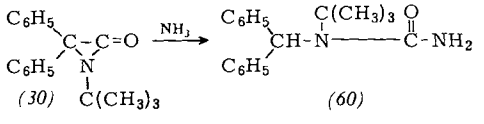
[32] *C. Kaiser*, *B. M. Trost*, *J. H. Beeson*, and *J. Weinstock*, J. org. Chemistry *30*, 3972 (1965).

3. Reactions of α-Lactams with Nucleophilic Reagents

a) Reactions with Aprotic and Protic Reagents

In general, α-lactams are very reactive. Their properties lie between those of the "Favorskii-intermediates" and those of the very stable di-*tert*-butyldiaziridinone, prepared by *Greene* and *Stowell*[33]. The chemical reactivity of α-lactams is indeed closer to that of the former than to the latter. Except for the very stable and unreactive 1,3-di-*tert*-butylaziridinone *(34)*, all α-lactams isolated and investigated to date react completely with nucleophiles already at room temperature. Depending on the nucleophilie, a strong selectivity is observed in the type of ring opening. Reaction with proton-containing nucleophiles, *e.g.* water, alcohols, thiols, amines, and mineral acids (HZ) leads exclusively to amides, corresponding to an alkyl-nitrogen bond splitting. On the other hand, reaction of α-lactams with aprotic nucleophiles ($Z^{\ominus}$) gives amino acid derivatives as the only products, corresponding to a ring opening at the acyl-nitrogen bond[34].

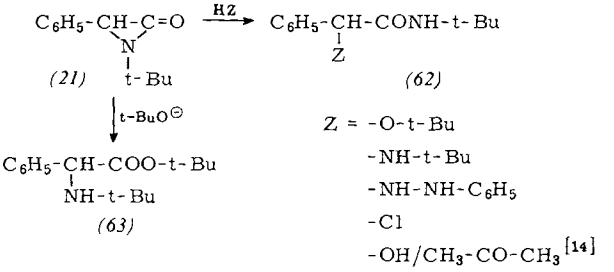
Products such as urethanes, urea derivatives, *etc.*, which could arise from α-lactams with nucleophiles *via* CC scission (the third possible way of opening the ring) have been observed only the in reaction of 1-*tert*-butyl-3,3-diphenylaziridinone *(30)* with liquid ammonia, in which *N*-benzhydryl-*N*-*tert*-butylurea *(60)* is the major product. Also, treatment of the same



(30) *(60)*

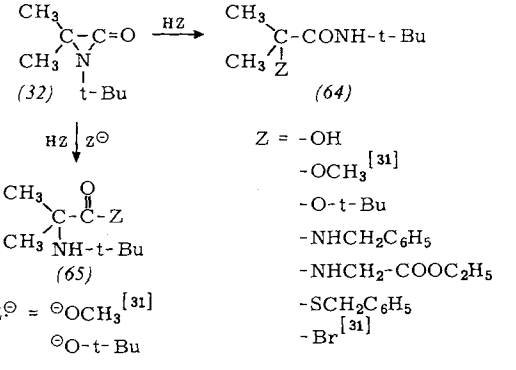
α-lactam with potassium *tert*-butoxide leads to benzhydryl-*tert*-butylamine *(61)* and not to an α-amino acid ester[35].

Reaction of 1-*tert*-butyl-3-phenylaziridinone *(21)* with *tert*-butyl alcohol, *tert*-butylamine, phenylhydrazine, or hydrochloric acid and solvolysis in different acetone/water mixtures gave the corresponding α-substituted *N*-*tert*-butylphenylacetamide *(62)*, whereas reaction of *(21)* with potassium-*tert*-butoxide produced *tert*-butyl *N*-*tert*-butylphenylglycinate *(63)* [10,11].



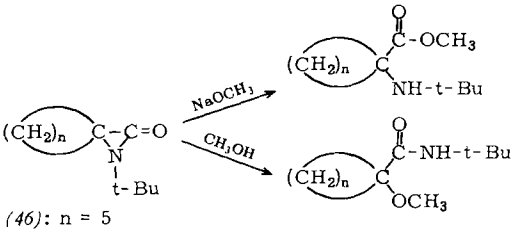
(21) *(62)* *(63)*

The α-lactam *(32)* was treated with water, methanol, *tert*-butyl alcohol, benzylamine, ethyl glycinate, 2-toluenethiol, and hydrobromic acid and from all these reactions the product was the corresponding α-substituted *N*-*tert*-butylisobutyramide *(64)* [17,18]. Sodium methoxide and potassium *tert*-butoxide converted the α-lactam *(32)* into the corresponding ester of *N*-*tert*-butyl-α-aminoisobutyric acid *(65)*.



(32) *(64)* *(65)*

The reaction of the three spiro-α-lactams *(46)*, *(51)*, and *(52)* with methanol or methoxide ion showed the same type of selective ring opening[30] as observed earlier[31] with the 3,3-dimethyl derivative *(32)*.



(46): n = 5
(51): n = 4
(52): n = 7

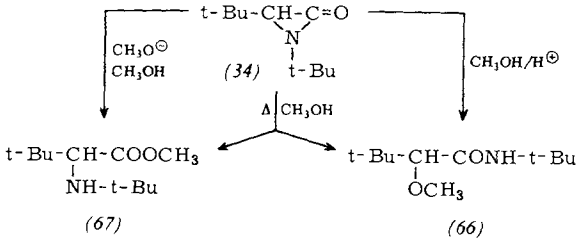
In contrast to the α-lactams *(21)* and *(32)*, 1,3-di-*tert*-butylaziridinone *(34)* is remarkably resistant toward nucleophiles (HZ). Several days' refluxing is necessary to solvolyze α-lactam *(34)* with methanol. The methanolysis products are amide *(66)* and ester *(67)* in the molar ratio 3:2[19,20]. This is the first recorded case in which an α-amino acid derivative was formed in the "uncatalyzed" solvolysis of an α-lactam. In

[33] *F. D. Greene* and *J. C. Stowell*, J. Amer. chem. Soc. *86*, 3569 (1964).

[34] The Favorskii reaction of α-chlorodibenzyl ketone is similarly selective: the 2,6-lutidine catalyzed methanolysis of this compound leads to the corresponding α-methoxy ketone; the sodium methoxide catalyzed methanolysis on the other hand gives the rearranged methyl ester [13].

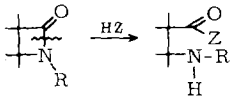
[35] *H. E. Baumgarten* and *R. D. Clark*, unpublished results; see reference [14], p. 88.

agreement with earlier findings for 1-*tert*-butyl-3,3-dimethylaziridinone, the α-lactam *(34)* gave only the ester *(67)* on treatment with sodium methoxide. Acid-catalyzed methanolysis led exclusively to amide *(66)*.

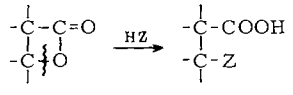


b) Nucleophilic Ring Opening of Other Small-ring Heterocycles

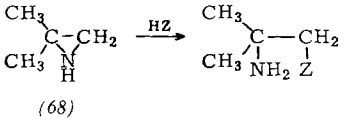
Monocyclic β-lactams are relatively stable compounds. They are solvolyzed only under drastic conditions and then yield products corresponding exclusively to scission of the amide bond [36].



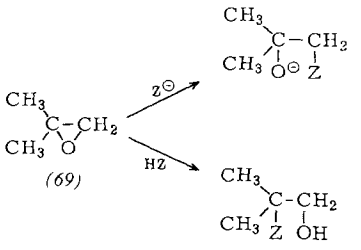
β-Lactones, on the other hand, are opened by nucleophiles preferentially at the alkyl-oxygen bond [37], a type of ring opening that resembles more that of α-lactams.



The type of ring opening of 2,2-dimethylaziridine *(68)* is also in sharp contrast to that of the α-lactams investigated to date. 2,2-Dimethylaziridine *(68)* is opened by protic nucleophiles (HZ) in such a way that substitution occurs exclusively at the primary carbon, *i.e.* nitrogen atom remains attached to the tertiary carbon [38].

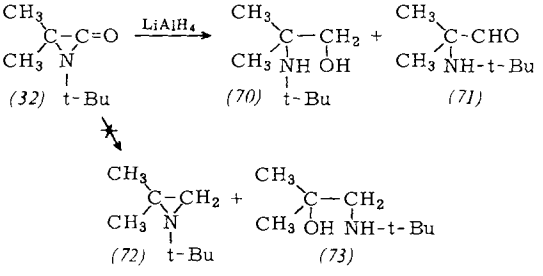


The observations made to date on the ring opening of α-lactams parallel the corresponding reactions of epoxides. Thus 2,2-dimethyloxirane *(69)* is opened by acids (HZ) to a primary alcohol and by bases or ionic nucleophiles to a tertiary alcohol [39].



c) Reduction of α-Lactams with $LiAlH_4$

Reaction of the α-lactam *(32)* with $LiAlH_4$ affords a mixture of 2-*tert*-butylamino-2-methyl-1-propanol *(70)* and 2-*tert*-butylamino-2-methylpropionaldehyde *(71)* [40]. Neither the anticipated 1-*tert*-butyl-2,2-dimethylaziridine *(72)* nor the structurally isomeric



amino alcohol, 1-*tert*-butyl-2-methyl-2-propanol *(73)*, could be detected in the product [40].

Applying the considerations [41] generally accepted for the reduction of acyclic tertiary amides to α-lactams with $LiAlH_4$ (and presuming a genuine α-lactam structure), three products are anticipated: a tertiary amine *(72)*; an *N,N*-disubstituted amino alcohol *(70)*; and a similar amino aldehyde *(71)*. In fact, the reaction produced only the last two. The possibility that the first product is indeed 1-*tert*-butyl-2,2-dimethylaziridine *(72)*, which is then converted into more stable secondary products, can be excluded since 2,2-dimethyl-*N*-alkylaziridines are known [42] to be stable even to an excess of $LiAlH_4$ when refluxed in ether.

d) Reduction of Larger Lactams with $LiAlH_4$

N-Aryl- and *N*-alkyl-β-lactams are reduced by an excess of $LiAlH_4$ to the corresponding *N,N*-disubstituted amino alcohol [43,44] in analogy to the α-lactam *(32)*. *N*-Alkyllactams

[36] See for example, *J. A. Moore*: Trimethyleneimines, in *A. Weissberger*: Heterocyclic Compounds with Three- and Four-Membered Rings. Interscience, New York 1964, Volume II, p. 942–49.

[37] *Y. Etienne* and *N. Fischer*: β-Lactones in [36], Volume II, p. 808–29.

[38] *L. B. Clapp, et al.*, J. Amer. chem. Soc. *70*, 184 (1948); *73*, 2121, 2584 (1951).

[39] See, for example, a) *A. A. Petrov*, Ž. obšč. Chim. *10*, 931 (1940); *14*, 1038 (1944); *23*, 737 (1953); Chem. Abstr. *35*, 3603 (1941); *40*, 7153 (1946); *48*, 3898 (1954); b) *M. S. Malinowski*, Ž. obšč. Chim. *17*, 1559 (1947); Chem. Abstr. *42*, 2229 (1948); c) *C. A. Vander Werf, R. Y. Heisler*, and *W. E. McEwen*, J. Amer. chem. Soc. *76*, 1231 (1954); d) *F. A. Long* and *J. G. Pritchard*, J. Amer. chem. Soc. *78*, 2663, 2667 (1956); e) *E. L. Eliel* and *D. W. Delmonte*, J. Amer. chem. Soc. *80*, 1744 (1958).

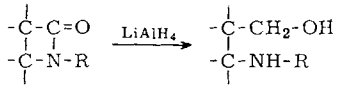
[40] *J. C. Sheehan* and *I. Lengyel*, α-Lactams III, J. org. Chemistry *31*, 4244 (1966).

[41] a) *F. Weygand et al.*, Angew. Chem. *65*, 525 (1953); b) *H. C. Brown* and *A. Tsukamoto*, J. Amer. chem. Soc. *83*, 2016, 4549 (1961).

[42] a) *H. M. Kissman* and *D. S. Tarbell*, J. Amer. chem. Soc. *74*, 4317 (1952); b) *A. T. Bottini* and *J. D. Roberts*, *ibid.*, *80*, 5203 (1958).

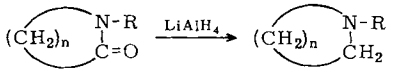
[43] a) *M. E. Speeter* and *W. H. Maroney*, J. Amer. chem. Soc. *76*, 5810 (1954); b) *F. F. Blicke* and *W. A. Gould*, J. org. Chemistry *23*, 1102 (1958).

[44] It should be mentioned here that *N-unsubstituted* β-lactams can be reduced by an excess of $LiAlH_4$ in high yields to the corresponding cyclic imine [*E. Testa*, *L. Fontanella*, and *G. F. Cristiani*, Liebigs Ann. Chem. *626*, 114 (1959)]. In fact, this reduction serves as an excellent method for the preparation of 3,3-disubstituted azetidines.



R = Alkyl, Aryl

with five- to nine-membered rings normally give the corresponding heterocycles *(74)* in good yield on reduction with $LiAlH_4$[45].



n = 3-7 *(74)*

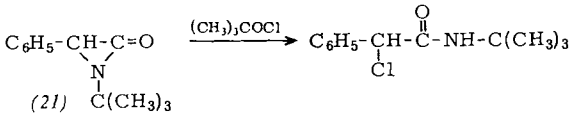
4. Miscellaneous Reactions of α-Lactams

a) Reaction with Diazomethane

In the hope of obtaining a ring-enlargement product, *Sheehan* and *Lengyel* treated 1-*tert*-butyl-3,3-dimethylaziridinone *(32)* with an ethereal solution of diazomethane at 0 °C[18]. No reaction was observed. *Baumgarten* and *Fuerholzer* attempted[46] to bring about a reaction between 1-*tert*-butyl-3-phenylaziridinone *(21)* and diazomethane in boiling ether; they could not, however, isolate or identify a product indicating a reaction.

b) Reaction with *tert*-Butyl Hypochlorite

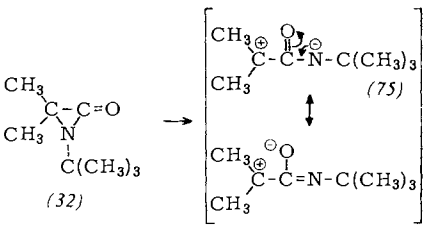
Addition of an ethereal solution of the α-lactam *(21)* to a solution of *tert*-butyl hypochlorite in ether initiates a rapid reaction[46]. One obtains *N*-*tert*-butyl-α-chlorophenylacetamide as the only product in 76% yield. In view of the polarization of *tert*-butyl hypochlorite ($tert\text{-}Bu\overset{\delta\ominus}{O}-\overset{\delta\oplus}{Cl}$), with the chlorine atom carrying a partial positive charge, the product obtained is surprising.



(21)

c) Reaction with Dimethyl Fumarate and Dimethyl Acetylenedicarboxylate

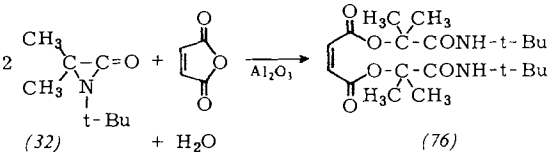
To examine the question whether α-lactams can function as 1,3-dipoles *(75)*[47], the α-lactam *(32)* was treated with dimethyl fumarate and dimethyl acetylenedicarboxylate, respectively[17,18]. No reaction was observed at 0 °C in chloroform solution. The α-lactam could be detected unchanged after two days.



(32) *(75)*

d) Reaction with Maleic Anhydride

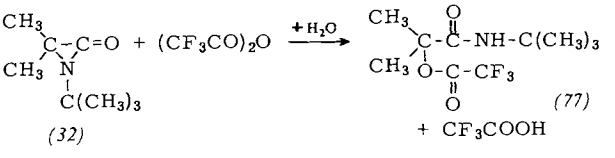
Surprisingly, the α-lactam *(32)* does react at 0 °C in chloroform with maleic anhydride. The product isolated after chromatography on alumina has been characterized[17] by elemental analysis, molecular-weight determination, and IR, UV, NMR, and mass spectrometry[48] as di[1-*tert*-butylcarbamoyl)-1-methylethyl)] maleate *(76)*.



(32) + H_2O *(76)*

e) Reaction with Trifluoroacetic Anhydride

α-Lactam *(32)* reacts vigorously with trifluoroacetic anhydride even at −5 °C to yield 1-(*tert*-butylcarbamoyl)-1-methylethyltrifluoroacetate *(77)*[48]. The mechanism has not been investigated.



(32) *(77)* + CF_3COOH

IV. Influence of the Substituents on Preparation, Stability, and Reactivity of α-Lactams

1. Variation of the Substituent on Nitrogen

As shown by *Sheehan* and *Lengyel*[17,18], the *N*-substituent decisively affects the reactivity of the "aliphatic" α-lactams. Exchanging the *N*-*tert*-butyl group in the starting amide for an *n*-propyl group *(78)* yielded the much more reactive α-lactam *(79)*, which has been detected by IR spectroscopy, but it reacted vigorously, even in the cold, with the potassium *tert*-butoxide present, thus precluding isolation. The two end products isolated were *tert*-butyl 2-methyl-2-*n*-propylaminopropionate *(80)* and 2-*tert*-butoxy-2-methyl-*N*-*n*-propylpropionamide *(81)*.

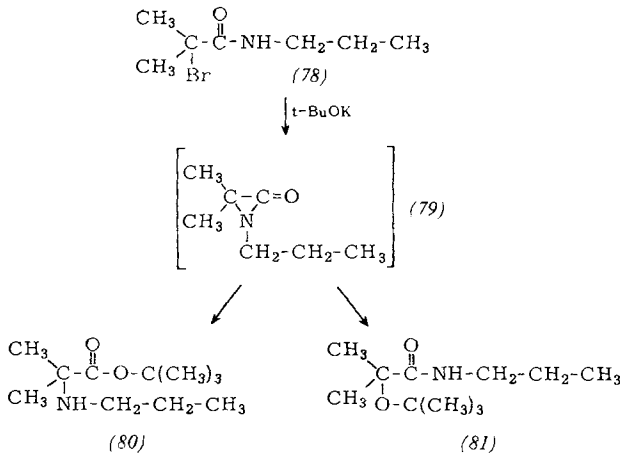
During the course of their attempts to prepare stable 3-phenyl-α-lactams[14,35] *Baumgarten* and co-workers also noticed the decisive influence of the *N*-substituent on ease of formation and stability of α-lactams.

[45] See, for example, a) *R. Lukes* and *J. Malek*, Chem. Listy *45*, 72 (1951); b) *P. G. Gassman* and *B. L. Fox*, J. org. Chemistry *31*, 982 (1966).

[46] Reference [14], p. 49.

[47] *R. Huisgen*, Angew. Chem. *75*, 604 (1963); Angew. Chem. internat. Edit. *2*, 565 (1963).

[48] *I. Lengyel*, unpublished results.



a) Replacement of the *N-tert*-Butyl Group in *(21)* by Secondary Alkyl Groups

Pure α-lactams could not be isolated from *N*-isopropyl-α-chlorophenylacetamide, *N*-isopropyl-α-bromophenylacetamide, *N*-cyclohexyl-*N*-chlorophenylacetamide, *N*-cyclohexyl-α-chlorophenylacetamide, or *N*-cyclohexyl-α-bromophenylacetamide [14]. The α-lactam was in most cases detected by IR, but in no case isolable because of its high reactivity. Replacement of the bulky *tert*-butyl group by primary and/or secondary alkyl or cycloalkyl groups – substituents with smaller steric requirement – in the starting amides also enhances the reactivity of the corresponding α-lactam.

b) Replacement of the *N-tert*-Butyl Group in *(21)* by *N*-2,6-Dimethylphenyl Group

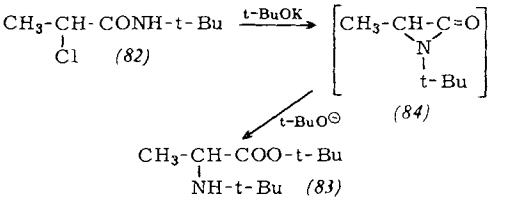
On the basis of the findings just described, one might expect that other bulky substituents on nitrogen would also lead to stable, moderately reactive α-lactams. In contrast to this expectation, it was found by *Baumgarten* and co-workers [14] that treatment of *N*-2,6-dimethylphenyl-α-bromophenylacetamide with potassium *tert*-butoxide in ether does not give an α-lactam; no IR band characteristic for an α-lactam could be detected in the spectrum of the reaction product, which was a yellow glassy mass that could not be identified.

This observation suggests that the ease of formation of an α-lactam (under otherwise identical conditions) is dependent not only on the degree of steric hindrance around the nitrogen, since both the *tert*-butyl and the 2,6-dimethylphenyl groups are bulky substituents with large steric requirements.

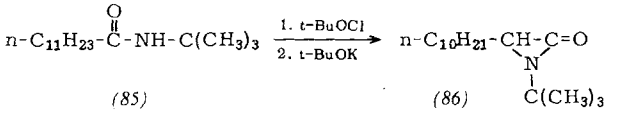
2. Variation of the Substituents on C-3

a) Aliphatic Series

Although the α-lactam formed from 2-bromo-2-methyl-*N-tert*-butylpropionamide with potassium *tert*-butoxide was stable enough to be isolated [17,18], replacement of one of the two methyl groups at C-3 by a hydrogen in the starting amide drastically changed the course of the reaction [18]. On treatment with potassium *tert*-butoxide, *N-tert*-butyl-α-chloropropionamide *(82)* gave a single product, *tert*-butyl-*N-tert*-butylalaninate *(83)*, in high yield. The intermediate α-lactam *(84)* could be detected by IR methods but was not isolated in pure form [18].

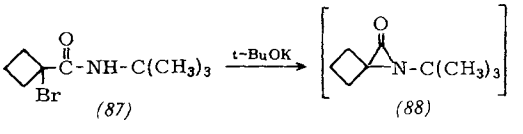


Attempts of *Baumgarten* and co-workers [14] to prepare a stable α-lactam from a long-chain fatty-acid amide were also unsuccessful. The reaction of *N-tert*-butyl-1-undecanecarboxamide *(85)* with *tert*-butyl hypochlorite and potassium *tert*-butoxide gave the α-lactam *(86)* (ν_{CO} = 1847 cm^{-1} in pentane) in such a low yield that it could not be isolated in pure form, since it is more reactive than the other components of the mixture and therefore decomposed on work-up. (For the formation of the unusually stable α-lactam *(34)* [19,20], compare Section III.1.)



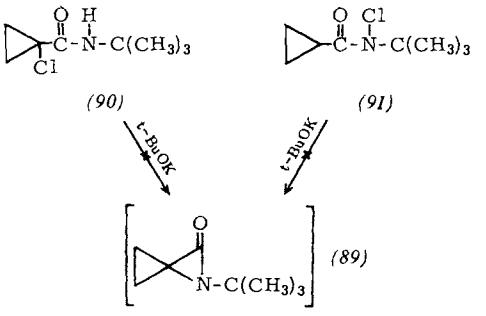
b) Variation of the Substituents on C-3 in Spiro-α-lactams

As mentioned in Section III.1., it was possible [19,25,30] to isolate – at least in crude form – α-lactams in good yield from *N-tert*-butyl-1-bromo-1-cycloalkane carboxamides with five-, six-, and eight-membered rings at C-3. However, decreasing the ring size of the spiro moiety in the starting amide produced a significant change in the reaction course: treatment of *N-tert*-butyl-1-bromo-1-cyclobutanecarboxamide *(87)* with potassium *tert*-butoxide in pentane at 0 °C gave – in low yield – the expected α-lactam *(88)*, but this was too reactive to be isolated [19].



Attempts [19] to prepare the interesting double-ring lactam *(89)* from the corresponding cyclopropyl precursors *(90)* and *(91)* on treatment with potassium *tert*-butoxide did not yield detectable quantities of compound *(89)* [19].

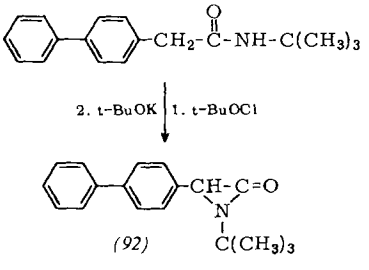
Only unchanged starting material was recovered from *(91)*, and starting with *(90)*, a mixture of unchanged starting material and *N-tert*-butylcyclopropane carboxamide was obtained.



c) Variation of the Substituents on C-3 in the Aromatic Series

As was mentioned in Section II.1., *Baumgarten* and co-workers prepared besides *N-tert*-butyl-3-phenylaziridinone *(21)*, the 3-*p*-chlorophenyl *(28)* and 3-*p*-bromophenyl *(29)* analogs. By using very fast work-up procedures they could also isolate 1-*tert*-butyl-3,3-diphenylaziridinone *(30)* [14].

Further attempts to prepare other α-lactams with aryl groups on C-3 did not lead to isolable quantities of the desired products [14]. Thus, it was not found possible to prepare or even to detect an α-lactam from *N-tert*-butyl-*p*-nitrophenylacetamide under the usual conditions. The reaction product was a dark-brown tar [14]. 1-*tert*-Butyl-3-(4-biphenylyl)aziridinone *(92)* could be prepared *via* the corresponding *N*-chloroamide only in impure form (m.p. 77–82 °C) [14].



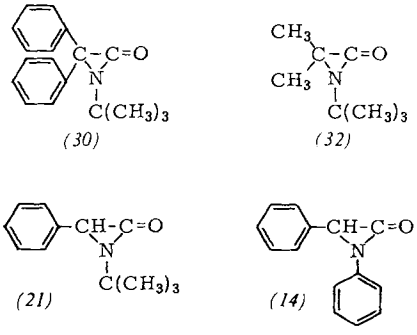
3. Thermal Stability and Chemical Reactivity of α-Lactams as a Function of Substitution Pattern

i) The greater the steric requirements of the substituents on N and on C-3 in the aliphatic series, the easier the preparation and purification of the α-lactam and the greater its thermal stability and lower the reactivity towards nucleophiles.

ii) Under otherwise identical conditions, C-3-disubstituted α-lactams are more stable than C-3-monosubstituted ones.

iii) The ease of thermal decomposition and the type of products formed is dependent not only on the steric factor but also on the presence or absence of at least one β-hydrogen in the alkyl group on C-3. α-Lactams possessing at least one such β-hydrogen in this alkyl group [such as *(32)*] decompose even on short warming in refluxing ether; the major products are α,β-unsaturated amides, formed *via* elimination of a β-hydrogen and subsequent rearrangement. α-Lactams that do not have a β-hydrogen in one of the alkyl groups on C-3 are more resistant to heating and give different products on thermal decomposition. Thus, the α-lactam *(21)* starts to decompose only at 105 °C [14], whereupon it fragments to benzaldehyde and *tert*-butyl isocyanide [14]. Similarly, the thermal decomposition of 1,3-di-*tert*-butylaziridinone *(34)*, which does not have a β-hydrogen and is further stabilized by the two bulky *tert*-butyl groups, does not start below 140 °C and leads to an aldehyde and a nitrile [19, 20].

iv) If the properties of α-lactams were determined and influenced only by steric factors, one would expect the α-lactam *(30)* to be more stable and easier to prepare than the α-lactam *(32)* because the two phenyl groups are bulkier than the two methyl groups. In fact, however, diphenyl-α-lactam *(30)* is the more difficult one to prepare. Furthermore, the α-lactams *(21)* and *(14)*

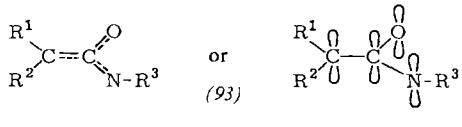


would then be expected to have a comparable stability, since the steric requirements of the *tert*-butyl and the phenyl group are not very different. In fact, the α-lactam *(14)* could not be prepared, in spite of considerable effort [4a,4b].

This leads to the conclusion that there are other factors (*e.g.* electronic effects) besides the steric one influencing the stability of α-lactams.

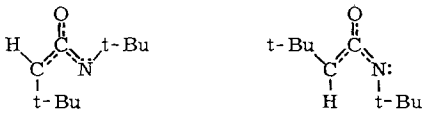
v) It appears reasonable to assume that both the preparation and the chemical and thermal reactions of α-lactams are decisively influenced by the geometry of an "acyclic" intermediate or transition state. The observations made hitherto concerning the properties of α-lactams can, at least qualitatively, be explained by invoking an intermediate or transition state of this type.

Such an intermediate *(93)* has recently been suggested by *Sheehan* and *Beeson* [30] (compare Section III.1.). This intermediate is acyclic, planar or quasi-planar,



and charge-delocalized. Substituents which contribute to the charge delocalization and thereby to the stabilization of this intermediate (or transition state), effect a destabilization of the real α-lactam ground state, *i.e.* render the preparation more difficult and enhance the reactivity of α-lactams.

Phenyl and aryl substituents considerably extend the charge delocalization of the transition state. In compounds with phenyl substituents on both C-3 and nitrogen [*e.g. (14)* and *(9)*], the π-electron system is extended throughout the whole molecule, thereby greatly facilitating formation of such an intermediate and enhancing its stability. This would explain why 1,3-diphenyl- and 1,3,3-triphenylaziridinone could not be prepared: the acyclic form is so stable that cyclization does not occur. Alkyl substituents, *e.g.* methyl [17,18] or *tert*-butyl groups [19,20], which do not significantly contribute to an extension of charge delocalization in the intermediate, destabilize this form and consequently enhance the stability of the α-lactam structure. As scale models clearly show, steric hindrance is very pronounced around the O–C–N atoms



in both possible conformations of the transition state of di-*tert*-butylaziridinone [20]. This may well explain the low reactivity and high thermal stability of this α-lactam.

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The Photolysis of Iodoaromatic Compounds

BY R. K. SHARMA AND N. KHARASCH [*]

Under appropriate conditions, the photolysis of iodoaromatic compounds yields derivatives of biphenyl and phenanthrene, as well as organometallic compounds. Ring closures of o-terphenyls to triphenylenes and of benzanilides to phenanthridones are described. The formation of dehydrobenzene (benzyne) on photolysis of 1,2-diiodobenzene in solution has been established. The photolysis of various substituted iodoaromatic compounds or of substances such as CH_3I, ICN, ICH_3, COOH, or $RC{\equiv}CI$, provides a general method for the generation of a large variety of free radicals in solution. The potential uses of photochemically initiated exchanges of iodine in ArI for ^{131}I, Li, D, Cl, or Br are noted.

1. Introduction

There are many early references [1] to the photochemistry of iodoaromatic compounds in the published literature and the free-radical nature of such processes was early recognized, especially by *Bryce-Smith* and co-workers. However, the synthetic potentialities of these reactions were not realized until comparatively recently. This review summarizes the main features of recent work on photolysis of iodoaromatic and other iodo compounds (ICN, ICH_2COOH, CH_3I, *etc.*) as well as selected bromoaromatic compounds. The mechanism of the photolysis is also commented on.

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[1] *A. Job* and *G. Emschwiller*, C. R. hebd. Séances Acad. Sci. *179*, 52 (1924); *G. Z. Razuvaev* and *M. A. Shubenko*, Ž. obšč. Chim. *21*, 1974 (1951); *O. P. Semenova* and *G. S. Tshiknnou*, J. Phys. Chem. (USSR.) *18*, 311 (1944); Chem. Abstr. *39*, 3206 (1945); *M. Badoche*, Bull. Soc. chim. France *9*, 393 (1942); Chem. Abstr. *37*, 4970 (1943); *N. A. Prilezhaeva*, Ž. fiz. Chim. *30*, 1044 (1956).

The following compounds can be synthesized by the photolysis of iodoaromatic compounds

a) Substituted biphenyls
b) Phenanthrenes (from *o*-iodostilbenes)
c) Various radio-isotope labeled compounds (by exchange reactions)
d) Specifically labeled deuterium compounds (by exchange reactions)
e) Organometallic compounds
f) Benzynes in solution (from 1,2-diiodoaromatic compounds).

2. Light Sources and the Nature of the Excited State

Perusal of the literature relating to the photolysis of iodoaromatic compounds reveals that a variety of light sources, frequently without filters, have been used – especially in qualitative studies. Mercury lamps have been most popular, and a summary of the

various types of commercial lamps is available [2]. A modified version of a cold-cathode, low-pressure mercury-vapor lamp was described by *Heidt* and *Boyles*, and an adaptation of such a lamp, now commercially available as the "W–K lamp" [74], has been found to be especially effective in synthetic work [3]. Monochromatic light, though less often used, has provided important information about details of reaction mechanisms.

A complete description of the initial excited state attained by iodoaromatic compounds on absorption of a quantum of light, as well as of the state which culminates in the cleavage of the carbon-iodine bond, is available only for a few cases, and the general picture is not complete. *Iredale* and co-workers examined the spectra of a number of iodo-organic compounds [4–7]. The first absorption band of iodobenzene in cyclohexane solution has a maximum at 2560 Å ($\varepsilon = 665$), and the second has a maximum at 2320 Å ($\varepsilon = 10000$). The second band has been said to correspond to the 2100 Å band (N → V, or π-π^*) of benzene [5]. It has been suggested that the first band is not due to absorption of a light quantum by the π-electrons of the aromatic system, but to absorption by the carbon-iodine bond or one of the electrons of iodine. Excitation to the A-level takes place, leading to the loss of an iodine atom.

This suggestion is supported by the fact that under the influence of nitric oxide, which inhibits the back reaction

$$C_6H_5^{\bullet} + I^{\bullet} \rightarrow C_6H_5I$$

by means of the side-reaction

$$C_6H_5^{\bullet} + NO \rightarrow C_6H_5NO,$$

a quantum yield of approximately unity has been found for the photodecomposition of iodobenzene by light of wavelength 2500 Å to 1800 Å. Practically all the light-affected molecules must have absorbed by way of the carbon-iodine bond, and not in the π-electrons of the benzene ring, since it is very unlikely that NO would have reacted by way of excited molecules at room temperature [4,5].

Substitution in the aromatic ring changes the spectral characteristics of the molecule. It has been pointed out that a molecule may absorb in the same spectral regions in one or more ways, in one or another of different groups, and to an extent dependent upon transition moments in these groups and on the influence of these groups on one another [5].

Wilkinson has studied the photosensitized decomposition of 1-iodonaphthalene. Degassed solutions of 1-iodonaphthalene do not show appreciable decomposition at 3600 Å. However, in the presence of benzophenone as sensitizer (when the triplet state of 1-iodonaphthalene is formed at a quantum yield of 0.9) the quantum yield of iodine formation, Φ_{I_2}, is only about 0.05, *i.e.* about one-half of the value when iodonaphthalene itself is irradiated at 3100 Å. It was suggested, therefore, that the triplet state of 1-iodonaphthalene is capable of dissociation, but does not always do so [8].

3. Photochemical Aspects

3.1. The Free-Radical Nature of the Photolysis

On absorption of light of suitable wavelength, an iodo compound dissociates into a free radical and an iodine atom. The quantum yield of this process in the liquid phase or in solution is less than unity. This has been ascribed to the back reaction (2).

$$Ar{-}I \rightarrow Ar^{\bullet} + I^{\bullet} \quad (1)$$
$$Ar^{\bullet} + I^{\bullet} \rightarrow ArI \quad (2)$$
$$Ar^{\bullet} + I_2 \rightarrow Ar{-}I + I^{\bullet} \quad (3)$$
$$Ar^{\bullet} + O_2 \rightarrow ArO_2^{\bullet} \quad (4)$$
$$Ar^{\bullet} + NO \rightarrow ArNO \quad (5)$$

The formation of free radicals by photolysis of ArI compounds has been proposed by several workers. The principal evidence for the homolytic nature of the process can be summarized as follows.

a) If the photolysis is carried out in the presence of the radical scavengers oxygen or nitric oxide, which inhibit the back reaction, the quantum yield of the reaction increases. *Olaerts* and *Jungers* have shown that the presence of oxygen raises the quantum yield in the photodecomposition of iodobenzene ten-fold, as compared with the value in absence of oxygen [28]. It was also shown that the quantum yield was independent of the amount of iodine produced, so reaction (3) cannot be very significant [52]. Similarly, a quantum yield of almost unity has been achieved in the presence of nitric oxide [5].

b) When the photolysis is conducted in aromatic solvents, the isomer distribution in the arylation product is in good agreement with that obtained with thermally generated aryl radicals [9,10].

c) Free radicals are known to participate in abstraction reactions. When aryl radicals are produced photochemically, they can also abstract hydrogen, chlorine, and bromine from cyclohexane [3], carbon tetrachloride, and bromoform [11], respectively.

The photolysis of iodobenzene in fluorocarbon and hydrocarbon solvents at 77 °K has been studied by ESR methods. The results suggest the formation of "free" phenyl radicals on photolysis [12].

The carbon-iodine bond energy in ArI compounds is about 55 kcal/mole. The photolysis of these bonds can thus be achieved readily; and with proper precautions – under conditions which allow other sen-

[2] *J. G. Calvert* and *J. N. Pitts jr.*: Photochemistry. John Wiley and Sons, New York 1966.

[3] *W. Wolf* and *N. Kharasch*, J. org. Chemistry *26*, 283 (1961); *30*, 2493 (1965).

[4] *R. A. Durie*, *T. Iredale*, and *A. H. Kingsbury*, Nature (London) *164*, 786 (1949).

[5] *R. A. Durie*, *T. Iredale*, and *J. M. S. Jarvie*, J. chem. Soc. (London) *1950*, 1181.

[6] *T. M. Dunn* and *T. Iredale*, J. chem. Soc. (London) *1952*, 1592.

[7] *J. Ferguson* and *T. Iredale*, J. chem. Soc. (London) *1953*, 2959.

[8] *F. Wilkinson*, J. physic. Chem. *66*, 2569 (1962).

[9] *J. M. Blair*, *D. Bryce-Smith*, and *B. W. Pengilly*, J. chem. Soc. (London) *1959*, 3174.

[10] *N. Kharasch* and *R. K. Sharma*, Abstracts 150th Meeting of Amer. chem. Soc. 1965, p. 10s.

[11] *N. Kharasch* and *P. G. Naylor*, unpublished results.

[12] *R. B. Ingalls*, *W. Wolf*, and *N. Kharasch*, Abstracts 146th Meeting of Am. Chem. Soc. 1964, p. 6 D.

sitive functional groups to remain intact – the photochemical decompositions of iodoaromatic compounds should provide a convenient source of free radicals of many different types.

3.2. Arylation by Photochemically Generated Aryl Radicals

It was shown by *Bryce-Smith* and co-workers that photolysis of iodobenzene, in isopropylbenzene [9] or as the neat liquid [13], leads to the phenylation of the isopropylbenzene or the iodobenzene. It was also found that hydrogen transfer to phenyl radical occurs on photolysis in isopropylbenzene.

Wolf and *Kharasch* have demonstrated that useful yields of substituted biphenyls and similar compounds can be obtained by this method [3] (see Table 1).

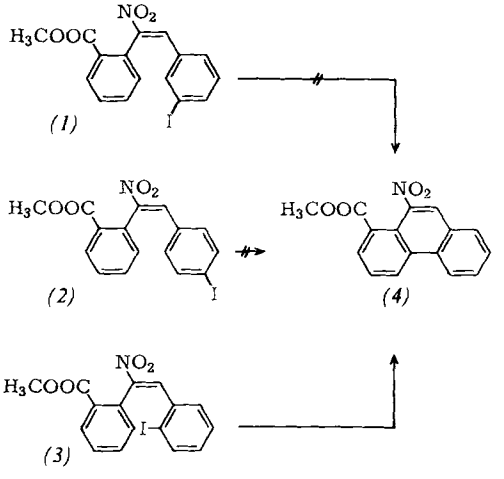
$$Ar{-}I + C_6H_6 \rightarrow Ar{-}C_6H_5 + {}^1/_2\, I_2 + [H] \qquad (6)$$

Table 1. Photolysis of aromatic iodo compounds in benzene.

Substrate	Conc. (M)	I_2 released (%)	Product	Yield (%)
Iodobenzene	0.03	98	Biphenyl	65
4-Iodobiphenyl	0.02	100	*p*-Terphenyl	91
1-Iodo-naphthalene	0.03	75	1-Phenyl-naphthalene	50
2-Iodotoluene	0.02	90	2-Methylbiphenyl	13
3-Iodotoluene	0.02	90	3-Methylbiphenyl	50
4-Iodotoluene	0.02	80	4-Methylbiphenyl	75
2-Iodothiophene	0.04	100	2-Thienylbenzene	70
2-Iodophenol	0.01	100	2-Hydroxybiphenyl	60
3,5-Diiodo-4-hydroxy-benzaldehyde	0.02	100	3,5-Diphenyl-4-hydroxy-benzaldehyde	25
2-Iodobenzoic acid	0.02	100	2-Phenylbenzoic acid	73
4-Iodobenzoic acid	0.03	100	4-Phenylbenzoic acid	80
4-Iodonitro-benzene	0.02	53	4-Nitrobiphenyl	–
2-Iodoaniline	0.01	60	2-Aminobiphenyl	20
4-Iodoaniline	0.02	75	4-Aminobiphenyl	38
2,4,6-Triiodophenol	0.015	100	2,4,6-Triphenylphenol	75

With many iodo substrates in aromatic solvents, iodine release is essentially quantitative. A plot of iodine release against time, however, shows a decrease in the rate of reaction in the later stages [14]. This may be due either to screening of light by the iodine released or to an increased amount of back reaction. Attempts have sometimes heen made to minimize such effects by carrying out the reaction in the presence of copper [16], silver [13], mercury [17], or silver trifluoroacetate [18]. In the photolysis of 1-iodo-2-phenylacetylene in benzene, the yield of diphenylacetylene was increased from 50 to 70 % when silver trifluoracetate was added. There are some problems caused by adherence of precipitated metallic iodides to the walls of the photolysis tube but satisfactory yields can generally be obtained in dilute solutions, even when the iodine released is not removed.

In the reaction, as carried out by *Wolf* and *Kharasch*, the incoming phenyl group always takes the position vacated by iodine; rearrangement of the aryl radical or the product has never been found. In those cases where a rearranged product has been isolated [19,20], the results can be attributed either to the isomerization of the iodo compound prior to the cleavage of the carbon-iodine bond or to rearrangement of the product subsequent to its formation. An ingenious experiment, which was planned to detect the slightest amount of rearrangement of the radical, while providing the greatest opportunity for it to do so, was conducted by *Kupchan* and *Wormser* [21]. It was shown that photolysis of methyl 3′-iodo-α-nitro-*cis*-stilbene-2-carboxylate *(1)* and methyl 4′-iodo-α-nitro-*cis*-stilbene-2-carboxylate *(2)* afforded no phenanthrene product, whereas the 2′-iodoisomer *(3)* gave the phenanthrene product *(4)* in 50 % yield.



Wynberg and *van Driel* [19], while attempting to use iodothiophene as a radical source, discovered that 2-phenylthiophene rearranges to 3-phenylthiophene on irradiation. In this paper, however, it was not made explicit whether isomeric products were isolated when iodothiophene was photolyzed in benzene.

The photochemical phenylation reaction has been extended to the direct synthesis of polyphenyl products. The synthesis of *(8)* and *(9)* from readily available 2,4,6-triiodophenol *(7)* further illustrates the scope of the photochemical technique [22].

A simple synthesis of *(10)* was achieved by *Nickon* and *Aaronoff* by the photolysis of 2,4-dimethyl-6-iodo-

[13] *J. M. Blair* and *D. Bryce-Smith*, J. chem. Soc. (London) *1960*, 1788.

[14] *J. Heidt* and *H. B. Boyles*, J. Amer. chem. Soc. *73*, 5728 (1951).

[15] *N. Kharasch* and *R. K. Sharma*, unpublished results.

[16] *I. P. Gragerov* and *M. Ya. Turkina*, Ž. obšč. Chim. *33*, 1843 (1963).

[17] *D. H. Hey*, *D. A. Shingleton*, and *G. H. Williams*, J. Chem. Soc. (London) *1963*, 1958.

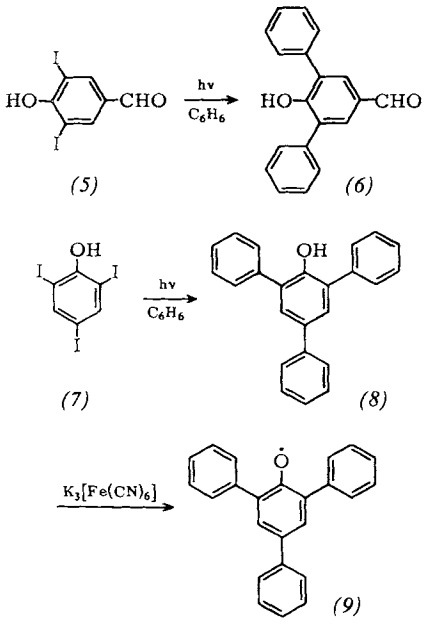
[18] *N. Kharasch* and *L. Göthlich*, unpublished results.

[19] *H. Wynberg* and *H. van Driel*, J. Amer. chem. Soc. *87*, 3998 (1965).

[20] *R. A. Bowie* and *O. C. Musgrave*, J. chem. Soc. (London) *C 1966*, 566.

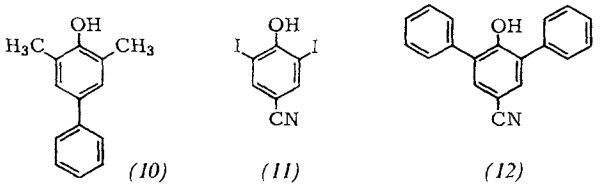
[21] *S. M. Kupchan* and *H. C. Wormser*, J. org. Chemistry *30*, 3792 (1965).

[22] *N. Kharasch*, *W. Wolf*, *T. J. Erpelding*, *P. G. Naylor*, and *L. Tokes*, Chem. and Ind. *1962*, 1720.



(5) (6) (7) (8) (9)

phenol in benzene[23], and recently the synthesis of 2,4,6-tri(pentadeuteriophenyl)phenol, in 45.5 % yield, by the photolysis of 2,4,6-triiodophenol in hexadeuteriobenzene has been reported by *Dimroth*, *Berndt*, and *Volland*[67].



(10) (11) (12)

Ioxynil *(11)*, a herbicide and molluscicide, is more toxic to plants in the light than in the dark. Since ioxynil undergoes photolytic reaction in benzene solution to give a phenylated product *(12)*, it has been suggested that the toxic action might be due to the free radicals produced in the cell on exposure to light, which seriously interfere with the reactions essential for the life of the plant[24].

Table 2. Some other synthetic results in the photolysis of iodo compounds in benzene [25].

Substrate	Time (h)	Product	Yield (%)
1-Iodo-2-phenylacetylene	12	Diphenylacetylene	50
1-Iodo-2-tolylacetylene	12	Tolylphenylacetylene	62
Benzoyl iodide	60	Benzophenone	12 [a]
2-Iodobenzaldehyde	48	2-Phenylbenzaldehyde	95 [a]
4-Iodobenzaldehyde	48	4-Phenylbenzaldehyde	90 [a]
Monoiodoacetic acid	24	Phenylacetic acid	67
Cyanogen iodide	10	Benzonitrile	50 [b]

[a] As 2,4-dinitrophenylhydrazone.

[b] As benzoic acid.

The phenomenon of photolytic decomposition in benzene is not limited to aryl iodides. *Kharasch* and *Göthlich* have shown that the reaction can be extended to other types of organic iodides to give fair to good yields of substituted benzenes (cf. Table 2)[25].

Photolysis of methyl iodide in benzene leads to the formation of toluene in 66 % yield, but with ethyl iodide and isopropyl iodide the yields of alkylation products are low[26]. Photolysis of benzyl iodide[17] in isopropyl benzene and of benzyl iodide and allyl iodide[27] in benzene also result in poor yields. In general, radicals that are not very susceptible to disproportionation can be produced effectively, and used for synthetic purposes, by photolysis of the appropriate iodo compounds.

3.3. Effect of Oxygen

Reference was made earlier to the fact that the presence of oxygen increases the quantum yield of decomposition of iodobenzene[28]. In the photolysis of iodoacetic acid in hexane, it was found by *Hacobian* and *Iredale*[29] that $\Phi_{I_2} = 0.49$ when no special efforts were made to remove oxygen. After an extensive removal of oxygen by transferring the solution under vacuum from one vessel to another by evaporation and condensation at least six times, the iodine release on photolysis was negligible ($\Phi_{I_2} = 0$) although the amount of light absorbed was practically the same as in the presence of oxygen. Similarly, the photolysis in hexane of such iodides as methyl, ethyl, isoamyl, iodobenzene, and *p*-iodotoluene gave $\Phi_{I_2} = 0.5$ in the presence of oxygen and $\Phi_{I_2} = 0.05$ after its extensive removal.

$$p\text{-}C_6H_5\text{-}C_6H_4\text{-}I \rightleftharpoons p\text{-}C_6H_5\text{-}C_6H_4^{\bullet} + I^{\bullet}\ (1/2\ I_2) \quad (7)$$

$$p\text{-}C_6H_5\text{-}C_6H_4^{\bullet} + C_6H_6 \longrightarrow p\text{-}C_6H_5\text{-}C_6H_4\text{-}C_6H_6^{\bullet} \quad (8)$$

$$p\text{-}C_6H_5\text{-}C_6H_4^{\bullet} + p\text{-}C_6H_5\text{-}C_6H_4\text{-}C_6H_6^{\bullet} \longrightarrow C_6H_5\text{-}C_6H_5 + p\text{-}C_6H_5\text{-}C_6H_4\text{-}C_6H_5 \quad (9)$$

$$p\text{-}C_6H_5\text{-}C_6H_4\text{-}C_6H_6^{\bullet} + \tfrac{1}{2}I_2 \longrightarrow p\text{-}C_6H_5\text{-}C_6H_4\text{-}C_6H_5 + HI \quad (10)$$

$$p\text{-}C_6H_5\text{-}C_6H_4^{\bullet} + HI \longrightarrow C_6H_5\text{-}C_6H_5 + I^{\bullet} \quad (11)$$

$$2\ I^{\bullet} \rightleftharpoons I_2 \quad (12)$$

The effect of oxygen on the product distribution in the arylation of benzene has been demonstrated by *Kharasch* and *Sharma*[30]. It was found in the photolysis of 4-iodobiphenyl in benzene that the yield of the hydrogen-transfer product (biphenyl) increased at the expense of the arylation product (*p*-terphenyl) with

[23] *A. Nickon* and *B. R. Aaronoff*, J. org. Chemistry *29*, 3379 (1964).

[24] *E. N. Ugochukwu* and *R. L. Wain*, Chem. and Ind. *1965*, 35.

[25] *N. Kharasch* and *L. Göthlich*, Angew. Chem. *74*, 651 (1962); Angew. Chem. internat. Edit. *1*, 459 (1962).

[26] *N. Kharasch*, *W. Wolf*, and *H. B. Lewis*, unpublished results.

[27] *N. Kharasch* and *H. Dien*, unpublished results.

[28] *E. Olaerts* and *J. C. Jungers*, Discussion Faraday Soc. *2*, 222 (1947).

[29] *S. Hacobian* and *T. Iredale*, Nature (London) *166*, 156 (1950).

[30] *N. Kharasch* and *R. K. Sharma*, Chem. Commun. *1966*, 106.

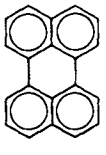
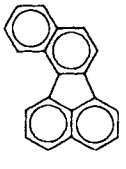
more efficient removal of oxygen by freeze-pump-thaw cycles. The ratio of biphenyl/*p*-terphenyl increased from 0.1 when the solution was not degassed to 0.5 when the solution was rigorously degassed. The decrease in the yield of biphenyl in the presence of oxygen has been explained in terms of the ability of oxygen to interfere with hydrogen transfer processes (equations (9) and (11)).

As mentioned earlier, oxygen can trap the radicals formed. In the above photolysis, 4-hydroxybiphenyl was formed in up to 26 % yield if the solution was kept saturated with oxygen during photolysis. The route to the phenol can be visualized as proceeding *via* a hydroperoxide, which is cleaved by the hydrogen iodide.

3.4. Arylation in Other Media

Bryce-Smith and co-workers, and *Kharasch* and *Naylor* [31], have studied the isomer distributions in the photochemical phenylation of various aromatic solvents. The results show that the isomer distribution is characteristic of "normal" free radicals, since a "hot" radical would have shown less selectivity. Thus any excess energy associated with the radical when first formed is rapidly dissipated in the condensed phase.

Badger and *Whittles* have photolyzed 1-iodonaphthalene in molten naphthalene. The products found were 1,1-binaphthyl, 1,2′-binaphthyl and small amounts of perylene *(13)* and benzofluoranthene *(14)* [32]. A control experiment showed that perylene is not formed by cyclodehydrogenation of 1,1′-binaphthyl.

(13)   *(14)*

Photolysis of 2-, and 3-, and 4-iodobiphenyl in biphenyl has been studied by *Hutchinson*, *Hudson*, and *Doss* in order to determine partial rate factors for substitution of biphenyl by biphenylyl free radical [33].

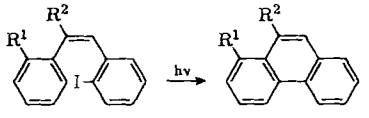
The photolysis of iodobenzene in thiophene gives 2- and 3-phenylthiophene, besides 2,2′-bithienyl and 2,3′-bithienyl [34]. In view of the recently established isomerization of 2-phenylthiophene to 3-phenylthiophene, the low yield of 3-phenylthiophene is rather surprising.

Preliminary experiments in our laboratory indicated that in the photolysis of 4-iodobiphenyl in 1-hexene an appreciable addition of 4-biphenylyl radicals to the double bond of 1-hexene occurs. This addition of a photochemically generated radical to a double bond has now been further studied toward developing a general synthesis of carboxylic acids from olefins.

Carboxymethyl radicals produced by photolysis of iodoacetic acid add to 1-hexene to give a mixture of saturated and unsaturated C_8 acids. Extraction with dilute sodium carbonate, acidification, and hydrogenation gives a 60 % yield of *n*-octanoic acid. A similar photolysis in cyclohexene gives 1- and 2-cyclohexenylacetic acid (24 %), cyclohexylacetic acid (3 %), and acetic acid (29 %) [35]. However, when bromoacetic acid was photolyzed in 1-hexene and in cyclohexene, *n*-octanoic acid and cyclohexylacetic acid were obtained in 60–70 % yields; unsaturated acids were not found in these cases.

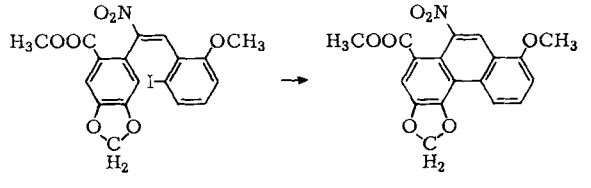
3.5. Intramolecular Arylation

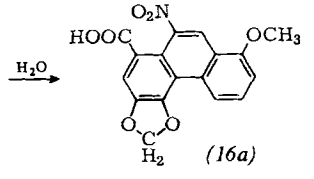
Based on the general studies of *Wolf* and *Kharasch*, *Kupchan* and *Wormser* have developed a general synthesis of substituted phenanthrene derivatives, which uses substituted 2-iodostilbenes in an intramolecular reaction to effect photocyclization [21].

(15)  *(16)*

$R^1 = R^2 = H$, 90 %
$R^1 = CH_3$, $R^2 = H$, 96 %
$R^1 = H$, $R^2 = COOCH_3$, 71 %
$R^1 = CH_3$, $R^2 = COOCH_3$, 62 %
$R^1 = H$, $R^2 = NO_2$, 40 %
$R^1 = COOCH_3$, $R^2 = NO_2$, 45 %

The effectiveness of this method for the synthesis of nitrophenanthrenes that are not readily accessible by other approaches is illustrated by an elegant synthesis of the naturally occurring tumor inhibitor, aristolochic acid *(16a)*.





(16a)

In the presence of dissolved oxygen or iodine, *cis*-stilbenes give phenanthrenes on photolysis in solution [36]. It was suggested that the cyclization proceeds through an unorthodox *trans*-dihydrophenanthrene derivative, and strong evidence for this has been presented [37, 38]. Photolysis of methyl α-nitro-*cis*-stil-

[31] *N. Kharasch* and *P. G. Naylor*, unpublished results.

[32] *G. M. Badger* and *C. P. Whittles*, Australian J. Chem. *16*, 440 (1963).

[33] *W. M. Hutchinson*, *P. S. Hudson*, and *R. C. Doss*, J. Amer. chem. Soc. *85*, 3358 (1963).

[34] *C. E. Griffin* and *K. R. Martin*, Chem. Commun. *1965*, 154.

[35] *N. Kharasch*, *P. Lewis*, and *R. K. Sharma*, Abstracts 152nd Meeting of Amer. Chem. Soc. 1966, p. 64u.

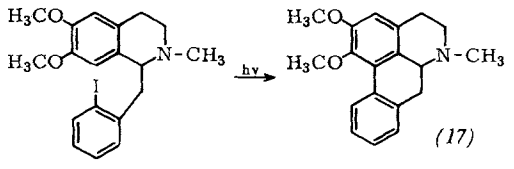
[36] *F. B. Mallory*, *C. S. Wood*, and *J. T. Gordon*, J. Amer. chem. Soc. *86*, 3094 (1964).

[37] *W. M. Moore*, *D. D. Morgan*, and *F. R. Stermitz*, J. Amer. chem. Soc. *85*, 829 (1963).

[38] *G. S. Hammond*, *J. Saltiel*, *A. A. Lamola*, *N. J. Turro*, *J. S. Bradshaw*, *D. O. Cowan*, *R. C. Counsell*, *V. Vogt*, and *C. Dalton*, J. Amer. chem. Soc. *86*, 3197 (1964).

bene-2-carboxylate fails to effect cyclization in the presence of oxygen or iodine, whereas the 6- or 2'-iodo compound gave the cyclization product in 45 % yield. This makes the intermediacy of a dihydrophenanthrene in the photocyclization of 2-iodostilbene very unlikely and an intramolecular cyclization *via* a free radical path seems the more likely route. It should be noted that on irradiation *trans*-stilbenes isomerize to *cis* compounds and may therefore be used as starting materials in some syntheses.

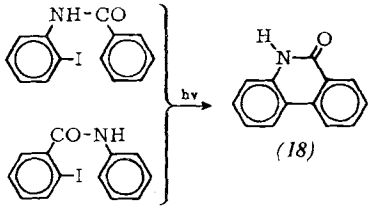
The method has been extended to the photochemical synthesis of noraporphines and of aporphines, by photolysis of 1-(2-iodobenzyl)-1,2,3,4-tetrahydroisoquinoline derivatives. Photolysis of suitable precursors gave DL-nuciferine *(17)*. It was found that the yield



(17)

was much better when the hydrochloride salt was photolyzed in aqueous solution [39]. While photolyses in aqueous solutions have not been generally studied, a report of the photolysis of 2-iododeoxyuridine in aqueous media has been made by *Prusoff* in a study of considerable chemical and biochemical interest.

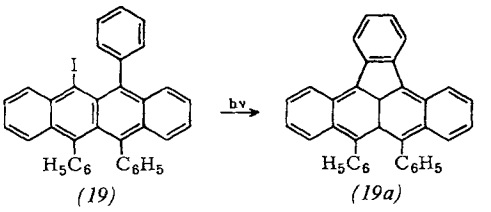
Similar intramolecular cyclizations leading to heterocyclic systems have been effected by *Kharasch* and coworkers [40]. For example, 2-iodo-*N*-benzoylaniline or 2-iodo-*N*-phenylbenzamide gave phenanthridone *(18)* on photolysis in benzene solution. Of special interest was the finding that benzanilide itself could undergo photocyclization to give phenanthridone in even better yields than from the iodo compounds.



(18)

The stereochemistry for the ring closures in these reactions would be favored on starting from the lactim forms of the amides. Further studies of the photolysis of sulfonamides are in progress to define these points more fully.

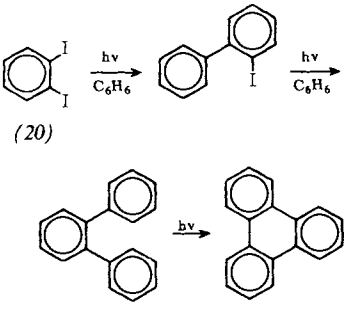
Formation of a five-membered ring – the first intramolecular cyclization to be effected by photolysis of an iodoaromatic substrate – was reported in 1942 by *Badoche* [1] who converted compound *(19)* into compound *(19a)*.



(19) *(19a)*

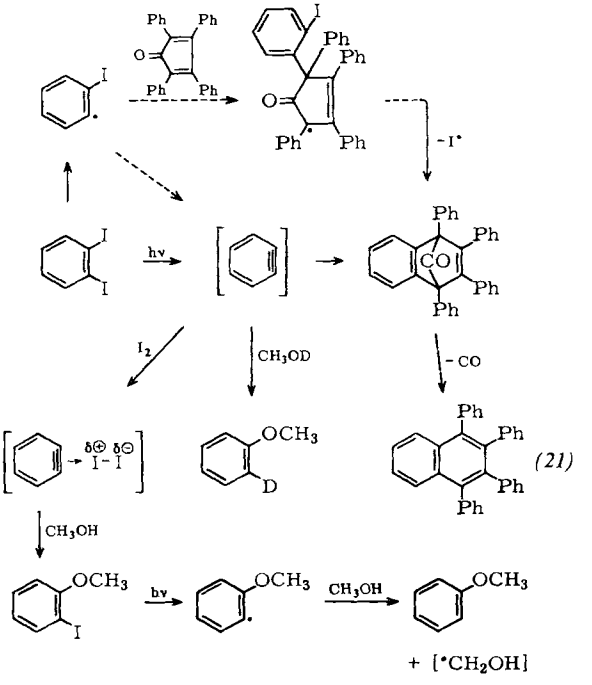
3.6. Polyiodo Compounds

Photolysis of *o*-diiodobenzene in benzene gave mainly 2-iodobiphenyl and small amounts of biphenyl and triphenylene [41]. Recent work has clearly demonstrated that triphenylene is formed by cyclodehydrogenation of *o*-terphenyl [42].



(20)

There is, of course, the interesting possibility that both iodine atoms will be lost on photolysis of diiodobenzene giving rise to benzyne. In the case of *o*-diiodobenzene, it was shown independently by *Kampmeier* and *Hoffmeister* and by *Kharasch* and *Alston* [43] that photolysis in the presence of tetracyclone gives the expected Diels-Alder adduct of benzyne and tetracyclone, *i.e.* 1,2,3,4-tetraphenylnaphthalene.



(21)

[39] *S. M. Kupchan* and *R. M. Kanojia*, Tetrahedron Letters *1966*, 5353.

[40] *N. Kharasch*, *B. S. Thyagarajan*, and *H. B. Lewis*, unpublished results.

[41] *J. A. Kampmeier* and *E. Hoffmeister*, J. Amer. chem. Soc. *84*, 3787 (1962).

[42] *N. Kharasch*, *T. G. Alston*, *H. B. Lewis*, and *W. Wolf*, Chem. Commun. *1965*, 242.

[43] See footnote 14 in reference [41].

It is, however, conceivable that the adduct is formed in a two-stage radical process without involving benzyne at all. Further evidence has now been obtained by performing the photolysis in CH_3OD. Mass spectral analysis of the anisole formed showed it to contain 63.8 % of monodeuterated anisole, which can be interpreted as arising through the intermediacy of benzyne [15].

The formation of 2-iodoanisole was unexpected, and presents another possible route to anisole by reductive removal of iodine. Its formation in such amounts by solvolysis of 1,2-diiodobenzene seems quite unlikely, and a more reasonable route, involving a π-complex of iodine with benzyne, is suggested.

Presuming that *m*- and *p*-benzynes would also add methanol to give anisole, formation of appreciable amounts of anisole on photolysis of *m*- and *p*-diiodobenzene in methanol would indicate the presence of these transitory intermediates. However, only traces of anisole (< 0.1 %) were formed when the experiment was carried out. It was felt that anisole is formed by secondary solvolytic processes and that *m*- and *p*-benzynes are not involved [44–46].

As pointed out earlier, photolysis of other diiodo- and triiodobenzene derivatives in benzene gives rise to the expected phenylation products. Thus, 2,4,6-triiodophenol leads to 2,4,6-triphenylphenol and thence to 2,4,6-triphenylphenoxy radicals. This opens a route to the general synthesis of substituted phenoxy radicals, whose properties could then be studied in detail. Other polyiodo compounds have also been studied (Table 1), but much further work remains to be done. It may also be pertinent to mention here that photolysis of methylene iodide in solution has recently been shown to give carbene [47].

3.7. Steric Effects

Eliel [48] has pointed out that whereas biphenyl itself has a strong absorption maximum at 249 nm, $\varepsilon = 15000$, because of an excited state involving conjugation of the two benzene rings, the introduction of even a single methyl group in the *ortho* position shifts the absorption maximum to 237 nm and lowers the extinction coefficient to 10500. When there are two methyl groups in the *o,o'* positions, the biphenyl band disappears and the absorption spectrum of the molecule resembles that of *m*-xylene. The reason for this is that the excited state deviates from a planar conformation and the extended resonance is greatly dampened. From the ultraviolet spectrum of *o*-iodobiphenyl there is also some evidence that the substitution of iodine at the *o*-position forces the molecule out of the planar conformation [6]

It seems, therefore, that 2-iodobiphenyl should photolyze faster than 4-iodobiphenyl, since loss of iodine from a molecule of 2-iodobiphenyl would allow the resulting 2-biphenylyl radical to assume a more stable planar structure. It has, however, been observed that although the photolysis of 4-iodobiphenyl in benzene is more than 90 % complete, the similar photolysis of 2-iodobiphenyl proceeds to an extent of 45 % only [49]. It appears that iodine competes favorably with benzene for the 2-biphenylyl radical and that steric factors in formation of the transition state for the conversion to *o*-terphenyl may be decisive in determining the course of the reaction. This is also reflected in the photolysis of an equimolar mixture of 2- and 4-iodobiphenyl in benzene, where it is found that *p*-phenylation is 26 times faster than *o*-phenylation. For the latter case, however, the differences in the light absorption by the two compounds might also be responsible for the observed yields of the phenylation products.

3.8. Exchange

It was reported by *Noyes* [50] that hexane solutions of iodobenzene undergo exchange reaction on illumination with visible light, whereas duplicate solutions stored in the dark underwent no more than 1 % of exchange. A direct substitution by an iodine atom was suggested as a mechanism of this exchange reaction [51]. A recent study by *Anbar* and *Rein* [52], utilizing a high-pressure mercury lamp and cut-off filters at 2850 Å and 3400 Å, reports that in the case of isotopic exchange with iodine the rate of de-iodination is independent of the concentration of molecular iodine and that the rate of isotopic exchange varies as the square root of the iodine concentration.

The observed square root dependence of the rate of exchange on iodine concentration is in accord with a mechanism *via* (13) and (14).

$$I_2 \xrightarrow{h\nu} 2\,I^{\bullet} \qquad (13)$$

$$I^{\bullet} + PhI \longrightarrow PhI + I^{\bullet} \qquad (14)$$

The exchange reaction appears to be distinctly faster than the corresponding exchange of ethyl iodide [57], while the rate of reaction with sodium suggests that the relative rates of exchange by a displacement of iodine which results in the formation of a radical would be in the opposite order. Moreover, the fact that the rate of de-iodination is independent of the iodine concentration suggests that reaction (15) is of little importance at the iodine concentration employed.

$$C_6H_5{-}I + I^{\bullet} \longrightarrow C_6H_5^{\bullet} + I_2 \qquad (15)$$

$$C_6H_5I \xrightarrow{h\nu} C_6H_5^{\bullet} + I^{\bullet} \qquad (16)$$

$$C_6H_5^{\bullet} + I_2 \longrightarrow C_6H_5I + I^{\bullet} \qquad (17)$$

Exchange *via* reaction (16) and (17) would require a first order dependence on the iodine concentration.

It may be pointed out that although the contribution of a reaction such as (17) is considered to be negligible during the exchange, the reaction can occur under appropriate conditions, the iodine then acting as a radical trap [57].

[44] *N. Kharasch* and *R. K. Sharma*, Abstracts 152nd Meeting of Amer. Chem. Soc. 1966, p. 128 S.

[45] *M. Stiles, R. G. Miller*, and *U. Burckhardt*, J. Amer. chem. Soc. *85*, 1792 (1963).

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[47] *D. C. Blomstrom, K. Herbig*, and *H. E. Simmons*, J. org. Chemistry *30*, 959 (1965).

[48] *E. L. Eliel*: Stereochemistry of Carbon Compounds. McGraw Hill, New York 1962, p. 177.

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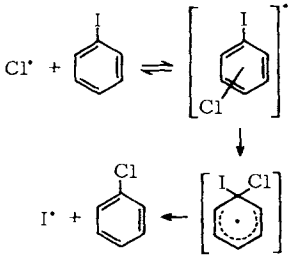
The displacement of iodine by chlorine or bromine atoms under illumination has also been studied.

$$Ar{-}I + Cl^{\bullet} \rightarrow ArCl + I^{\bullet} \quad (18)$$

$$Ar{-}I + Br^{\bullet} \rightarrow ArBr + I^{\bullet} \quad (19)$$

The reactions proceed smoothly in carbon tetrachloride or other inert solvents at room temperature on illumination with visible light, but do not take place at a noticeable rate in the dark. When a substituent is present, the entering halogen atom invariably occupies the position of the atom displaced. Dissociation of iodoarene followed by subsequent reaction with the halogen, or a mechanism involving a displacement on halogen to give an aryl radical are considered to be unlikely; direct displacement on carbon is favored. This may proceed through the formation of a π- or σ-complex intermediate[54]. Formation of complexes between aromatics and halogen atoms is indirectly supported by the selectivity studies of *Russell*[55] and *Walling* and *Mayahi*[56].



3.9. Abstraction Reactions

Replacement of iodine by hydrogen has been effected by conducting the photolysis in cyclohexane[3] or methanol[53]; in most cases the yield is good[53]. Water, methyl iodide, and dimethoxymethane were also identified among the reaction products. The following sequence of reactions has been proposed for the reductive de-iodination process.

$$ArI \rightarrow Ar^{\bullet} + I^{\bullet} \quad (20)$$

$$Ar^{\bullet} + CH_3OH \rightarrow ArH + {}^{\bullet}CH_2OH \quad (21)$$

$${}^{\bullet}CH_2OH + I \rightarrow (ICH_2OH) \rightarrow HI + H_2C{=}O \quad (22)$$

$$CH_3OH + HI \rightarrow CH_3I + H_2O \quad (23)$$

$$H_2C{=}O + 2\,CH_3OH \rightarrow H_2C(OCH_3)_2 + H_2O \quad (24)$$

These reactions especially when perdeuterioacetone is used as a solvent provide a general synthesis of specifically labeled deuterium compounds from iodo precursors.

The photolysis of chloro or bromo compounds under conditions where exchange of hydrogen for halogen can occur was reported by *Szychlinski*[58].

Using a procedure similar to that of *Bridger* and *Russell*[59], photolysis of 4-iodobiphenyl in a mixture of benzene and other solvents containing hydrogen has been initiated. The purpose of such a study is to compare the hydrogen-donating abilities of various solvents. Preliminary studies show that the differences in hydrogen-donating abilities of the various solvents can be demonstrated, *e.g.* with methanol and cyclohexane, but further study is required before quantitative predictions can be made.

When the photolysis of 4-iodobiphenyl is carried out in carbon tetrachloride, 4-chlorobiphenyl is formed. However, the yield of this product diminishes as the photolysis progresses, probably because Cl or CCl_3 (which are present under conditions of photolysis) attack 4-chloro- or 4-iodobiphenyl converting them into other products. Bromine can also be abstracted when bromoform is used as the solvent in the photolysis. The yield of the bromobiphenyl was 93 %, and only about 1 % of hydrogen abstraction takes place, as measured by biphenyl formation[60]. This result is in excellent agreement with the findings of *Cadogan et al.*[66], who studied the similar reaction with bromoform of the thermally generated phenyl radical from benzoyl peroxide.

3.10. Synthesis of Organometallic Compounds

Formation of organometallic compounds by the attack of organic free radicals on a suitable substrate is known. The availability of a variety of free radicals by the photolyses of aryl iodides offers an attractive route for such syntheses and it has been effectively utilized in the synthesis of organophosphorous and organoboron compounds. *Griffin* and co-workers[61,62] have shown that the photolysis of iodobenzene, in a three- to five-fold excess of trimethyl phosphite at $-3\,^{\circ}C$, yields dimethylphenylphosphonate in quantitative yield. A mechanism involving the attack of phenyl radical on trimethyl phosphite has been proposed.

$$\begin{aligned} C_6H_5I &\xrightarrow{h\nu} C_6H_5^{\bullet} + I^{\bullet} \\ C_6H_5^{\bullet} + P(OR)_3 &\longrightarrow C_6H_5P^{\bullet}(OR)_3 \\ C_6H_5P^{\bullet}(OR)_3 + I^{\bullet} &\longrightarrow [C_6H_5P(OR)_3]^{\oplus}I^{\ominus} \\ [C_6H_5P(OR)_3]^{\oplus}I^{\ominus} &\longrightarrow C_6H_5P(O)(OR)_2 + RI \\ R = CH_3 & \end{aligned} \quad (22)$$

The phosphonium salt *(22)* has been isolated. Vinyl iodide has also been shown to undergo photolysis with formation of dialkyl vinyl phosphonate.

[53] *N. Kharasch* and *P. Friedman*, Abstracts 148th Meeting of Amer. Chem. Soc. 1964, p. 27 S.

[54] *B. Milligan, R. L. Bradow, J. E. Rose, H. E. Hubbert*, and *A. Roe*, J. Amer. chem. Soc. *84*, 158 (1962).

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[61] *J. B. Plumb* and *C. E. Griffin*, J. org. Chemistry *27*, 4711 (1962).

[62] *J. B. Plumb, R. Obrycki*, and *C. E. Griffin*, J. org. Chemistry *31*, 2455 (1966).

Recently *Drawe* and *Caspari* [63] have shown that gamma-irradiation (Co-60 source) of mixtures of aryl halides with triphenylphosphine or triphenylarsine gives phosphonium or arsonium halides. Although photolyses of aryl iodides have not been carried out in the presence of triphenylarsine, formation of arsonium iodides, and hence of carbon-arsenic bonds, in this manner should be feasible. Photolysis of iodobenzene with phosphorous trichloride and tribromide is reported to give phenylphosphorous dichloride and the dibromide, respectively, after irradiation for 50–53 hours [20].

It was found by *Bowie* and *Musgrave* [20] that photolysis of iodobenzene in the presence of boron halides results in the formation of phenylboron dihalides and diphenylboron halides by free-radical substitution reactions. Hydrolysis of the products gives the corresponding boronic or borinic acids, the yields decreasing in the series $BI_3 > BBr_3 > BCl_3$. Boron tribromide is used most frequently; and by using suitable iodo compounds a variety of boronic and borinic acids or anhydrides has been obtained. There is also some evidence that BBr_2 radicals are also present in the above photolyses.

The reaction of 1-iodonaphthalene gives rise to a 2-naphthyl derivative that is formed by rearrangement of the 1-naphthyl radical or of the intermediate 1-naphthylboron dibromide. The rearrangement of the 1-naphthyl radicals seems ruled out, particularly in view of the study of *M. S. Kharasch* and *Danenberg* [64], who found that isomerization of this radical to 2-naphthyl radical does not occur in boiling carbon tetrachloride. Since it is known that ionic paths are available for isomerizations of 1-naphthyl to 2-naphthyl compounds, it seems that such a path may be involved for the rearrangement of 1-iodonaphthalene or of 1-naphthylboron dibromide under the conditions of the experiment.

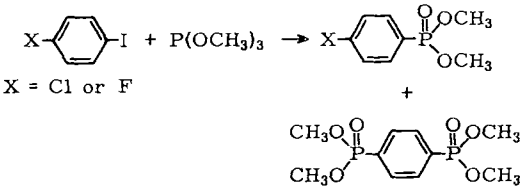
Bowie and *Musgrave* [20] also attempted the photolysis of iodobenzene in the presence of silicon tetrabromide or stannic bromide but could not isolate any definitive products.

3.11. Photolysis of Other Halides

As the strength of the carbon-halogen bond increases, the photolysis is expected to proceed with increasing difficulty. This is borne out by the results of the photolysis of 4-halobiphenyls [65]. Whereas the photolysis of 4-iodobiphenyl is more than 90 % complete, under the same conditions 4-fluorobiphenyl and 4-chlorobiphenyl decompose only to the extent of 1–2 %. 4-Bromobiphenyl, however, photolyzes to the extent of 70–80 %, under conditions where 4-iodobiphenyl photolysis is essentially complete, to yield the following products: *p*-terphenyl, biphenyl, and hydrogen bromide (20–30 %), and bromobenzene (1 %). Recently, *Matsura* and *Omura* have been able to obtain biphenyl derivatives in 20–40 % yields by photolysis of variously substituted bromobenzenes in benzene [68]. (The photolysis of chloro- and bromoarenes under reductive conditions [58] was mentioned in Section 3.9.)

A recent report by *Joschek* and *Miller* [69] indicates that a steady irradiation of 4-bromophenol in deaerated water with a low-pressure mercury-vapor lamp gives 4,4'-dihydroxybiphenyl and hydroquinone. Similar results are obtained with 2- and 3-bromophenols.

Although there is little significant photochemical cleavage of C–Cl and C–F bonds in aryl halides, *Obrycki* and *Griffin* have reported that photolysis of *p*-chloroiodobenzene and *p*-fluoroiodobenzene in the presence of trimethyl phosphite gives an appreciable amount of *p*-phenylenebisphosphonate *(23)* as well as the expected *p*-chlorophenyl-or *p*-fluorophenylphosphonate.



(23)

This unexpected lability of the carbon-chlorine and carbon-fluorine bonds has been ascribed to the activating influence of the dimethoxyphosphono group in the *ortho* or *para* position [70].

The predominant process in the photolysis of oxygen-free aqueous solutions of fluorobenzene is the one that leads to the disappearance of the absorption band of fluorobenzene in the 260 nm region. This photochemical change has a quantum yield of 0.2 and is almost entirely reversible on admission of oxygen. A similar phenomenon is observed in ethanol or *n*-heptane solutions. The quantum yield of the process has a first-order dependence on concentration. In view of these results, formation of a dimer has been proposed [71]. It is interesting to note that vapor-phase photolyses of hexafluorobenzene has been reported to give hexafluoro(Dewar benzene) [72, 73].

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The Cool Flames of Hydrocarbons

BY A. FISH [*]

This review describes the properties of the cool-flame and two-stage ignition processes that characterize the gaseous oxidation of hydrocarbons and discusses the chemical reactions that are responsible for these phenomena. Cool flames result from a chain-thermal acceleration of reaction rate. It is probable that the free-radical chain involved is propagated by the reaction of an alkyl radical with oxygen to give an alkylperoxy radical which isomerizes to a hydroperoxyalkyl radical. The decomposition of this radical produces a hydroxyl radical, which attacks the hydrocarbon rapidly and unselectively to regenerate an alkyl radical. Branching probably results from the pyrolysis of mono- and dihydroperoxides, from the oxidation of aldehydes, and from radical-molecule reactions. This reaction scheme explains the existence of a low-temperature ignition peninsula and the relation of the extent and shape of this peninsula to the molecular structure of the hydrocarbon. The chemical relevance of cool flames to abnormal combustion phenomena, such as knock, in gasoline engines is discussed.

1. Introduction

The gaseous oxidation of a hydrocarbon is a complex free-radical chain reaction which involves a multiplicity of chain carriers and branching agents with widely different lifetimes and modes of reaction. The resulting variation with temperature and pressure of the reaction rate leads to a complex pressure/temperature ignition profile that exhibits distinct high-temperature and low-temperature regions with an intermediate region of negative temperature coefficient of reaction rate.

The low temperature region of ignition is associated with cool flames; in this region, ignition is a two-stage process, the propagation of a cool flame being followed by that of a hot flame. These two stages are evident both in "static" experiments, in which the two flames pass in succession through the stationary mixture of gases, and in flow experiments, in which each flame can be stabilized at a given point in a flowing gas. In the latter type of experiment, the cool flame appears as a pale blue reaction zone upstream from the bright hot flame; it exhibits many of the properties of a true flame. In static experiments, at pressures too low for ignition, cool flames still propagate; the properties of these flames are continuous across the ignition boundary [1,2] showing that the isolated cool flame and the first stage of two-stage ignition are one and the same phenomenon. In contrast, ignition in the high-temperature region is a one-stage process; no cool flame precedes the hot flame and no cool flames propagate at pressures too low for ignition.

In addition to being readily distinguished from one-stage ignition, the region of cool-flame and two-stage ignition may itself be divided into several parts. The pressure/temperature locus of the limiting condition for ignition exhibits fine structure. As temperature is increased, the necessary pressure for ignition passes through several minimum and maximum values; the region surrounding a particular minimum is referred to as a "lobe". The existence of several lobes shows that the cool-flame region is a very complex kinetic system, several successive increases and decreases of reaction rate occurring within a quite narrow temperature region. Further evidence of this kinetic complexity is provided by the formation of periodic cool flames. In fuel/oxidant mixtures of suitable pressure, temperature, and composition, several cool flames may propagate, one following another after a discrete time interval during which little non-isothermal reaction occurs. Cool-flame reaction is, therefore, one of the few examples of periodic phenomena in chemistry.

The régime of two-stage ignition is of considerable practical significance. It is established [3] that a close qualitative relationship exists between the tendency of a pure hydrocarbon fuel to cause knock in an engine and the shape and extent of its low-temperature ignition profile.

2. The Properties of Cool Flames

2.1. The Pressure/Temperature Ignition Profile

The nature of the ignition profile of the oxidation of a hydrocarbon has been discussed in general terms in the Introduction. All the phenomena described are exemplified by the oxidation of 2-methylpentane [2], a typical alkane having primary, secondary, and tertiary C–H bonds. The pressure/temperature (p_o/T_o) ignition profile for the reaction of this alkane with twice the molar quantity of oxygen is shown in

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[1] *A. S. Sokolik*: Self-ignition, Flame and Detonation in Gases. Israel program for Scientific Translations, Jerusalem 1963.

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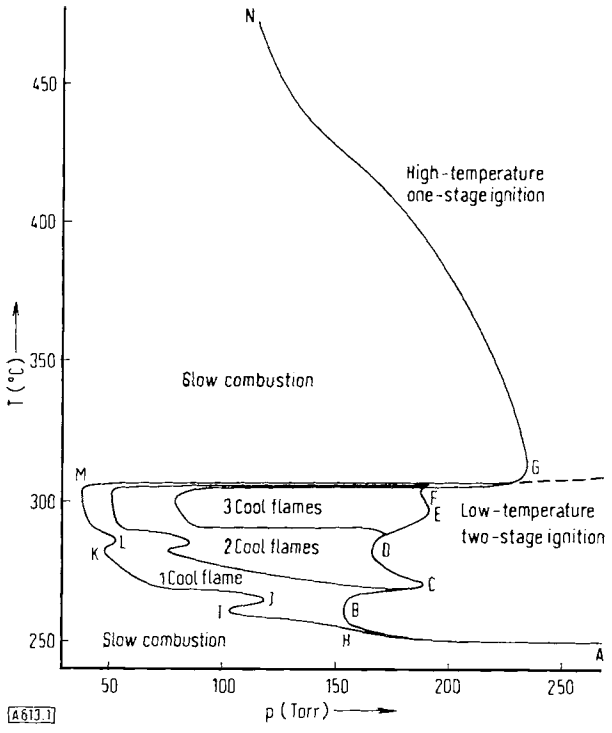

Fig. 1. Pressure/temperature ignition profile for 2-methylpentane/O_2 in a molar ratio of 1:2 (spherical Pyrex vessel of 450 ml capacity) [2].

Figure 1. Oxidation proceeds slowly and almost isothermally at temperatures below 250 °C.

The rate of reaction increases with temperature, and at 250 °C and at approximately 170 torr, is sufficient to lead to two-stage ignition; at lower pressures, cool flames propagate. This kind of behavior persists in the temperature range 250–307 °C, the low-temperature ignition peninsula (ABCDEFG, Figure 1) consisting of three lobes (ABC, CDE, and EFG). Similarly, three corresponding lobes (HIJ, JKL, and LMF) comprise the limiting condition for cool flames. Periodic cool flames are formed at sufficiently high temperatures and pressures within the cool-flame region. At 307 °C, the rate of reaction falls quite sharply with further increase of temperature, *i.e.*, the temperature coefficient of reaction rate is negative. As a result the limiting pressure for ignition increases sharply. As temperature is increased still further, the rate of reaction again increases but the resulting ignition (GN, Fig. 1) is one-stage.

The precise nature and position of the pressure/temperature ignition profile depend, of course, on the experimental conditions. The nature and amount of oxidant, the nature and extent of the surface, and the molecular structure of the fuel all affect the ease and extent of cool-flame reaction.

2.1.1. The Oxidant

Cool flames are formed during the oxidation of hydrocarbons in air or oxygen (and also during certain other reactions of hydrocarbons, such as nitration by nitrogen dioxide). The temperature range involved is, in general, slightly higher for the reaction of a given fuel with air than for reaction with oxygen, but the major difference between the two oxidants is the pressure range within which the limiting profiles of two-stage ignition and of cool flames lie.

Hydrocarbon/oxygen systems at suitable temperatures produce cool flames at pressures which can be as low as 0.05 atm. The minimum total pressure at which cool flames can be observed in 2:1 mixtures of oxygen with 2-methylpentane, for example, is 40 torr (Figure 1) while that in 4:5 mixtures of oxygen with hexane is 20 torr [4]. The limiting pressures even for two-stage ignition of such mixtures are much less than 1 atm, being about 155 torr and 175 torr respectively in these two cases. Cool flames are formed in hydrocarbon/air systems only at considerably greater pressures, however. Thus, for mixtures of air with pentane having $O_2:C_5H_{12} = 6.4:1$ (*i.e.* containing 0.8 × the stoichiometric quantity of oxygen) the lower pressure limit of cool flames is about 1 atm and of two-stage ignition is about 3.5 atm [5]. Mixtures of similar stoichiometry of the reactive fuel heptane with air [6] produce cool flames at about 100 torr total pressure but ignite only at pressures of about 1 atm.

Nevertheless, the cool flames of hydrocarbons in air and in oxygen are similar phenomena [7].

The properties of cool flames are affected not only by the nature of the oxidant but also by the amount. The mixture composition affects the cool flame intensity (defined in section 2.2.) which, in general, increases with the proportion of fuel present. This is to be expected from chemical considerations; the intensity is related to the amount of heat released and hence to the reaction rate of the oxidation. For hydrocarbons, this rate is a more sensitive positive function of fuel concentration than it is of oxygen concentration [8]. (It should be noted that for the oxidation of aldehydes, the opposite is true [1].)

Although the quantitative properties of cool flames are dependent upon the nature of the oxidant and the mixture composition, the basic chemical processes involved are independent of these factors, as is shown in Section 4.

2.1.2. The Surface of the Reaction Vessel

The nature and extent of reaction vessel surfaces have a profound effect on the rates of gaseous oxidation reactions. At low pressures, the predominant chain-termination steps in such reactions are heterogeneous, involving the removal at the wall of chain carriers and branching agents to give inactive products.

Thus, for example, it is well established that base- or salt-coated vessels destroy HO_2 radicals efficiently but boric acid-coated vessels do not [9]. Again, the destruction of hydrogen peroxide at the surface to give inactive products is inefficient

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in a boric acid-coated vessel, having an activation energy of about 5 kcal mole^{-1}, but is much more efficient in copper vessels[10], in which the activation energy is less than 3 kcal mole^{-1}.

The natures and amounts of the minor products can also depend to a marked extent on the nature of the reaction vessel surface[11]. The extent of the vessel surface, which is usually expressed as the ratio of surface to volume, S/V, also affects the rate of these heterogeneous processes. Diffusion-controlled wall reactions have rate constants which depend on the inverse square of the effective radius of the vessel[12], whereas those of kinetically-controlled wall reactions depend on the inverse first power of the effective radius[13]. These wall effects can produce dramatic changes in ignition profiles.

The one-stage ignition limits of heptane depend on both the nature and the extent of the surface, the primary factor involved probably being the mode of control of the termination steps[10]. The cool flames of heptane are inhibited in vessels coated with lead oxide but are unaffected by potassium chloride coatings[14]; those of cyclohexane are inhibited by both boric acid and sodium hydroxide[15]. Again, multiple cool flames characterize the oxidation of butane by oxygen between 280 °C and 320 °C in a silica vessel but are strongly inhibited when the vessel walls are coated with metal oxides (PbO, NiO, Cu_2O, Fe_2O_3, Pb_3O_4) or metal halides ($MnCl_2$, $NiCl_2$, $CuCl_2$, $PbCl_2$, KCl, and KI)[16]. In the presence of these coated surfaces, the ignition limits are much higher than in silica vessels. The most effective inhibitor studied was lead oxide; there seems little reason to doubt that the mode of action involves an increase in the rate of heterogeneous chain termination or in the rate of heterogeneous destruction branching agents. In contrast, however, etching the Pyrex reactor with hydrofluoric acid and/or coating it with potassium chloride does not materially affect the cool flame region of the oxidation of 1:1 propane/oxygen mixtures[17].

Although the nature and extent of the vessel surface profoundly affect the morphology of the two-stage ignition region by altering the kinetic balance of the reactions involved, it seems likely[18] that they do not alter qualitatively the predominant chemical routes by which oxidation occurs.

2.1.3. The Molecular Structure of the Fuel

The profound effect of the molecular structure of a fuel on the ease with which cool flames are formed during its oxidation was evident from the first published study of these phenomena.

Perkins[19], in 1882, described the "blue lambent flames" which could be obtained in air from the vapours of certain organic fuels. He noted that as the molecular weight of a paraffinic fuel was increased, the tendency to give such flames increased. A similar result was obtained from a series of aliphatic acids, but no such flames could be obtained for simple aromatic hydrocarbons, aromatic acids, or phenols.

More recent studies have shown that the nature and position of the low-temperature ignition diagram is a sensitive function of molecular size and shape. The two-stage ignition limit (cf. curve ABCDEFG, Fig. 1) may be divided into a maximum of three lobes; for some hydrocarbons, certain of these are absent. In other words, the "fine structure" of the low-temperature ignition diagrams is related to molecular structure.

If the lobes are designated L_1, L_2, and L_3 in order of increasing temperature[3], *n*-alkanes with four or more carbon atoms exhibit all three lobes, although L_3 is sometimes ill-defined. Propane, however, shows two lobes only and the temperatures at which these occur show that they are L_2 and L_3. Ethane shows L_3 only and methane is unique in this series in possessing no low-temperature region. (Methane does exhibit a two-stage ignition limit at temperatures of *ca.* 500 °C[20] but the mechanism of this combustion is not the same as that of the low-temperature ignition of higher hydrocarbons[21].) Some branched-chain alkanes also have certain lobes absent.

Although 2-methylpentane and 2,2-dimethylbutane have all three lobes, isobutane exhibits L_2 and L_3 only, while 2,3-dimethylbutane shows no well-defined low-temperature ignition régime. Neopentane has L_2 and L_3 lobes but the latter is at a high temperature and is probably not a real lobe at all but corresponds to the two-stage ignition of methane[21].

Cyclic hydrocarbons also have "incomplete" diagrams. Cyclohexane exhibits only two lobes, as does methylcyclopentane; there is disagreement about the nature of the low-temperature ignition diagram of cyclopentane. It is difficult meaningfully to compare ignition diagrams for different hydrocarbons obtained under different conditions of oxidant, fuel:oxidant ratio, and vessel size and material.

The available data do suggest, however, that the complexity of the low-temperature ignition diagram varies with molecular structure in a systematic way and that it is not merely a function of experimental conditions. These data are summarized in Table 1.

The lower pressure/temperature limit of cool-flame formation (see curve HIJKLM, Fig. 1) also exhibits lobes. Fewer detailed studies of the relation of these to molecular structure have been made than for the ignition limit, but it seems likely that the numbers of lobes in the cool-flame limit and in the ignition limit correspond.

2.2. Pressure Change

The propagation of a cool flame in a reacting hydrocarbon-oxygen mixture is accompanied by a rise in pressure, Δp_{cf}. The use of transducers to detect this

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Table 1. The fine structure of low-temperature ignition limits.

Hydrocarbon	Lobes observed experimentally			Reference	Number of H atoms available for intramolecular H-transfer in derived alkylperoxy radicals				Lobes predicted by alkylperoxy radical rearrangement theory		
	L_1	L_2	L_3		1:6	1:5	1:4	1:7, 1:8 *etc.*	L_1	L_2	L_3
Methane	–	–	–	[20, 21, 22]	0	0	0	0	–	–	–
Ethane	–	–	+	[22, 23]	0	0	3	0	–	–	+
Propane	–	+	+	[22, 24]	0	3	2	0	–	+	+
Butane	+ (weak)	+	+	[22]	3	5	7	0	+	+	+
		+	+	[16, 25]							
Pentane	+	+	+	[26]	5	10	11	3	+	+	+
Hexane	+	+	+	[27, 28]	7	9	11	8	+	+	+
	+	+	–	[4, 29]							
Heptane	+	+	+	[30]	12	13	15	15	+	+	+
Octane	+	+	+	[30]	11	13	15	24	+	+	+
Isobutane	–	+	+	[31]	0	6	10	0	–	+	+
Isopentane	+	+	+	[32]	6	15	15	0	+	+	+
Neopentane	–	+	–	[32, 33]	0	9	0	0	–	+	–
2-Methylpentane	+	+	+	[2]	12	19	19	9	+	+	+
3-Methylpentane	–	+	+	[28]	8	12	10	3	+	+	+
2,2-Dimethylbutane	+	+	+	[28]	12	17	5	0	+	+	+
2,3-Dimethylbutane	–	–	–	[28]	6	13	8	0	–	–	–
2,2,4-Trimethyl-pentane	–	+	+	[30]	10	28	10	15	+	+	+
	+	+	+	[34]							
Cyclohexane	+	+	–	[27, 28]	(2)	4	(4)	0	–	+	–
Methylcyclopentane	+	+ (weak)	–	[28, 35]	7	7+(11)	4+(11)	0	+	+	+
Cyclopentane	+	+	+	[32]	0	(4)	(4)	0	–	–	–
	–	–	–	[36]							

pressure change is one of the most common methods of studying cool-flame reactions. If the gases behave ideally, the magnitude of this rise in a constant volume reactor is given by the equation

$$\Delta p_{cf} = p_o \left(\frac{\bar{n}\bar{T}}{n_o T_o} - 1 \right)$$

where p_o, T_o, n_o are the pressure, temperature, and molecular concentration of the unchanged mixture and $\bar{T}$, $\bar{n}$ are the mean temperature and molecular concentration at the instant when the pressure rise is Δp_{cf}.

At low concentrations of oxidant, the pressure falls, after the cool flame has passed, to a value only slightly greater than the original value, p_o (Fig. 2a); in other words, $\bar{n}$ is not significantly greater than n_o and the transient pressure rise is

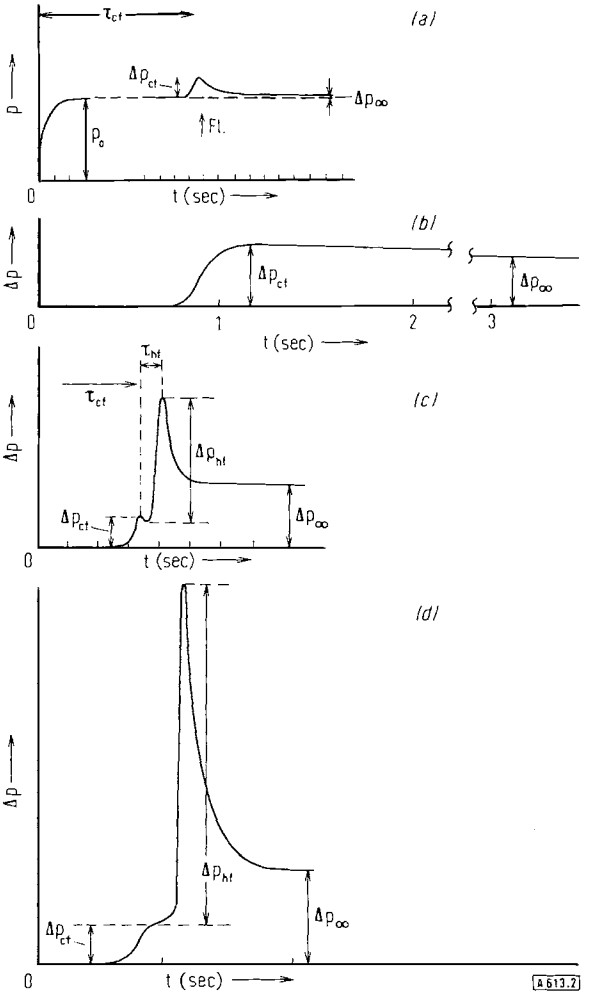

Fig. 2. Pressure development during cool flames and two-stage ignition.
(a) The propagation of one cool flame in 2-methylpentane/oxygen ($RH:O_2 = 1:2$, $T_o = 265$ °C, $p_o = 158$ torr) [2]. Fl. = cool flame.
(b) The propagation of one cool flame in iso-octane/air ($RH:O_2 = 1:10$, $T_o = 370$ °C, $p_o = 1368$ torr) [6].
(c) Two-stage ignition in 2-methylpentane/oxygen. ($RH:O_2 = 1:2$, $T_o = 255$ °C, $p_o = 154$ torr) [2].
(d) Two-stage ignition in 2-methylpentane/oxygen. ($RH:O_2 = 1:2$, $T_o = 294.5$ °C, $p_o = 195$ torr) [2].

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largely due to the exothermic character of the reaction ($\bar{T} > T_o$). At higher oxidant concentrations, however, Δp_∞ is quite large (Fig. 2b); it is evident that both $\bar{n}$ and $\bar{T}$ exceed the values n_o and T_o.

If the pressure is sufficiently high, the passage of a cool flame may be followed by that of a hot flame, giving an overall pressure/time record as in Fig. 2c. The passage of the cool flame is followed by a further induction period and a rapid non-isothermal increase in pressure, which is defined as the hot flame. Subsequently the pressure falls exponentially from its maximum value until the contents of the reaction vessel are again in thermal equilibrium with their surroundings. The final pressure change, Δp_∞, is considerable, showing that a substantial increase in molecular concentration has occurred during hot ignition. If the pressure and temperature are sufficiently high, the "second-stage" induction period is so short that no intermediate decrease in pressure between the two stages of ignition is noticed (Fig. 2d).

For a given fuel and oxidant in a mixture of given stoichiometry the relationships between $\bar{n}$ and n_o and $\bar{T}$ and T_o will be functions of pressure; it should therefore be possible to express Δp_{cf} as a function of p_o alone. It has been shown [1,6] that the relation

$$\Delta p_{cf} = Cp_o + Kp_o^2$$

where C and K are constants, holds for iso-octane/air mixtures. Approximately, then,

$$\Delta p_{cf} = kp_o^m$$

where $1 < m < 2$ and k is constant. The accuracy of this empirical relationship is illustrated for 2-methylpentane/oxygen mixtures [2,18] in Figure 3, from which it is evident that for this system $m \simeq 1.65$. This value compares quite closely with that for the iso-octane/air system [6], for which $m \simeq 1.5$. Moreover, this kind of relationship holds not only for different hydrocarbon/oxidant systems under similar conditions but also for a given fuel under very widely different conditions (see Section 4).

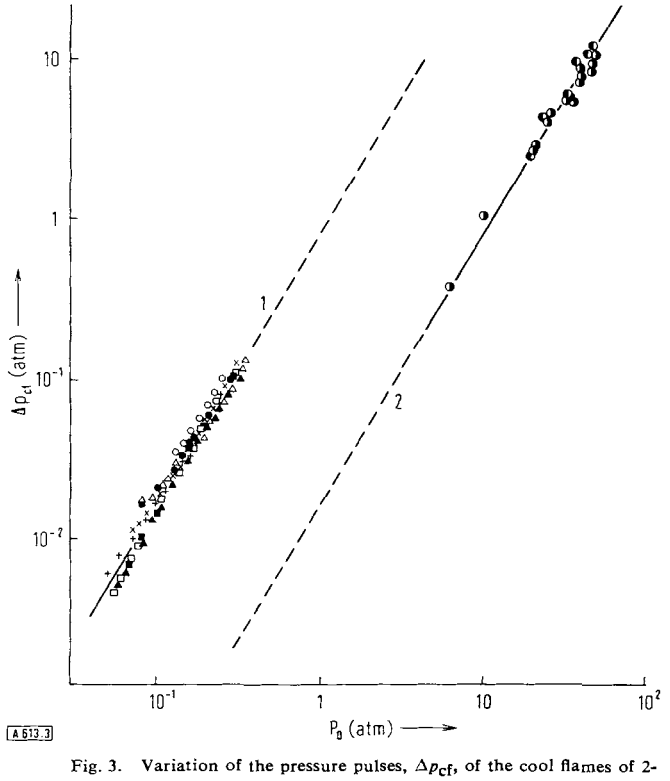

Fig. 3. Variation of the pressure pulses, Δp_{cf}, of the cool flames of 2-methylpentane with initial pressure p_o [18].

1: Pyrex reactor, $RH:O_2:N_2 = 1:2:0$
○, 260 °C; ●, 269 °C; ×, 275 °C; +, 282 °C;
■, 289 °C; □, 291 °C; ▲, 299 °C; △, 306 °C.

2: Rapid compression machine
◑, $RH:O_2:N_2 = 1:19:76$, 433 °C;
◐, $RH:O_2:N_2 = 1:30.6:122$, 457 °C.

The relationship between Δp_{cf} and p_o is a measure of the intensity I_{cf} of the cool flame:

$$I_{cf} = (p_o + \Delta p_{cf})/p_o$$

The intensities of cool flames in different hydrocarbon-oxidant systems are quite similar. For example, those of the first cool flame of heptane in air [34] are 1.04 to 1.35 while those for the first cool flame of 2-methylpentane in oxygen [2] are 1.1 to 1.4. The intensities of the second-stage hot flames, which may be defined similarly, have values from about 2.5 to 4.0 [2,34].

A further important parameter which may be derived from the pressure change accompanying the propagation of a cool flame is the maximum rate of pressure increase, $(dp/dt)_{max,cf}$. Whereas Δp_{cf} is not a good kinetic measure of the chemical reactions occurring during a cool flame, $(dp/dt)_{max,cf}$ is, because it is proportional to $(d\bar{T}/dt)_{max}$ (where T is the average temperature at time t) which is in turn related to the rate of liberation of heat per unit volume of the reactor and hence to the rate of chemical transformation [1]. It is likely, therefore, that if the complex low-temperature ignition limit is related to the rate of chemical transformation in the cool flame, it will be related to $(dp/dt)_{max,cf}$. This is indeed so [2,34]. For the first cool flame of the 2-methylpentane/oxygen system, for example, the variation of $(dp/dt)_{max,cf}$ with temperature and pressure exhibits a system of three "lobes", the positions of which correspond well with those of the lobes in the loci of the limiting conditions for ignition and for cool flames (Fig. 4). The complex dependence on p_o and T_o of the *limiting* conditions for igni-

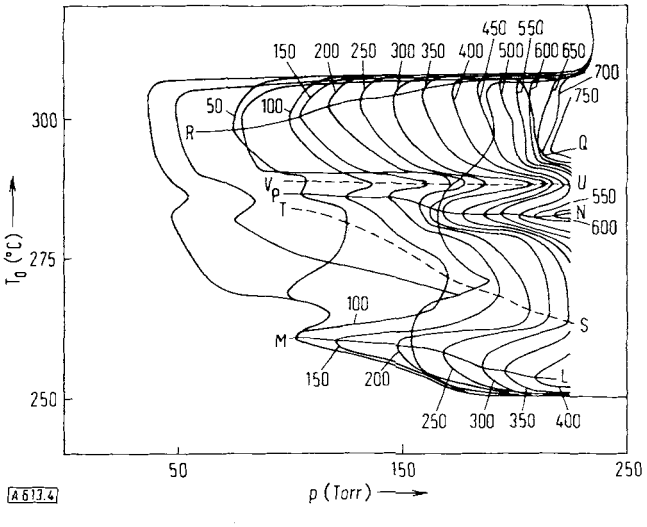

Fig. 4. Pressure/temperature "contour" map of the rate of pressure rise during the first cool flame in 2-methylpentane/oxygen ($RH:O_2 = 1:2$). LM, NP, and QR are loci of maximum rate; ST and UV are loci of minimum rate; contours are lines of equal rate (torr/sec) [2].

tion is closely related, therefore, to the rate of the overall chemical reaction responsible for the cool-flame step.

2.3. Induction Periods

The induction period for two-stage ignition is divisible into two parts, τ_{cf} and τ_{hf} (see Fig. 2c), the relative magnitudes of which depend on stoichiometry, pressure, and temperature.

Some authors [1] distinguish three stages, denoting τ_{cf} as the time from the completion of the filling of the vessel to the beginning of the sharp pressure rise, Δp_{cf}; the "second stage" is then the time for cool-flame propagation, *i.e.* the time elapsing during this sharp change in pressure, and the third stage is τ_{hf}. At low pressure, this alternative definition of τ_{cf} does not substantially affect its measured variations with the independent variables, as the time for cool-flame propagation is relatively small, corresponding to an average flame velocity of about 30 cm/sec, and does not vary markedly [1].

As p_o is increased at constant T_o, τ_{cf} becomes shorter, obeying the equation

$$\tau_{cf} = k' p_o^{-n} + c'$$

where n is positive and k' and c' are constants. This equation holds both at low [1,2,18] and at high [18,34] pressures. The value of n varies with T_o in a way that reflects the shape of the ignition limit [2,34]. At temperatures at which the limiting value of p_o for ignition is minimized, so is the value of n.

The effects of p_o and T_o on τ_{hf} are complex. Two factors may be distinguished, *viz*: the effects of p_o and T_o themselves on the second-stage ignition process and their effects on cool-flame intensity which cause the actual values of pressure and temperature under which the second stage occurs to vary. In general, the second effect is more important at the lower temperatures within the two-stage ignition régime (*i.e.*, where Δp_{cf} is highest [2]) and the first effect more important at higher temperatures [1].

At high pressures, for iso-octane cool flames [34], τ_{hf} is related to p_o by a power law similar to that which holds for τ_{cf} and, for hot flames, n also exhibits maximum and minimum values as T_o is altered. The temperatures at which these values occur, however, are not identical with those at which n for cool flames exhibits turning values. For the cool flames of hexane at high pressures [37], τ_{cf} depends primarily on temperature and τ_{hf} primarily on pressure. The variation of $\ln\tau_{cf}$ with $1/T_o$ has been used to calculate an "effective activation energy", E_{eff}, for the cool flame process [1,34]. In the case of many fuels, this plot is linear over a considerable range of temperature and the values of E_{eff} obtained correlate quite well with the octane numbers of those fuels [1]. In other cases, however, the plot of $\ln\tau_{cf}$ against $1/T_o$ is non-linear [2,34]. In view of the chemical complexity of the overall cool flame process, the precise significance of E_{eff} is not clear.

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2.4. Temperature Change

As has been mentioned, the pressure increase attendant upon the passage of a cool flame is associated with an increase in the temperature of the gases due to the heat liberated by their chemical reaction. In a "static" reactor, this temperature increase can be measured directly by suitably positioning the hot junction of a thermocouple in the reactor and comparing the output of this with that of a second thermocouple, the hot junction of which is maintained at the temperature of the reactor wall [38,39]. Similarly, in a flow system, the difference in temperature of the inlet and exhaust gases can be measured [40]. This thermometric technique is a useful one for distinguishing cool-flame reaction from slow combustion; although slow combustion is not entirely isothermal, the rate of temperature change is much less than that of cool-flame reaction. The variation of ΔT with T_o exhibits a sharp maximum in the cool-flame region [40]; at a given temperature T_o,

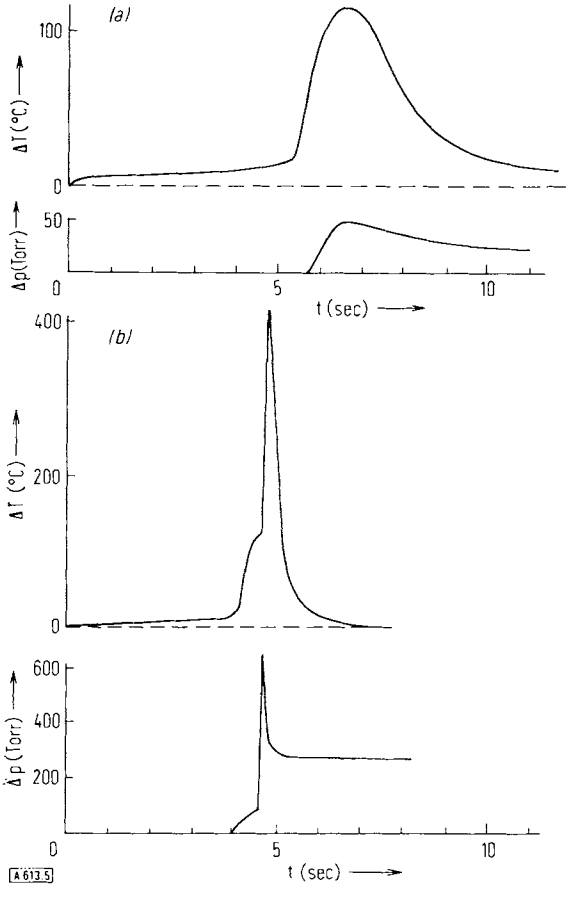

Fig. 5. Changes in pressure and temperature during the oxidation of neopentane (T_o = 310 °C, RH:O_2 = 1:2).
(a) Cool flame reaction at p_o = 200 torr;
(b) Two-stage ignition at p_o = 260 torr [33].

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ΔT_{cf} varies with the reactant concentrations according to the equation

$$\Delta T_{cf} = k''[RH]([O_2] - [O_2]_c)$$

where $[O_2]_c$ is a critical concentration of oxygen below which non-isothermal reaction does not develop.

As would be expected, the changes in temperature and in pressure during the propagation of a cool flame and of two-stage ignition run closely parallel (Fig. 5) [33]. At low concentrations of oxidant, comparison of the measured ΔT_{cf} with that calculated from Δp_{cf} using the ideal gas law and assuming negligible change in molecular concentration gives agreement within 15%.

The magnitude of ΔT_{cf} varies from about 10 °C to about 200 °C, being higher for fuel/oxygen mixtures than for fuel/air mixtures because of the lower thermal capacity per mole of fuel of the former. For a given system, ΔT_{cf} is highest at high pressures but low temperatures.

It has been suggested that low-temperature two-stage ignition results solely because the increase in temperature ΔT_{cf} raises the temperature of the reacting mixture so that it reaches the high-temperature one-stage ignition curve GN (Figure 1). If this were so, GN would describe the pressure locus of $(T_o + \Delta T_{cf})$ for reactions of which the T_o/p_o relationship is BCDEFG. In fact, the locus of $(T_o + \Delta T_{cf})$ generally lies above GN; it would appear that the thermal effect of cool flames on the conditions for the second-stage ignition is considerable but that there is a marked chemical effect too.

2.5. Light Emission

The passage of a cool flame is accompanied by the emission of light [41]. The detection of this radiation, with the aid of a photomultiplier, has been used as a diagnostic test of cool-flame formation [42,43], although a faint light emission may accompany slow combustion also [44]. The source of this chemiluminescence is excited formaldehyde [45–47]. It is very difficult to envisage a radical-molecule reaction which would give formaldehyde with an energy of 77 kcal mole^{-1} in excess of the ground electronic state. It is likely, therefore, that a radical-radical reaction is involved. Studies of the thermal decomposition of alkyl nitrites and nitrates [48] have suggested that alkoxy radicals are involved; a possible reaction is

$$RCH_2O^{\bullet} + {}^{\bullet}OH \rightarrow H_2CO^{*} + ROH, \quad \Delta H = -75 \text{ kcal mole}^{-1}.$$

As the concentrations of radicals in cool-flame systems are fairly low, it would be expected that radical-radical reactions would be infrequent. It is consistent with this that the extent of the conversion of fuel to excited formaldehyde in the cool flame is very low indeed. During the oxidation of butane [42] about 5×10^{15} molecules react per quantum emitted; the corresponding figure during the oxidation of acetaldehyde is 3×10^6 molecules/quantum [49]. The light emission from cool flames is unlikely, therefore, to provide information regarding the nature of the major chemical paths by which the fuel is oxidized.

An interesting, recently discovered aspect of light emission during hydrocarbon oxidation occurs during slow combustion of mixtures in which the mole fraction of oxygen is low, at temperatures just too low for cool-flame formation. A sudden acceleration of the variation of pressure with time occurs [26,50] in the last stages of the slow oxidation. Simultaneously, a sharp jump in the emission of light occurs [43,50] (the *pic d'arrêt*) after which the reaction stops very quickly. The *pic d'arrêt* is probably due to radical-radical reactions when the oxygen is nearly all consumed.

2.6. The Chemical Products of Cool Flames

Oxidation in the cool-flame region is a very unselective process, producing a wide variety of stable or moderately stable products. It has been shown gas-chromatographically that the products of alkane cool flames include alkenes, alcohols, saturated and unsaturated aldehydes and ketones, and O-heterocyclic compounds (Table 2) [51].

A further class of compounds which are important in cool-flame products is that of the organic peroxides. Although some of these can be analyzed satisfactorily by gas chromatography [52], it is difficult to effect an estimation under conditions that are suitable for analyzing products with other functional groups. Peroxides have usually been analyzed, therefore, by chemical means or by paper chromatography. The latter technique [53] has shown that, in addition to alkyl monohydroperoxides, peracids, and hydrogen peroxide, the products of oxidation in the cool flame region contain unsaturated hydroperoxides [15] and alkyl dihydroperoxides [14]. This last class of compounds can, indeed, become the major peroxidic

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Table 2. Products of the cool-flame reaction of 2-methylpentane with twice the molar quantity of oxygen [51].

Saturated ketones	Saturated aldehydes	Unsaturated carbonyls	O-heterocycles	Alkenes	Alkanes	Alcohols
Acetone	Formaldehyde	Acrolein	Oxirane	Ethylene	Isopentane	None
Butanone	Acetaldehyde	Methacrolein	Methyloxirane	Propylene	Butane	
2-Pentanone	Propionaldehyde	3-Buten-2-one	2,2-Dimethyloxirane	Isobutene	Ethane	
3-Methyl-2-butanone	Isobutyraldehyde	*trans*-3-Penten-2-one	2,2-Dimethyl-3-ethyloxirane	2-Methyl-1-butene	Methane	
2-Methyl-3-pentanone	Butyraldehyde	4-Methyl-4-penten-2-one	2-Methyl-2-*n*-propyloxirane	*cis*- and *trans*-2-Pentene		
3-Methyl-2-pentanone	2-Methylpentanal	4-Methyl-3-penten-2-one	2-Isopropyl-3-methyloxirane	2-Methyl-2-butene		
2-Hexanone	4-Methylpentanal	1-Penten-3-one	3-Methyloxetane	1-Pentene		
3-Hexanone			2,2-Dimethyltetrahydrofuran	3-Methyl-1-butene		
			2,4-Dimethyltetrahydrofuran	2-Methyl-1-pentene		
				2-Methyl-2-pentene		

component of the product mixture [14]. In addition to the many organic products of cool-flame oxidation, oxides of carbon and water are formed, the amounts increasing with the availability of oxygen.

The natures of the products do not change suddenly at the boundaries between slow combustion and cool flames but change gradually with experimental conditions.

Thus, in the oxidation of 2-methylpentane [51], the yield of titratable peroxide is high during slow combustion at low temperatures (near H, Fig. 1) but decreases along HIJKLM, being very small at M. The yields of certain other products are, however, low in low-temperature slow combustion but increase with temperature and reach maximum values in the cool-flame region. In the oxidation of hexane, the yields of 2,5-dimethyltetrahydrofuran, 2-ethyl-4-methyloxetane, and 2-methyl-3-propyloxirane all maximize under cool-flame conditions [4] (Fig. 6).

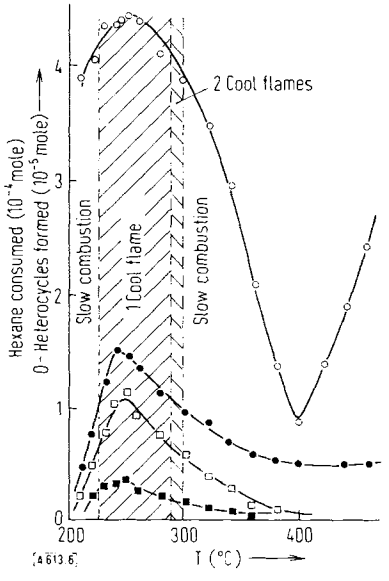

Fig. 6. Amount of fuel consumed during the oxidation of hexane with oxygen (75:60 torr) and yield of O-heterocycles as a function of temperature.
○, *n*-hexane; ●, 2,5-dimethyltetrahydrofuran;
□, 2-ethyl-4-methyloxetane; ■, 2-methyl-3-*n*-propyloxirane [4].

Even within the cool-flame region itself, significant changes in the relative yields of various products occur with change in temperature and can be tentatively related to the fine structure of the region. These variations thus provide a clue to the nature of the subtile mechanistic changes which lead to the formation of several lobes (Fig. 7) [51]. The reactions leading to a given product can be assigned to a given lobe (or lobes). Thus, in Figure 7, reactions producing 2,4-dimethyltetrahydrofuran are most important in lobes

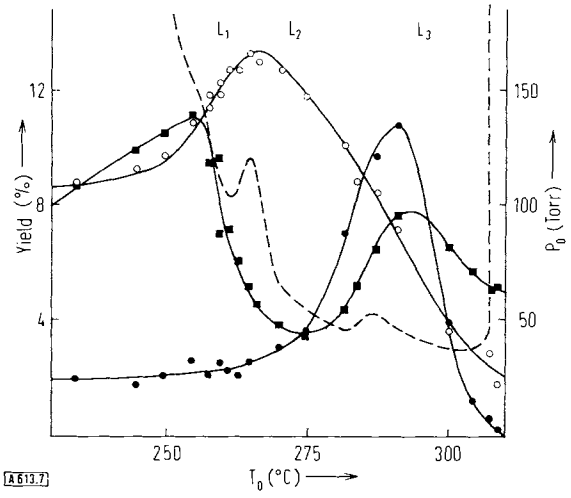

Fig. 7. Examples of the yields of products from slow combustion just outside the cool flame limit in 2-methylpentane/O_2 (1:2).
○, 2,4-dimethyltetrahydrofuran; ●, 2,2-dimethyl-3-ethyloxirane(×10); ■, acetone; – – – p_0/T_0 locus of cool flame limit (HIJKL, Fig. 1) [51].

L_1 and L_2, those producing 2,2-dimethyl-3-ethyloxirane are most important in L_3, and those producing acetone in L_1 and L_3.

At temperatures above the maximum temperature for cool-flame formation, the yields of oxygenated organic products gradually decrease while those of alkenes and of hydrogen peroxide increase.

The products of ignition are very different from those of cool flames. During the highly exothermic second stage of ignition, the wide variety of oxygenated products produced in the cool-flame stage is largely destroyed. The concentrations of water, of oxides of carbon, and of certain hydrocarbons of low molecular weight increase, however. In fuel-rich mixtures, extensive cracking of the excess fuel occurs, giving high yields of simple aliphatic and of aromatic hydrocarbons and, in very rich mixtures, depositing soot.

Techniques, such as electron paramagnetic resonance spectroscopy, for identifying and estimating radicals in the gas phase are as yet insufficiently sensitive to deal with the low radical concentrations and complex mixtures found in the early stages of hydrocarbon oxidation. Indirect evidence, based upon the natures of the more stable products and on known modes of radical reaction to give such products, suggests strongly, however, that chain reactions involving alkyl, alkylperoxy, hydroperoxyalkyl, and hydroxyl radicals are important in the cool flame region.

2.7. The Periodicity of Cool Flames

Multiple cool flames have often been observed at pressures below those necessary for two-stage ignition. These non-isothermal events occur at intervals during an otherwise isothermal oxidation reaction. As many as seven successive cool flames have been observed during the oxidation of propane [24,50]; similarly, the oxidations of pentane [50] and butane [25] are characterized by a maximum of five cool flames. Other fuels for which multiple cool flames have been observed include hexane [4], heptane [14], 2-methylpentane [2], acetaldehyde [54], and butanone [55].

Periodic phenomena of this sort are rare in chemistry [56] and are not well understood. It has been commonly supposed that a cool flame occurs when some intermediate product reaches a critical concentration [57]; the concentration of the product involved should decrease precipitously during the passage of the cool flame. Peroxides do indeed exhibit this behavior in some systems [15,25,51,55]; dihydroperoxides, for example, are the major peroxidic product of the pre-cool-flame reaction of heptane with an equimolar quantity of oxygen at 160 torr and 255 °C, but are completely destroyed when the cool flame passes [14]. As these compounds have been considered to be the agents of degenerate branching of slow combustion at relatively low temperatures, it appears that cool flames are mechanistically similar to slow combustion and should not be regarded as side processes. Aldehydes, which also act as agents of degenerate branching during hydrocarbon combustion, are similarly instrumental in the formation of cool flames [58–60]. It seems, then, that the normal course of slow combustion can lead to a non-isothermal event and that this can occur several times in the same system. Two explanation of this have been advanced.

The "chain-thermal" theory [12,61] attributes the oscillations to the effect of the rise in temperature resultant from the cool flame on the rates of formation and destruction of a single intermediate (X) [55,58,59].

This intermediate product X can lead, under suitable conditions of p_0 and T_0, to multiple cool flames if its formation and destruction reactions, *viz.*

$$\text{reactants} \xrightarrow[E_1]{\Delta H_1} \text{X}$$

$$\text{X} \xrightarrow[E_2]{\Delta H_2} \text{products}$$

are such that $\Delta H_2 > \Delta H_1$ and $E_2 > E_1$. As X accumulates, the second reaction becomes more rapid; this increases the rate of liberation of heat and hence increases the temperature. The second reaction is therefore accelerated relative to the first, as $E_2 > E_1$, and [X] falls. When [X] becomes small, the temperature falls again and the first reaction is accelerated relative to the second leading to another increase in [X], and so to a periodic thermokinetic phenomenon.

The alternative explanation is that odd-numbered cool flames and even-numbered cool flames are due respectively to the production of critical concentrations of different intermediate products X and Y, each of which is involved in branching reactions [12,62]. This "two-product" explanation is therefore purely kinetic.

The necessary reaction scheme

$$\text{A} + \text{X} \xrightarrow{k_3} \text{B} + 2\,\text{X},$$

$$\text{X} + \text{Y} \xrightarrow{k_4} \text{B} + 2\,\text{Y},$$

$$\text{A} + \text{Y} \xrightarrow{k_5} \text{B}$$

(where A and B represent reactant and final product respectively) gives the rate equations

$$\mathrm{d}[\mathrm{X}]/\mathrm{d}t = k_3[\mathrm{A}][\mathrm{X}] - k_4[\mathrm{X}][\mathrm{Y}],$$

$$\mathrm{d}[\mathrm{Y}]/\mathrm{d}t = k_4[\mathrm{X}][\mathrm{Y}] - k_5[\mathrm{A}][\mathrm{Y}].$$

When [X] reaches the critical value $k_5[\mathrm{A}]/k_4$, $\mathrm{d}[\mathrm{Y}]/\mathrm{d}t$ becomes positive and [Y] increases at the expense of [X]. When [Y] in turn reaches the critical value $k_3[\mathrm{A}]/k_4$, $\mathrm{d}[\mathrm{X}]/\mathrm{d}t$ becomes negative and [X] will eventually fall below the value $k_5[\mathrm{A}]/k_4$. [Y] will then begin to fall in turn and when [Y] becomes less than $k_3[\mathrm{A}]/k_4$, [X] will rise again. If, therefore, the criterion for the first, third, *etc.* cool flames is that [X] exceeds a critical value and for the secund, fourth, *etc.* is that [Y] exceeds a critical value, the periodic phenomenon is explicable. It has been suggested [62,63] that the reaction X + Y → B + 2 Y is a condensation reaction which catalyzes the decomposition of hydroperoxide (X) to aldehyde (Y).

It is noteworthy that each of these explanations depends on the competition between two reactions, the first being dependent on the relative magnitudes of E_1 and E_2 and the second on those of k_3 and k_5. If, indeed, Y could be associated with the heat evolved by the reactions of X [64], the two theories could become quite similar. Neither of these theories explains satisfactorily all the features of cool-flame periodicity.

The two-product theory does not show why periodic phenomena occur in non-isothermal regions of oxidation but not in isothermal ones. The chain-thermal theory, however, demands that, owing to the gradual consumption of reactants,

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the intensities of successive cool flames must decrease, whereas the two-product explanation demands only that those of odd-numbered cool flames decrease and that those of even-numbered cool flames decrease. In certain systems, the "two-product" explanation of cool flames is supported by the fact that successive cool flames are not equivalent. Thus, for example, during the non-isothermal oxidation of butane[25], the passage of the second cool flame at 284 °C is accompanied by a precipitous decline in the concentration of peroxides, whereas that of the first cool flame is not. Again, comparison of the decreases in concentrations of products during the passage of each cool flame of 2-methylpentane[51] suggests that some are associated with reactions of peroxides and others with reactions of aldehydes.

3. Mechanism of Cool-Flame Formation

3.1. Elementary Steps in the Gaseous Oxidation of Hydrocarbons

The slow oxidations of hydrocarbons, in both gaseous and liquid phases, are the best-known examples of degenerately branched chain reactions. In such reactions, the four kinds of step involved are initiation, propagation, termination, and branching. If the branching process is to be truly degenerate, then the reciprocal of Φ (the net branching factor) must exceed the average lifetime of the chain-carrying radicals, *i.e.* branching must be slow. Hydrocarbon oxidation is thus characterized by very slow initiation, a reasonably rapid primary linear chain process leading to a metastable product P (the agent of degenerate branching), and slow breakdown of, or further reaction of, P to branch the chain. When the reaction conditions are such that Φ exceeds zero (or, more accurately, a small positive value, in order to overcome reactant consumption) the concentrations of chain carriers will increase exponentially and the mixture will increase in temperature, leading to chain-thermal ignition. At low temperatures, the first non-isothermal stage of such ignition is cool-flame reaction.

3.1.1. Initiation

The initial attack on saturated hydrocarbons by oxygen usually involves the abstraction of a hydrogen atom to yield an alkyl radical and a hydroperoxy radical:

$$RH + O_2 \rightarrow R^\bullet + HO_2^\bullet \qquad (1)$$

As the activation energies of such abstraction reactions are high (40–55 kcal mole^{-1}), they are both slow and selective. As would be expected from the strengths of C–H bonds in various intramolecular environments, the tertiary hydrogen atoms are by far the most vulnerable and the primary atoms are least readily attacked. Thus, the attack by oxygen on a typical hydrocarbon molecule such as isopentane, $(CH_3)_2CHCH_2CH_3$, produces a mixture of four alkyl radicals, but $(CH_3)_2\dot{C}CH_2CH_3$ predominates. These differences are most marked, of course, at low temperatures.

3.1.2. Propagation

Alkyl radicals may decompose, recombine, disproportionate, isomerize, or react with either fuel or oxygen. In the presence of large concentrations of oxygen, the last of these reactions is sufficiently rapid to occur to the virtual exclusion of the others. The first step in the interaction of $R^\bullet$ with O_2 must be the formation of some species which may be formally written as $R^\bullet....O_2$. This may be a fairly stable free radical which can exist for relatively long periods of time or it may be merely a collision complex which breaks down within the period of a single vibration. It is generally believed that at low temperatures (< 300 °C) $RO_2^\bullet$ radicals are quite stable but that at higher temperatures (> 400 °C) the initial collision complex breaks down almost immediately to give an HO_2 radical and an alkene. The competition between the reactions (2) and (3) is partly responsible for the observed influence of temperature on the pattern of product formation.

$$R^\bullet + O_2 \rightarrow RO_2^\bullet \qquad E = 0 \qquad (2)$$

$$R^\bullet + O_2 \rightarrow HO_2^\bullet + \text{alkene}, \quad E = 7\text{–}10 \text{ kcal mole}^{-1} \qquad (3)$$

The primary propagation process at low temperatures must be completed, therefore, by reactions of $RO_2^\bullet$ which lead eventually to the abstraction of hydrogen from another fuel molecule to regenerate an alkyl radical, $R^\bullet$. If the $RO_2^\bullet$ radicals formed at low temperatures have an appreciable lifetime, there are various fates which they can undergo.

The first of these is reaction (4) with the fuel to form a hydroperoxide; abstraction of tertiary hydrogen predominates as the activation energies for the rupture by $RO_2^\bullet$ of tertiary, secondary, and primary C–H bonds are 8, 10·5, and 14 kcal mole^{-1} respectively.

$$RO_2^\bullet + RH \rightarrow ROOH + R^\bullet \qquad (4)$$

This reaction is important in liquid-phase oxidation. In gas-phase oxidation, there is evidence for the formation of small amounts of ROOH from certain compounds RH[65,66] but such products may sometimes result from relatively unimportant side reactions and not from one of the main chain-propagation steps.

Thus, in the oxidations of ethane and isobutane[67,68] the corresponding hydroperoxides arise from the termination reaction (5),

$$RO_2^\bullet + HO_2^\bullet \rightarrow ROOH + O_2 \qquad (5)$$

and methyl hydroperoxide is formed during the oxidation of methane[69,70] by $CH_3O_2^\bullet$ radicals attacking formaldehyde

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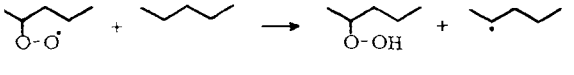
(and not methane). Furthermore, during the oxidation of isopentane no monohydroperoxides can be detected [71].

It is now generally believed that at fairly low temperatures $RO_2^{\bullet}$ radicals are formed which react further in such a way as to enable chains to be propagated without the $RO_2^{\bullet}$ radicals themselves reacting with a fuel molecule. Thus, they may isomerize by the transfer of hydrogen from a carbon atom to the outer oxygen of the peroxy group (reaction (6)).

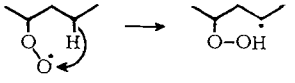
$$C_nH_{2n+1}OO^{\bullet} \rightarrow {}^{\bullet}C_nH_{2n}OOH, \quad E = 8\text{–}24 \text{ kcal mole}^{-1} \qquad (6)$$

This reaction is, in general, sufficiently rapid to compete successfully with intermolecular hydrogen abstraction at sub-atmospheric pressures and at temperatures of about 600 °K.

Consider, for example, the competition between reactions (4a) and (6a).



(4a)



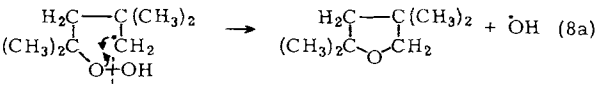
(6a)

The ratio of the rates of intramolecular and intermolecular H-abstraction by $RO_2^{\bullet}$ is $k_{6a}/k_{4a}[RH]$. When the partial pressure of RH is 200 torr, $[RH] = 10^{18.5}$ molecules cm^{-3}. If it is assumed that there is free rotation in the transition state of reaction (4a), $k_{4a} \simeq 10^{-13}e^{-10500/RT}$ cm^3 molecules^{-1} sec^{-1}. (If it is assumed that there is no free rotation, a considerably lower value is obtained.) As reaction (6a) involves transfer of secondary hydrogen around a six-membered ring, $k_{6a} \simeq 10^{11}e^{-11100/RT}$ sec^{-1}. At 600 °K, then, $k_{6a}/k_{4a}[RH] \simeq 10^{5.3}$ and intramolecular abstraction predominates. Even for less favored intramolecular H-transfer reactions, such as the transfer of the primary H around a five-membered ring, this ratio is as high as 10^2.

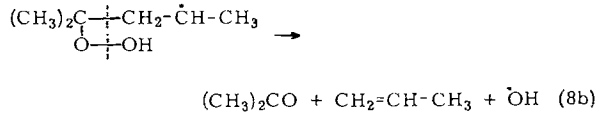
It has been amply demonstrated experimentally [4, 18, 51, 72–80] that this isomerization reaction is a major chain-propagating step during gaseous oxidation. Similarly, isomerization by transfer of an alkyl group occurs (reaction (7)) [51, 72, 77, 78], although this is much less common.

$$C_nH_{2n+1}OO^{\bullet} \rightarrow {}^{\bullet}C_{n-m}H_{2(n-m)}OOC_mH_{2m+1} \qquad (7)$$

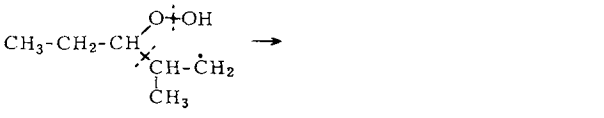
The hydroperoxyalkyl radical produced by reaction (6) may decompose in one of several ways or may react with further oxygen. The modes of decomposition of such radicals have been enumerated previously [51, 72]; only a few examples need be given here (reactions (8a)–(8e)).



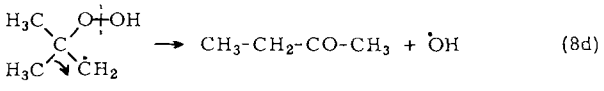
(8a)



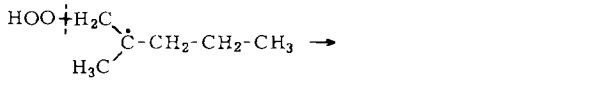
(8b)

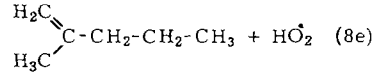


(8c)



(8d)





(8e)

It is evident from these examples that carbonyl compounds, alkenes and O-heterocycles (oxiranes, oxetanes, tetrahydrofurans, and tetrahydropyrans) are among the important products of decomposition of the hydroperoxyalkyl radicals. Moreover, as the O–O bond is the weakest in the decomposing radical, the radical usually (although not invariably) produced is the hydroxyl radical. The corresponding breakdown of the alkylperoxyalkyl radicals produced by the infrequent reaction (7) gives alkoxy radicals (and hence alcohols).

The hydroxyl radical attacks the hydrocarbon fuel molecule, abstracting a hydrogen atom to form water and thus regenerating an alkyl radical and completing the primary chain process. This abstraction reaction has a low activation energy (1–2 kcal mole^{-1}) [81]; attack by $^{\bullet}OH$ on the fuel molecule is, therefore, much less selective than attack by $RO_2^{\bullet}$ or $HO_2^{\bullet}$. When $^{\bullet}OH$ is the predominant chain-propagating entity, the formation of tertiary alkyl radicals will no longer predominate and the products of oxidation will include, in significant amounts, products of the further reaction of each possible alkyl radical derived from the fuel.

In oxidation régimes where isomerization is the usual fate of alkylperoxy radicals and decomposition of the

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hydroperoxyalkyl radicals so formed occurs readily, the primary linear chain process may be represented:

$$C_nH_{2n+1}^{\bullet} + O_2 \rightarrow C_nH_{2n+1}OO^{\bullet} \quad (9a)$$

$$C_nH_{2n+1}OO^{\bullet} \rightarrow {}^{\bullet}C_nH_{2n}OOH \quad (9b)$$

$${}^{\bullet}C_nH_{2n}OOH \rightarrow \text{products} + {}^{\bullet}OH \quad (9c)$$

$${}^{\bullet}OH + C_nH_{2n+2} \rightarrow H_2O + C_nH_{2n+1}^{\bullet} \quad (9d)$$

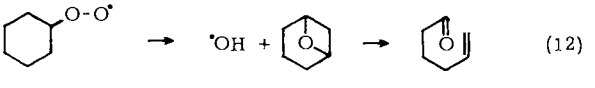
The further oxidation of hydroperoxyalkyl radicals, reaction (10), competes with their decomposition, becoming particularly important in the case of α-hydroperoxyalkyl radicals[51]; the hydroperoxyalkylperoxy radicals so formed may abstract hydrogen

$${}^{\bullet}C_nH_{2n}OOH + O_2 \rightarrow {}^{\bullet}OOC_nH_{2n}OOH \quad (10)$$

from a fuel molecule to give dihydroperoxides, propagating the chain, or may decompose to branch the chain. The formation of dihydroperoxides by a route involving intramolecular H-transfer is supported by the results of studies[14,82] in which a compound (HBr) with a readily-abstractable hydrogen was added to the system. Under these conditions, intermolecular H-transfer competes with intramolecular H-transfer, and monohydroperoxides, not dihydroperoxides, are formed.

Isomerization is not the only fate of alkylperoxy radicals during gaseous oxidation. In the presence of substantial amounts of alkenic products, addition of $RO_2^{\bullet}$ to these species may lead to oxiranes as products (*e.g.* reaction (11)) and it has been suggested[71,78] that $RO_2^{\bullet}$ may decompose without prior isomerization (*e.g.* reaction (12)).

$$RO_2^{\bullet} + R^1R^2C{=}CR^3R^4 \rightarrow R^1R^2\dot{C}\text{-}\underset{\underset{OOR}{|}}{C}R^3R^4 \rightarrow R^1R^2C\text{-}\underset{\diagdown O \diagup}{C}R^3R^4 + RO^{\bullet} \quad (11)$$



(12)

Each of these steps will also propagate the chain.

At higher temperatures, where alkyl radicals react with oxygen predominantly to give an olefin and an $HO_2^{\bullet}$ radical, some reaction of $HO_2^{\bullet}$ must be responsible for completing the primary chain. This radical abstracts a hydrogen atom from an alkane to give hydrogen peroxide (reaction (13));

$$HO_2^{\bullet} + RH \rightarrow H_2O_2 + R^{\bullet} \quad (13)$$

the activation energy has not been measured accurately but is probably[10,83] in the region of 6–14 kcal mole^{-1}. Attack of RH by $HO_2^{\bullet}$ is therefore more selective than attack by $^{\bullet}OH$ and, if reaction (13) becomes important at higher temperatures, the selectivity should increase with temperature.

It has been suggested[83], however, that the reaction of $HO_2^{\bullet}$ with alkenes (which are formed in the same propagation step as is $HO_2^{\bullet}$) to give α-hydroperoxyalkyl radicals is sufficiently rapid to become the major chain-propagating reaction of this radical in the temperature range 300–400 °C. The chain cycle (14) has thus been proposed[83]:

$$HO_2^{\bullet} + R_2C{=}CR_2 \rightarrow R_2\dot{C}\text{-}C(OOH)R_2 \quad (14a)$$

$$R_2\dot{C}\text{-}C(OOH)R_2 + O_2 \rightarrow R_2C(OO^{\bullet})C(OOH)R_2 \quad (14b)$$

$$HO_2^{\bullet} + R_2C(OO^{\bullet})C(OOH)R_2 \rightarrow R_2C(OOH)C(OOH)R_2 + O_2 \quad (14c)$$

$$R_2C(OOH)C(OOH)R_2 \rightarrow 2\,R_2CO + 2\,\dot{O}H \quad (14d)$$

$${}^{\bullet}OH + R_2CHCHR_2 \rightarrow R_2\dot{C}CHR_2 + H_2O \quad (14e)$$

$$R_2\dot{C}CHR_2 + O_2 \rightarrow R_2C{=}CR_2 + HO_2^{\bullet} \quad (14f)$$

In this cycle, $^{\bullet}OH$ is again the entity which attacks the fuel molecule and oxidation is unselective. It seems that unless (14d) is very fast step (14c) should properly be regarded as a termination step and step (14d) as a branching step, rather than each as a propagation step. This being so, scheme (14) does not represent a chain-propagation process but is merely a slow mechanism for conversion of $HO_2^{\bullet}$ to $^{\bullet}OH$. A true propagation process would result if the step (14g) were substituted for (14b–d) inclusive or if step (14h) were substituted for (14c–e) inclusive.

$$R_2\dot{C}\text{-}C(OOH)R_2 \rightarrow R_2C\text{-}\underset{\diagdown O \diagup}{C}R_2 + \dot{O}H \quad (14g)$$

$$R_2CH\text{-}CHR_2 + R_2C(O\dot{O})\text{-}C(OOH)R_2 \rightarrow R_2C(OOH)\text{-}C(OOH)R_2 + R_2\dot{C}\text{-}CHR_2 \quad (14h)$$

In this event, schemes resembling the propagation scheme involving alkylperoxy radical isomerization are produced, except that the hydroperoxyalkyl radicals involved necessarily have the hydroperoxy group and the unpaired electron on adjoining carbon atoms.

3.1.3. Degenerate Branching

Several types of compound produced in the propagation steps discussed above are capable of acting as agents of degenerate branching. Two kinds of branching reaction are possible, the first involving non-radical reactants (including molecular oxygen) only and the second involving radicals. The latter family of reactions, being of lower activation energy than the former, are probably important only in régimes of rapid reaction.

The pyrolysis of peroxides has frequently been postulated as a degenerate branching reaction in the oxidation of alkanes. Monohydroperoxides decompose to

[82] *L. V. Karmilova, N. S. Enikolopyan, A. B. Nalbandyan,* and *N. N. Semenov,* Ž. fiz. Chim. *34,* 562 (1960).

[83] *J. H. Knox,* Combust. and Flame *9,* 297 (1965).

give an alkoxy radical and a hydroxyl radical (reaction 15) with activation energies of *ca.* 35–40 kcal/mole^{-1} (*e.g. tert*-butyl hydroperoxide[84], $E = 37.8 \pm 0.7$ kcal mole^{-1}). Dihydroperoxides decompose similarly, by homolysis of both O–O bonds; in α-dihydroperoxides this scission process will be accompanied by that of a C–C bond, leading to two carbonyl compounds and two OH radicals (reaction (16)) whereas β-, γ-, or δ-hydroperoxides will decompose to dicarbonyl compounds (reaction (17)).

$$ROOH \rightarrow RO^{\bullet} + {}^{\bullet}OH \qquad (15)$$

$$HOO(R^1R^2)C\text{-}C(R^3R^4)OOH \longrightarrow R^1R^2C{=}O + R^3R^4C{=}O + 2\,{}^{\bullet}OH \qquad (16)$$

$$R^1R^2C(O\text{-}OH)\text{-}CH_2\text{-}C(O\text{-}OH)R^3R^4 \longrightarrow R^1C(=O)\text{-}CH_2\text{-}C(=O)R^3 + {}^{\bullet}R^2 + {}^{\bullet}R^4 + 2\,{}^{\bullet}OH \qquad (17)$$

Hydrogen peroxide decomposes with the assistance of a second body (reaction 18), the process having[85] an activation energy of 45 kcal mole^{-1}. This branching

$$HOOH + M \rightarrow 2\,\dot{O}H + M \qquad (18)$$

process is therefore likely to be important at temperatures somewhat higher than those at which organic peroxides decompose.

The attack by molecular oxygen on moderately stable products with weak C–H bonds is considerably faster than the corresponding attack on alkanes, (*i.e.* than the initiation reaction) and will act, therefore, as a degenerate branching reaction. By far the best example of such a class of products is the aldehydes; reaction (19) has frequently been supposed[58–60] to fill this role. For formaldehyde[82], $E_{19} = 32$ kcal mole^{-1} whereas for acetaldehyde[86] E_{19} may be as low as 14 kcal mole^{-1}. Higher aldehydes, including branched and unsaturated aldehydes, are in general less reactive than acetaldehyde[87].

$$RCHO + O_2 \rightarrow HO_2^{\bullet} + R\dot{C}{=}O \qquad (19)$$

The pyrolysis of peroxides and the oxidation of aldehydes are certainly the two best-established modes of degenerate branching during the oxidation of alkanes. Branching reactions involving free radicals as reactants have received less attention but it has recently been realized that these may play a considerable part. In the oxidation of heptane[14], for example, the hydroperoxyheptylperoxy radicals formed may decompose (reaction (20)) sufficiently rapidly to compete with hydrogen abstraction to give a dihydroperoxide. Also, the reactions of free radicals with molecules (*e.g.* reactions (21) and (22)) can lead to branching.

$$CH_3CH(OOH)CH_2CH(OO^{\bullet})C_3H_7 \rightarrow 2\,{}^{\bullet}OH + (CH_3)_2C{=}O + C_3H_7^{\bullet} + CO \qquad (20)$$

There is an important analogy between such reactions and the equation $X + Y \rightarrow B + 2\,Y$ involved in the two-product explanation of cool flames (section 2.7.).

$$RO_2^{\bullet} + R'CHO \rightarrow RO^{\bullet} + {}^{\bullet}OH + R'\dot{C}{=}O \qquad (21)$$

$$RO_2^{\bullet} + R''OOH \rightarrow RO^{\bullet} + {}^{\bullet}OH + R''O_2^{\bullet} \qquad (22)$$

3.1.4. Termination

Termination of chains in gaseous oxidation systems occurs in two ways. Radicals may react together in the gas phase to produce species which are inactive as chain-propagating agents, or may diffuse to the walls where they are either captured or converted to inactive products. During slow combustion the concentrations of radicals are low; homogeneous termination processes, which have rates proportional to the product of two radical concentrations, are therefore slow and heterogeneous termination predominates. At higher radical concentrations, such as those characteristic of non-isothermal oxidation, homogeneous termination by disproportionation of radicals having relatively long lifetimes, such as $RO_2^{\bullet}$ and $HO_2^{\bullet}$, may become appreciable, however. The effects of surface on the kinetics of the overall reaction provided evidence for the mode of termination.

The important homogeneous termination reactions during the gaseous oxidation of alkanes are

$$2\,C_nH_{2n+1}OO^{\bullet} \rightarrow C_nH_{2n+1}OOH + C_nH_{2n} + O_2 \qquad (23)$$

$$C_nH_{2n+1}OO^{\bullet} + HO_2^{\bullet} \rightarrow C_nH_{2n+1}OOH + O_2 \qquad (24)$$

$$2\,HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \qquad (25)$$

Heterogeneous termination occurs by diffusion to, and destruction at, the walls of chain carriers and branching agents (*e.g.* $HO_2^{\bullet}$, $C_nH_{2n+1}OO^{\bullet}$, ${}^{\bullet}C_nH_{2n}OOH$, ${}^{\bullet}OH$, H_2O_2, ROOH). These processes can be controlled either by the efficiency of the wall reaction (kinetic control) or by the rate of diffusion of species to the wall (diffusion control)[10,12].

3.2. The Steps Operative in the Cool Flame Region

The temperature region in which cool flames are formed (250–400 °C) is such that both modes of reaction of alkyl radicals with oxygen must be considered as

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[89] *W. S. Affleck* and *A. Fish*: Eleventh Internat. Symposium on Combustion. The Combustion Institute, Pittsburgh 1967, p 1003.

propagation steps. The particularly low selectivity of oxidation in the cool-flame region shows that, if the primary chain-propagating cycle be represented by the general equations

$$RH + X^{\bullet} \rightarrow R^{\bullet} + XH$$

$$R^{\bullet} + O_2 \rightarrow P + X^{\bullet}$$

then it is evident that the species X that predominates in the cool-flame region is different from that predominating at other temperatures and attacks RH less selectively. It is likely therefore that $X \equiv OH$ at cool-flame temperatures whereas at other temperatures $RO_2^{\bullet}$ or $HO_2^{\bullet}$ radicals act as X.

Two propagation schemes (schemes (9) and (14)) in which $X \equiv OH$ have been discussed. The basic difference between these is that the hydroperoxyalkyl radicals in scheme (14) are necessarily α-hydroperoxyalkyl radicals, whereas β-, γ-, and δ-hydroperoxyalkyl radicals, as well as α-hydroperoxyalkyl radicals, are formed in scheme (9). If only scheme (14) operates, the O-heterocyclic products with carbon skeletons corresponding to that of the fuel molecule will be oxiranes exclusively, whereas, if scheme (9) operates, oxiranes, oxetanes, tetrahydrofurans, and tetrahydropyrans can all be formed. The latter is found experimentally to be true, particularly in the cool-flame region [4, 18, 33, 51, 72, 90, 91].

The primary chain-propagation process during cool-flame oxidation of alkanes is thus probably (9), although the chain (14a, 14g, 14e, 14f) and the reaction sequence (11) may each contribute to the formation of oxiranes and the sequence (14b, 14h, 16) may increase the yields of carbonyl scission products. A detailed study [51] of this reaction scheme has shown that it is consistent with the complex product distribution resulting from the cool-flame oxidation of 2-methylpentane. It is probable that the chain (14a, 14g, 14e, 14f) competes quite effectively with the chain (9) during the oxidation of smaller alkanes such as isobutane and ethane.

The rate-determining step in cycle (9) is the alkylperoxy radical rearrangement reaction, reaction (9b). As the activation energies of the different modes of rearrangement differ, it is possible that this reaction explains the complex variation of the properties of cool flames with temperature and also the variation of the shape and extent of the low-temperature ignition diagram with the molecular structure of the fuel [3]. Two factors affecting the activation energy in question may be distinguished, namely, the strength of the C–H bond broken and the strain energy involved in forming the cyclic transition state.

Correlation of the temperature region in which the yield of each product maximizes during the cool-flame oxidation of 2-methylpentane [51] with the mode of rearrangement involved in the formation of the product shows that the three lobes of the two-stage ignition régime are predominantly associated, in order of increasing temperature, with 1:5, 1:6, and 1:4 H-transfer respectively, suggesting that the transition-state strain energy is the predominant factor. A given mode of H-transfer cannot be assigned exclusively to a given lobe, however. In particular, there is considerable intermixing of 1:5 and 1:6 H-transfer in the two lower lobes.

The strain energies involved in four-, five-, six-, seven-, and eight-membered cycloalkane rings are, respectively, 26, 6.5, 0.6, 6.5, and 10 kcal mole^{-1}. If it is assumed that the strain energies of transition-state rings of similar sizes run parallel to these, 1:5 H-transfer in alkylperoxy radicals should occur at the lowest temperature, followed by 1:6 and 1:4 H-transfer and, in turn, 1:7 H-transfer. The energetic requirements of the decomposition reactions of the hydroperoxyalkyl radicals so formed may, however, be sufficiently large to alter the effective sequence. For example, considerable strain energy is involved in reaction (8a), in which a ring is formed which has two fewer members than the ring involved in the corresponding reaction (6). Radicals which have been formed by the easy 1:5 H-transfer will decompose therefore only slowly, as a four-membered ring is involved, and this step may become rate-determining. The decomposition of radicals formed by 1:6 H-transfer involves, however, a five-membered ring and will be relatively rapid. Such considerations may explain the "mixing" of 1:5 and 1:6 H-transfer in the lobes L_1 and L_2 of the 2-methylpentane system and may, indeed, cause overall reactions involving 1:6 H-transfer to occur, in general, at lower temperatures than those involving 1:5 H-transfer.

The variation of the shape of the low-temperature ignition peninsula with the molecular structure of the fuel can be explained reasonably satisfactorily in chemical terms by considering the number of hydrogens which can be transferred around rings of a given size in each and every alkylperoxy radical derived from the fuel skeleton and adding these to give a picture of the properties of the fuel (see Table 1). It is necessary to consider every alkylperoxy radical derived from the fuel skeleton because $^{\bullet}OH$ attacks fuel unselectively.

For example, two alkylperoxy radicals can be derived from butane, *viz*, 1-butylperoxy and 2-butylperoxy. The 1-butylperoxy radical has two hydrogens available for 1:4 H-transfer, two for 1:5 H-transfer, and three for 1:6 H-transfer. The 2-butylperoxy radical has, respectively, five, three, and zero such hydrogens. The propensities (irrespective of energy requirements) of butane to react *via* propagation steps involving, respectively, 1:4, 1:5, and 1:6 H-transfer, are therefore in the ratios 7:5:3. The ignition limit of this fuel should therefore exhibit all three lobes. Ethane, however, gives only one alkylperoxy radical and this can isomerize only by 1:4 H-transfer. Only one lobe should therefore be present. Similarly, neopentane should exhibit one lobe only, corresponding to 1:5 H-transfer.

The predictions of this theory, if it is assumed that 1:6 and 1:5 H-transfer account respectively for lobes L_1 and L_2 and that 1:4 H-transfer (together with 1:n H-transfer where $n > 6$) accounts for L_3, are compared with experiment in Table 1. The increasing number and position of lobes as the molecular weight of an *n*-alkane is increased are correctly predicted, as are the "incomplete" diagrams of isobutane and neopentane. For 3-methylpentane, however, the theory predicts the existence of more lobes than have been found.

2,3-Dimethylbutane is a particularly interesting case; isomerization of alkylperoxy radicals by 1:6, 1:5, and 1:4 H-transfer is possible but it is doubtful whether such radicals will be formed. An alkyl radical derived from this fuel necessarily has a tertiary hydrogen atom attached to a carbon atom in a position α to the carbon atom bearing the free valency. The abstraction by oxygen of this hydrogen atom (reaction (3)) will be easy and may well compete successfully

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[91] *G. Kyryacos*, *H. R. Menapace*, and *C. E. Boord*, Analytic. Chem. *31*, 222 (1959).

with the addition of oxygen. If this is so, the low-temperature ignition region of 2,3-dimethylbutane will be either non-existent or very small, in agreement with experiment.

Cyclic hydrocarbons probably have "incomplete" diagrams because of the highly strained configuration of the transition state complex necessary to alkylperoxy radical rearrangement. In the oxidation of cyclohexane, 1:5 H-transfer occurs, leading to 5-hexen-1-al[78], and 1:6 H-transfer is possible in the boat form but 1:4 H-transfer is unimportant. Cyclopentylperoxy radicals, indeed, may not isomerize easily at all. In Table 1, isomerization reactions of cycloalkylperoxy radicals that may be excluded for this reason have been placed in parentheses and discounted in predicting the occurrence of lobes.

The alkylperoxy radical rearrangement theory describes quite successfully, then, both the natures of the products of cool flames of alkanes and the variation of the fine structure of the two-stage ignition region with molecular size and shape. Similarly, the variation with molecular structure of the oxidation characteristics of ketones and esters can be described by the theory[92]. The branching reactions involved in the cool-flame régime doubtless include both the pyrolysis of peroxidic compounds and the oxidation of aldehydes, both of which are found as products (see Sections 2.5 and 2.6).

Thus, the cool flames of butanone[55] and of cyclohexane[15] have been said to represent the pyrolytic explosion of accumulated peroxide. On the other hand, the opinion has been expressed[60] that the cool flames of oxidizing hydrocarbons correspond to the cool flames of aldehydes. The possible role of peroxides and aldehydes in a two-product explanation of the formation of cool flames is dependent on the existence of a mechanism for their interconversion. Branching by the homogeneous decomposition of peroxide/aldehyde addition compounds may also play some part, as may radical reactions such as (20), (21), and (22).

The probable mechanistic reasons for the changes in rate and selectivity of the gaseous oxidation of alkanes with temperature may therefore be summarized as follows. At low temperatures, alkyl radicals react with oxygen to give alkylperoxy radicals which, in turn, attack fuel molecules selectively to produce hydroperoxides. Branching results from the pyrolysis of the hydroperoxides. As the temperature is increased, the mode of reaction of alkylperoxy radicals changes and this is the basic reason for the formation of cool flames. Homogeneous isomerization reactions predominate, producing hydroperoxyalkyl radicals. The different activation energies of the various modes of this reaction may be responsible for the fine structure of the cool-flame region. The hydroperoxyalkyl radicals decompose, both directly and after addition of further oxygen, producing a wide variety of stable or moderately stable products. These decomposition reactions lead to the OH radical as the predominant chain-propagating entity; the resulting attack on the fuel molecule is rapid and unselective. The chain is branched by reactions of aldehydes, hydroperoxides, and dihydroperoxides. The existence of an upper temperature limit of cool flames is probably a result of the mode of attack of alkyl radicals by oxygen changing from addition to abstraction. At temperatures above those of cool flames, it is likely that the hydroperoxy radical propagates the chain, producing hydrogen peroxide and resulting in an increase in selectivity and a decrease in rate. Branching probably results from the homogeneous decomposition of the hydrogen peroxide so formed.

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4. Cool Flames and Combustion Processes in Engines

The properties of the self-ignition of hydrocarbon fuels at high pressures (> 15 atm) and temperatures ($> 700\,^{\circ}K$) are of primary importance in understanding abnormal combustion phenomena in internal combustion engines. Thus, self-ignition of the end-gas is widely held[93–95] to be responsible for knock in the gasoline engine and accounts also for the phenomenon of run-on. Again, in the diesel engine, the normal operation of the engine is determined by the length of the ignition delay period and the pattern of heat release during ignition. A close qualitative relationship exists between the tendency of a pure hydrocarbon fuel to cause knock in a gasoline engine and the shape and extent of its low-temperature ignition diagram[3, 72]. It would seem then that the two-stage ignition process is maintained even at pressures far into the ignition zone. Recent direct experimental work has shown that this is so.

Although the ignition delay is reduced, when the pressure is increased from about 1 to about 15 atm, by a factor of 10^3 to 10^4, the general shape of the ignition limit is reflected in the shape of isolag curves at high pressure[96], although the "fine structure" of the low-temperature limit is lost (Fig. 8a). Division of the total delay to ignition at high pressure of a stoichiometric mixture with air of 60% iso-octane + 40% heptane into τ_{cf} and τ_{hf}, and extrapolation of the pressure/temperature loci of the conditions $\tau_{hf} = 0$, τ_{total} = minimum, and τ_{hf} = maximum to the pressures and temperatures characteristic of the ignition limit, produces curves which reflect even the fine structure of the limit, as illustrated in Figure 8 (b) and (c). This relationship between two-stage ignition at low pressures and under engine conditions is reflected also in the indices n and m in the equations $\tau_{cf} = k'p^{o-n} + c'$ (Section 2.3.) and $\Delta p_{cf} = kp_o^m$ (Section 2.2.) which describe the variations of induction period and pressure rise with initial pressure. For the cool flames of 2-methylpentane, the index n at pressures relevant to combustion in engines (10–50 atm) is similar to the minimum value of n at the ignition limit[18]; the equality of m under these two widely different conditions of initial pressure is striking (Fig. 3).

A most dramatic demonstration of the similarity between two-stage ignition at low pressures and that under engine conditions has resulted from the analysis of the chemical products of the cool-flame step in each case[18].

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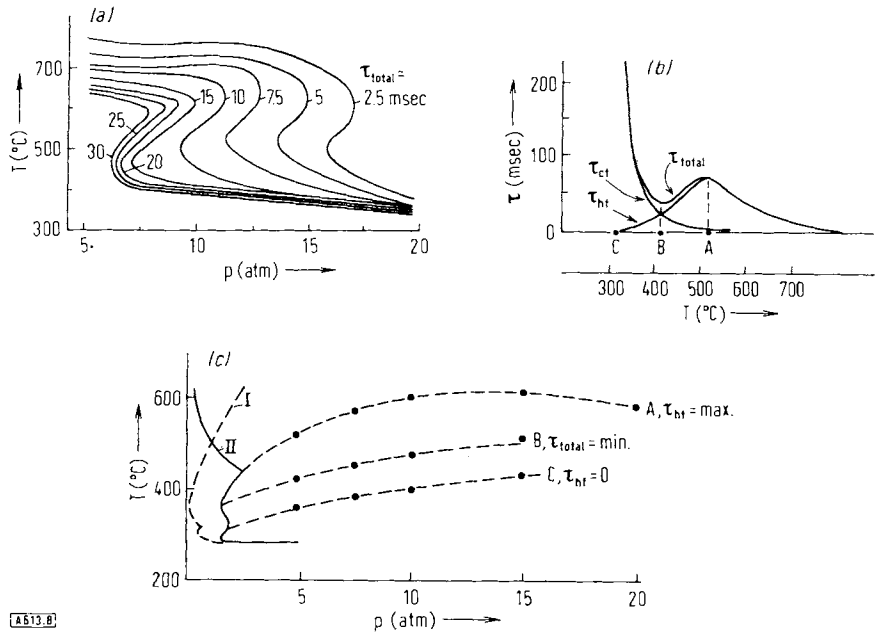

Fig. 8. The ignition at high pressures of a 40% heptane + 60% iso-octane mixture in stoichiometric concentration in air.

(a) Isolag curves.

(b) Variation of two-stage induction period with temperature at p_O = 5 atm.

(c) Extrapolation of loci of turning values of τ to the limiting conditions for ignition.

I = cool flame limit; II = ignition limit [96].

The cool flames of 2-methylpentane were isolated under two sets of conditions which differed very widely, low-pressure experiments being performed in a conventional Pyrex reactor and high-pressure experiments in a rapid-compression machine. A 15-fold range of reactant ratio was involved; the reactors differed by a factor of 100 in effective radius (calculated in terms of molecular mean free paths), the pressures were different by a factor of 5×10^2 and the induction period measured differed by a factor of 10^4. Despite these very large differences in conditions, the chemical products of the first stage of two-stage ignition are sufficiently similar in the two régimes for there to be little doubt that a common phenomenon is involved. Of 42 organic species in the products, no less than 39 are common to the two combustion régimes; this pattern is sufficiently complex to ensure that its duplication in the two régimes is mechanistically significant. The products of the cool-flame oxidation of 2-methylpentane at high pressures include dimethyltetrahydrofurans, which are diagnostic of the occurrence of alkylperoxy radical isomerization, in considerable quantities. The very low surface availability (radius of reactor about 10^6 mean free paths) and short reaction time (about 10^{-3} sec) ensure that isomerization is not (as has been suggested [11,83]) an unimportant wall reaction, but occurs homogeneously and is capable of propagating the chain. The high-pressure experiments have been extended to the cool-flame combustion of 2-methylpentane in a motored Ricardo E6 experimental engine [18]; again, the products are similar. Nor is the similarity peculiar to 2-methylpentane as a fuel. The preflame reaction products of iso-octane in a motored engine contain large amounts of 2,2,4,4-tetramethyltetrahydrofuran and 2-*tert*-butyl-3-methyloxetane [97]. These ring ethers, together with 2-isopropyl-3,3-dimethyloxetane and 2-*tert*-butyl-3,3-dimethyloxirane, are also present in the end products of slow oxidation of the end gas during the spark-ignited combustion of iso-octane in an engine [98]; small quantities of these products even survive the passage of the flame itself [99,100].

The relationship of the knock rating of a fuel to its low-temperature ignition diagram is hardly surprising for the same chemical paths which determine the latter are involved in the early stages of the autoignition process which leads to knock. A circle of correlation has therefore been established between the molecular structure of a fuel, the ease of formation of and subsequent isomerization of the alkylperoxy radicals derived from it, the shape and extent of its low temperature ignition diagram, and its octane rating.

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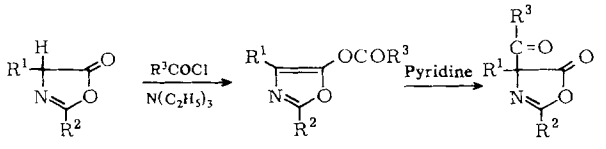
5-Acyloxyoxazoles and their Rearrangement to 4-Acyloxazol-5-ones

By *W. Steglich* and *G. Höfle* [*]

4-Substituted 2-phenyl-4*H*-oxazol-5-ones, on reaction with aliphatic carboxylic acid chlorides in the presence of one molar equivalent of triethylamine, give 2,4-disubstituted 5-acyloxyoxazoles *(1)* in high yield. As example we cite the reactions of 4-methyl-2-phenyloxazol-5-one with acetyl chloride or methyl chloroformate, in which 5-acetoxy-4-methyl-2-phenyloxazole *(1a)* and 4-methoxycarbonyloxy-4-methyl-2-phenyloxazole *(1b)*, respectively, are formed.

(1a): Yield 93 %; b.p. 140 °C/0.4 mm, m.p. 52 °C; IR (film) 1789 (vs), 1748 (s), 1718 (s), 1656 (vs), 1548 cm^{-1} (m); UV (in hexane, fine structure maximum with bands at 300, 286, 280, 275 (ε = 18600), 269 nm; NMR (in CCl_4) δ = 2.06 (singlet, 3 protons), 2.22 (singlet, 3), 7.3 (multiplet, 3), 7.9 ppm (multiplet, 2).

(1b): Yield 97 %; b.p. 150 °C/0.4 mm; IR (film) 1779 (vs), 1661 (s), 1548 cm^{-1} (m); NMR (in CCl_4) δ = 2.10 (singlet, 3 protons), 3.85 (singlet, 3), 7.3 (multiplet, 3), 7.9 ppm (multiplet 2).



(1) *(2)*

(a), $R^1 = R^3 = CH_3$, $R^2 = C_6H_5$
(b), $R^1 = CH_3$, $R^2 = C_6H_5$, $R^3 = OCH_3$

When kept or when warmed for a short time in pyridine, *(1a)* rearranges to 4-acetyl-4-methyl-2-phenyloxazol-5-one *(2a)*.

(2a): Yield 80 %; b.p. 135 °C/0.4 mm; IR (film) 1818 (vs), 1718 (s), 1639 cm^{-1} (s); NMR (in CCl_4) δ = 1.63 (singlet, 3 protons), 2.20 (singlet, 3), 7.5 and 8.0 ppm (multiplet, 5). Methyl 4,5-dihydro-4-methyl-5-oxo-2-phenyloxazole-4-carboxylate *(2b)* is obtained analogously from *(1b)* and is identical with a product obtained by another route [1].

Acylation of the oxazolone anion with acid chloride and triethylamine thus leads to the *O*-acyl derivative in a kinetically controlled reaction, whereas under the usual conditions of the Dakin-West reaction [2] (acetic anhydride and pyridine) only the thermodynamically more stable *C*-acyl derivatives have hitherto been isolated [3]. To establish whether 5-acyloxyoxazoles are formed also as intermediates in the classical Dakin-West reaction needs further study.

Huisgen and *Knorr* [4] detected 5-acetoxyoxazolium salts as the first stage of the Dakin-West reaction of mesoionic 3-alkyloxazolones. When *(1a)* is warmed with glacial acetic acid cleavage to *N*-benzoyl-DL-alanine occurs, whereas simultaneous addition of pyridine leads to formation of 3-benzoylamino-2-butanone.

Since 4-acyl-4*H*-oxazol-5-ones *(2)* are cleaved to α-acylamino ketones by acid hydrolysis, the sequence of reactions now described constitutes a method for the conversion of aliphatic halides into α-acylamino ketones in good yield.

Preparation of 2,4-Disubstituted 5-Acyloxyoxazoles (1): 50 mmoles of the acid chloride is added dropwise and with stirring into an ice-cooled solution of 50 mmoles of oxazolone and 7 ml of triethylamine (50 mmoles) in 70 ml of tetrahydrofuran. After 2 h the mixture is evaporated in a vacuum and the residue is partitioned between ether and N HCl. The ethereal phase is dried with $MgSO_4$ and, after removal of the ether in a vacuum, is distilled.

Preparation of 2,4-Disubstituted 4-Acyloxazol-5-ones (2): 20 mmoles of 5-acyloxyoxazole *(1)* is heated in 40 ml of anhydrous pyridine for 30 min at 95 °C. The pyridine is evaporated and the residue is distilled, both operations being carried out in a vacuum.

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[1] *W. Steglich, G. Höfle, W. König*, and *F. Weygand*, Chem. Ber., in press.

[2] *H. D. Dakin* and *R. West*, J. biol. Chemistry *78*, 91, 745, 757 (1928).

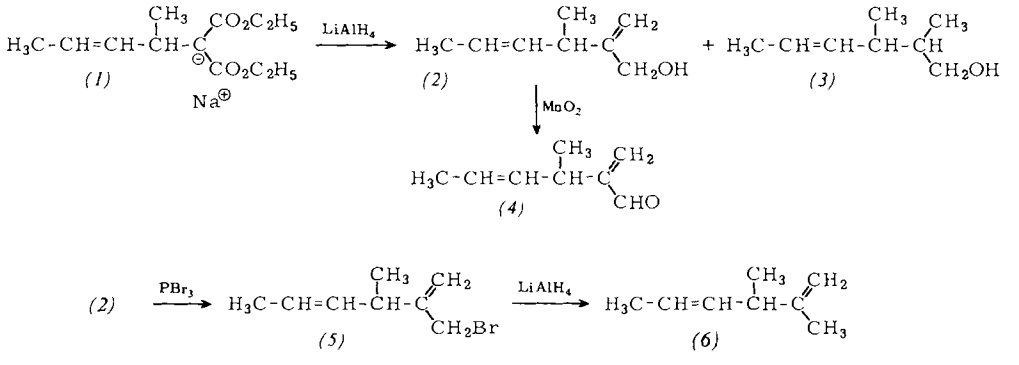
[3] *Y. Iwakura, F. Toda*, and *H. Suzuki*, J. org. Chemistry *32*, 440 (1967).

[4] *R. Huisgen* in Aromaticity. Special Publication No. 21, The Chemical Society, London 1967, p. 59.

Preparation of 1,4-Dienes by Reduction of Sodioallylmalonic Ester with Lithium Aluminum Hydride

By *W. Sucrow* [*]

1,4-Dienes are conveniently accessible if one applies to sodioallylmalonic ester the reduction process described by *Marshall et al.* [1] for substituted sodiomalonic esters. The single previous example of this type appears to be the reduction of a tricyclic malonic ester lactone in the synthesis of alantolactone [2]. An experiment with a model *(1)* (chosen with a view to synthesis of a steroid containing an unusual side chain [3]) showed that reduction occurs also with open-chain sodioallylmalonic esters, yielding the nonconjugated diene without isomerization. Further, the 1,4-diene-alcohol can be converted into the aldehyde or the hydrocarbon without isomerization.



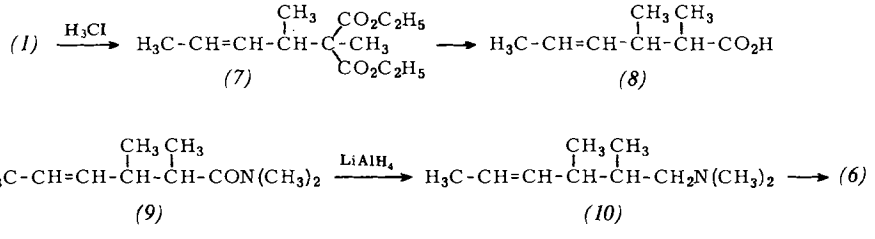
(1) *(2)* *(3)* *(4)* *(5)* *(6)*

Experimental:

The sodium salt *(1)* from 10 g of diethyl (1-methyl-2-butenyl)-malonate[4] is heated with 5.25 g of $LiAlH_4$ in 65 ml of dimethoxyethane for 20 min, thus giving 74% of a *ca.* 5:1 mixture of 3-methyl-2-methylene-4-hexen-1-ol *(2)* [b.p. 80 °C/18 mm; IR, $=CH_2$ 3090, 1650, 905, $-CH=CH-$ 968 cm^{-1}; NMR, $H_3C-C\leqslant$ (d) δ = 1.12; $H_3C-C=$ (split d) 1.65; $HC\leqslant$ (dq) 2.8; $-CH_2O-$ (broad s) 3.96; $=CH_2$ (m) 4.82, (m) 4.97; $-CH=CH-$ (m) 5.1–5.6 ppm; 3,5-dinitrobenzoate, m.p. 44 °C] and 2,3-dimethyl-4-hexen-1-ol *(3)*, which appears from its NMR spectrum to be a mixture of the *threo*- and the *erythro*-form. Compounds *(2)* and *(3)* can be separated by gas chromatography (20% Carbowax/Chromosorb W, H_2, 180 °C).

Oxidation of *(2)* with manganese dioxide gives a 60% yield of 3-methyl-2-methylene-4-hexenal *(4)* [b.p. 60 °C (bath temp.)/18 mm; UV, 212.5 nm (ε = 6800) in ether; IR, $=CH_2$ 3100, 1629, 941, $-CHO$ 2700, 1702, $-CH=CH-$ 972 cm^{-1}; NMR, $H_3C-C\leqslant$ (d) δ = 1.13, $H_3C-C=$ (split d) 1.65, $HC\leqslant$ (m) around 3.3, $-CH=CH-$ (m) around 5.3, $=CH_2$ (m) 5.85, (m) 6.10, $-CHO$ (s) 9.42 ppm; dinitrophenylhydrazone, m.p. 137 °C]. With PBr_3 in petroleum ether *(2)* affords 2-bromomethyl-3-methyl-1,4-hexadiene *(5)* [b.p. 80 °C (bath temp.)/18 mm; IR $=CH_2$ 3095, 1641, 912, $-CH=CH-$ 970 cm^{-1}; NMR, $H_3C-C\leqslant$ (d) δ = 1.16, $H_3C-C=$ (d) 1.67, $HC\leqslant$ (m) 2.8–3.3, $-CH_2Br$ (s) 3.90, $=CH_2$ (m) 4.94, (m) 5.13; $-CH=CH-$ (m) around 5.3 ppm], and thence by 3.5 hours' boiling with $LiAlH_4$ in ether an 80% yield of 2,3-dimethyl-1,4-hexadiene *(6)* [b.p. 107 °C; IR, $=CH_2$ 3090, 1642, 892; $-CH=CH-$ 970 cm^{-1}; NMR, $H_3C-C\leqslant$ (d) δ = 1.06, $H_3C-C=$ (m) 1.65 (6 H), $HC\leqslant$ (m) 2.4–3.0, $=CH_2$ (m) 4.62 (2 H), $-CH=CH-$ (m) around 5.3 ppm; mass spectrum, M^+ at *m/e* = 110.10996, fragments at *m/e* = 95 ($M-CH_3$, m* = 82.0), 93 ($95-2H$, m* = 91.0), 91 ($93-2H$, m* = 89.0), 67 ($95-C_2H_4$, m* = 47.3), 41 ($67-C_2H_2$, m* = 25.1), 39 ($41-2H$, m* = 37.1)].

For control, compound *(6)* was also prepared by the following route: Methylation of *(1)* gives the dialkylmalonic ester *(7)* [b.p. 100 °C (bath temp.)/0.1 mm; NMR new (s) δ = 1.23, no longer (d) at 3.08 ppm], which was hydrolyzed (m.p. 142 °C) and then decarboxylated to *(8)* [b.p. 100 °C (bath temp.)/18 mm; IR, $-COOH$ 1710, $-CH=CH-$ 969 cm^{-1}]. Reduction of the derived dimethylamide *(9)* [b.p. 50 °C (bath temp.)/0.1 mm; IR, $-CON\leqslant$ 1650, $-CH=CH-$ 970 cm^{-1}] leads to *N,N*-dimethyl-2,3-dimethyl-4-hexenylamine



(10) [b.p. 90 °C (bath temp.)/18 mm]. The NMR spectrum of *(10)* [4 doublets from CH_3 on saturated C at δ = 0.73, 0.75, 0.84, 0.93 ppm; $H_3C-C=$ (d) 1.61; $-N(CH_3)_2$ (s) 2.08; $-CH=CH-$ (m) around 5.3 ppm] shows that *(8)*, *(9)*, and *(10)* occur as mixtures of *threo*- and *erythro*-forms. Oxidation of *(10)* to the amine oxide and Cope degradation[5] gives *(6)* [40% yield calculated on *(1)*]. IR and NMR spectra were measured for CCl_4 solutions.

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[1] *J. A. Marshall, N. H. Andersen,* and *A. R. Hochstetler,* J. org. Chemistry *32*, 113 (1967).

[2] *J. A. Marshall* and *N. Cohen,* J. Amer. chem. Soc. *87*, 2773 (1965).

[3] *N. A. Poulos,* Diss. Abstr. *17*, 2824 (1957); *W. Sucrow,* Chem. Ber. *99*, 3559 (1966).

[4] *E. Bergmann,* Helv. chim. Acta *20*, 590 (1937); *R. J. Lewina* and *N. N. Godowikow,* Ž. obšč. Chim. *24*, 1572 (1954).

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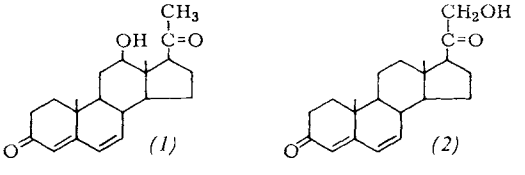
Protective Materials in the Secretion from the Prothoracic Protective Gland of a Mexican Cybister Species [1]

By *H. Schildknecht* and *W. Körnig* [*]

During an excursion by boat on the water ditches of the floating garden of Xochimilco (Mexico City) we were able to catch four *Cybister* (as well as many *Hydrophylidae*). We succeeded in bringing three of the water beetles alive to Heidelberg. Their milky cervical secretion was sucked up in glass capillaries. 1.5 mg of a crystalline substance of m.p. 196 °C was isolated from this secretion by repeated preprarative thin-layer chromatography on silica gel (GF_{254} Merck) with 1:1 cyclohexane/ethyl acetate.

Since we had found cybisterone[2] as protective material in the corresponding secretion of *Cybister lateralimarginalis* occurring, above all, in Southern Europe, we assumed that the ingredient of the prothoracic gland of this, as yet inexactly characterized, Mexican *Cybister* would also be a steroid. This was at once confirmed by the absorption maximum at 284 nm in ethanol and the absorption bands at 1655 cm^{-1} ($\nu_{C=O}$), 1612 cm^{-1} ($\nu_{C=C}$), and 1580 cm^{-1} ($\nu_{C=C}$). Further, a band at 1680 cm^{-1} ($\nu_{C=O}$) indicated a second carbonyl group, this one exocyclic. In agreement with this we found a positive Cotton effect with two circular dichroism maxima at 363 and 303 nm. A hydroxyl group, identified by acetate formation, was evidenced by a strong absorption band at 3350 cm^{-1} (ν_{O-H}) and ν_{C-OH} vibrations at 1038 cm^{-1} (s) and 1070 cm^{-1} (m). A molecular weight of 328 (calculated from the mass spectrum) showed that the protective material from the Mexican *Cybister*, like cybisterone, is in fact a C_{21} steroid. The fragmentation pattern in the mass spectrum showed that the side chain of the steroid must be a CH_3CO group. These results suggest the presence of a 4,6-pregnadiene-3,20-dione hydroxylated in ring C.

The 11β- and 12α-position for the OH can be excluded since such steroids do not form acetates in pyridine/acetic anhydride. Comparison of the IR spectra of 11α-hydroxy-4,6-pregnadiene-3,20-dione and the natural product excludes further the 11α-position. Finally, study of the absorption data of *Heller*[3] for numerous hydroxylated progesterones showed the *Cybister* steroid to have the structure of a 12β-hydroxy-4,6-pregnadiene-3,20-dione *(1)*. We propose the name cybisterol for this new insect steroid, of which the beetle can store more than 1 mg.



Alongside this material, we isolated from the prothoracic protective glands traces of 21-hydroxy-4,6-pregnadiene-3,20-dione *(2)*, which was identified spectroscopically after isolation by thin-layer chromatography.

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[1] Part XXX of Arthropod Protective Substances. – Part XXIX. *H. Schildknecht* and *D. Hotz*, Angew. Chem. *79*, 902 (1967); Angew. Chem. internat. Edit. *6*, 881 (1967). – The investigations were made possible by support of the Deutsche Forschungsgemeinschaft. We thank Dr. *M. Molina*, Facultad de Quimica U.N.A.M., for leading the collecting expedition.

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[3] *K. Heller*, Z. Naturforsch. *14b*, 300 (1959).

Sulfur Dichloride (Chlorosulfonyl)imide and *N,N'*-Hydrazodisulfonyl Difluoride[1]

By *H. W. Roesky*[*]

Reaction of chlorosulfonamide *(1)* and thionyl chloride *(2)* affords sulfur dichloride (chlorosulfonyl)imide *(3)*.

$$\underset{(1)}{ClSO_2NH_2} + 2\ SOCl_2 \longrightarrow \underset{(3)}{ClSO_2\text{-}N{=}S(Cl)Cl} + 2\ HCl + SO_2$$
$$\qquad\qquad (2)$$

Compound *(3)* can also be obtained by boiling amidosulfuric acid *(4)* and *(2)* under reflux for 5 days, the yield being 35%.

$$\underset{(4)}{HOSO_2NH_2} + 3\ SOCl_2 \rightarrow (3) + 3\ HCl + 2\ SO_2$$

Experimental:

0.1 mole of *(1)* and 0.22 mole of *(2)* are heated (oil-bath temperature 100 °C) under reflux for 12 h. HCl and SO_2 are given off as gaseous products and a brown residue formed, which on fractional distillation affords compound *(3)* in 70% yield. Compound *(3)* is a yellow liquid, b.p. 72 °C/0.2 mm (65–66 °C/0.02 mm), which reacts with a little water to yield crystalline amidosulfuric acid as a precipitate. With an excess of anhydrous hydrogen fluoride at 80 °C the product *(3)* affords fluorosulfonamide *(5)*

$$\underset{(3)}{ClSO_2N{=}S(Cl)Cl} + 5\ HF \longrightarrow \underset{(5)}{FSO_2NH_2} + SF_4 + 3\ HCl$$

With sodium fluoride in TMSO, *(3)* reacts at 100–120 °C to give chlorosulfonyl fluoride and thiazyl fluoride, NSF.

The IR spectrum of compound *(3)* (capillary film) in the NaCl and KBr region shows bands at 1800 w, 1395 vs, 1170 vs, 1110 vs, 980 w, 678 vs, 585 vs, 548 s with shoulders at 523 w, and 440 vs cm^{-1} [2]. These are provisionally allotted to the following vibrations: ν_{as}(SO) 1395, ν_s(SO) 1170, ν(S=N) 1110, ν(SN) 678, ν(SCl) 585, 548, 440.

When a mixture of 1.0 mole of *(5)* and 1.0 mole of *(2)* is boiled under reflux, for 24 h, *N,N'*-hydrazodisulfonyl difluoride *(6)* is precipitated and can be separated by filtration from the sulfur oxide (fluorosulfonyl)imide, FSO_2NSO (24.5 g), and sulfur dichloride (fluorosulfonyl)imide, FSO_2NSCl_2, that are also formed. Compound *(6)* (yield as above, 11 g) is a yellow solid, m.p. 77 °C, that is soluble in methanol with decomposition. The ^{19}F–NMR spectrum measured at 100 °C contains a singlet at $\delta_F = -54.4$ ppm (CCl_3F as external standard). In the ^1H–NMR spectrum there is a sharp triplet (relative intensities 1:1:1) at $\delta_H = 6.18$ ppm, $J_{H-N} = 54$ Hz [$(CH_3)_4Si$ as external standard], probably caused by spin coupling of the nitrogen. The IR spectrum of *(6)* was measured in Kel-F oil at 4000–1350 and in Nujol at 1350–400 cm^{-1}: 3100 vs, 1400 vs, 1360 vs, 1175 vs, 1060 s, 840 s, 765 s, 740 s, 550 vs cm^{-1} [2].

$$(5) + SOCl_2 \longrightarrow \underset{(6)}{FSO_2\text{-}\overset{H}{N}\text{-}\overset{H}{N}\text{-}SO_2F}$$

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[1] Part VI of Sulfur-Nitrogen Compounds. – Part V: *H. W. Roesky*, Angew. Chem. *79*, 904 (1967); Angew. Chem. internat. Edit. *6*, 882 (1967).

[2] w = weak, s = strong, vs = very strong.

Preparation of *N*-(Trifluoromethyl)fluorosulfonamide and its Salts [1]

By *H. W. Roesky*[*]

N-(Dichloromethylene)chlorosulfonamide *(1)*, prepared by treatment of chlorosulfonyl isocyanate with phosphorus pentachloride[2], reacts with anhydrous hydrogen fluoride[3] to give *N*-(trifluoromethyl)fluorosulfonamide[4] *(2)*.

$$\underset{(1)}{ClSO_2N{=}C(Cl)Cl} + 4\ HF \longrightarrow \underset{(2)}{FSO_2\text{-}\overset{H}{N}\text{-}CF_3} + 3\ HCl$$

Experimental:

0.3 mole of *(1)* and 2.2 mole of HF are condensed in a 300-ml Monel cylinder. After thawing to room temperature, the cyclinder is warmed to 80 °C for 2 h; then it is cooled to 0 °C and most of the HCl formed is allowed to escape. The crude product is poured into a second cyclinder containing 2 moles of dry sodium fluoride and left overnight (absorption of the excess of hydrogen fluoride). The product *(2)* is obtained by pumping off and condensation in a high vacuum (methanol/solid carbon dioxide). For further purification, compound *(2)* is fractionally distilled through a 20-cm long column. Yield: 11 g (crude product 21 g); b.p. 100–101 °C.

Compound *(2)* is a water-clear liquid that can be distilled undecomposed in glass apparatus. It is very soluble in water and on titration with 0.1 N NaOH it takes up two equivalents of alkali. The fluorine atom on the sulfonyl group is hydrolyzed by dilute sodium hydroxide solution. With tetraphenylphosphonium and tetraphenylarsonium chloride it gives the salts

$[(C_6H_5)_4P]^{\oplus}[FSO_2NCF_3]^{\ominus}$, m.p. 192 °C and
$(C_6H_5)_4As]^{\oplus}[FSO_2NCF_3]^{\ominus}$, m.p. 190 °C (dec.),

which are precipitated as white solids.

The IR spectrum of compound *(2)* (capillary film) in the NaCl and KBr region shows bands at 3130 s, 1460 vs, 1410 vs, 1265 vs, 1205 vs, 1170 vs, 990 m (?), 860 m, 810 vs, 712 w, 606 vs, 537 m, 425 m cm^{-1} [5] [*(2)* decomposes KBr disks]. These are provisionally assigned to the following vibrations: 3130 ν (NH), 1460 or 1410 ν_{as} (SO) (in the IR spectra of the salts the two bands appear shifted to lower wavelengths, at 1350 and 1322 cm^{-1}), 1265 ν_s (SO), 1205 ν_{as} (CF), 1170 ν_s (CF), 810 ν (SF), 606 ν (SN).

The ^{19}F–NMR spectrum contains for the CF_3 group two doublets at $\delta_F = 58.0$ ppm (CCl_3F as external standard) with coupling constants $J_{F-SF} = 6$ Hz and $J_{F-H} = 3$ Hz. The FSO_2 group gives rise to two quartets at $\delta_{SF} = -55.4$ ppm with coupling constants $J_{SF-H} = 4$ Hz and $J_{F-SF} = 6$ Hz. The doublet:quartet intensity ratio 3:1. The ^1H–NMR spectrum contains a broad signal at $\delta_H = 7.45$ ppm [$Si(CH_3)_4$ as external standard]. The NMR data accord with structure *(2)*. According to the IR and NMR spectra the isomeric form $F-OS(OH)=NCF_3$ is unlikely.

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[1] Part VIII of Sulfur-Nitrogen Compounds. Part VII: *H. W. Roesky, O. Glemser,* and *A. Hoff*, Chem. Ber., in press.

[2] *H. W. Roesky* and *U. Biermann*, Angew. Chem. *79*, 904 (1967); Angew. Chem. internat. Edit. *6*, 882 (1967).

[3] We thank Farbenfabriken Bayer for a supply of hydrogen fluoride.

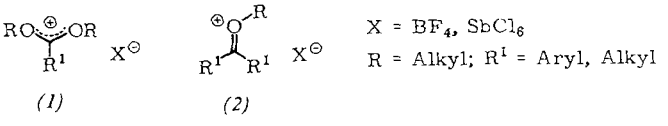
[4] Cf. *E. Kühle, B. Anders,* and *G. Zumach*, Angew. Chem. *79*, 663 (1967); Angew. Chem. internat. Edit. *6*, 649 (1967).

[5] m = medium, s = strong, vs = very strong.

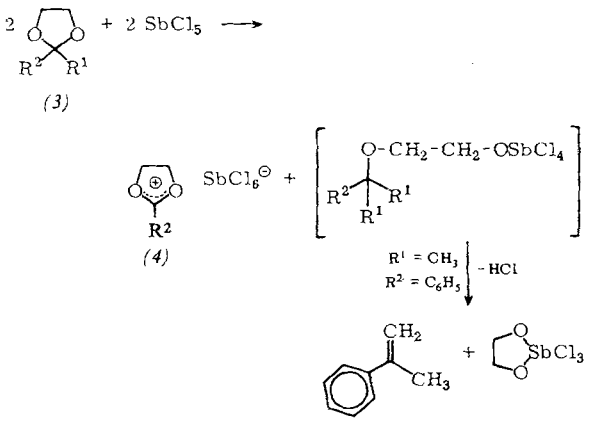
Formation of Dialkoxycarbonium Ions from Ketals by Removal of Alkyl Groups by means of Carbonium Ions [1]

By *S. Kabuss* [*]

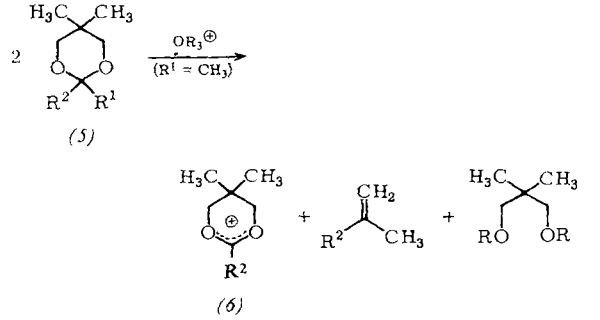
Whereas dialkoxycarbonium salts *(1)* are, in general, obtained in good yield from orthocarboxylic esters by the action of Lewis acids [2], monoalkoxycarbonium salts *(2)* are only exceptionally accessible by the analogous reaction of ketals with Lewis acids [2b].



(1) *(2)*



(3) *(4)*



(5)

(6)

Ketal *(3)* R²	Ketal *(3)* R¹	Reagent	Yield of *(4)* (%)
CH_3	CH_3	BF_3/OR_2	20
CH_3	CH_3	$SbCl_5$	15
CH_3	CH_3	$O(C_2H_5)_3^+BF_4^-$	33
CH_3	C_2H_5	$O(C_2H_5)_3^+BF_4^-$	24 [a]
CH_3	n-C_5H_{11}	$O(C_2H_5)_3^+BF_4^-$	19 [a]
C_6H_5	CH_3	BF_3/OR_2	41
C_6H_5	CH_3	$SbCl_5$	*ca.* 30
C_6H_5	CH_3	$O(C_2H_5)_3^+BF_4^-$	42
C_6H_5	CH_3	$HC(OC_2H_5)_2^+SbCl_6^-$	49
C_6H_5	CH_3	$C_6H_5-C(OC_2H_5)CH_3^+SbCl_6^-$	52
C_6H_5	CH_3	p-$CH_3-C_6H_4-C(OC_2H_5)CH_3^+SbCl_6^-$	38 [b]
C_6H_5	C_2H_5	$O(C_2H_5)_3^+BF_4^-$	24
C_6H_5	i-C_3H_7	$O(C_2H_5)_3^+BF_4^-$	< 5
p-$CH_3-C_6H_4$	CH_3	$C_6H_5-C(OC_2H_5)CH_3^+SbCl_6^-$	10 [c]

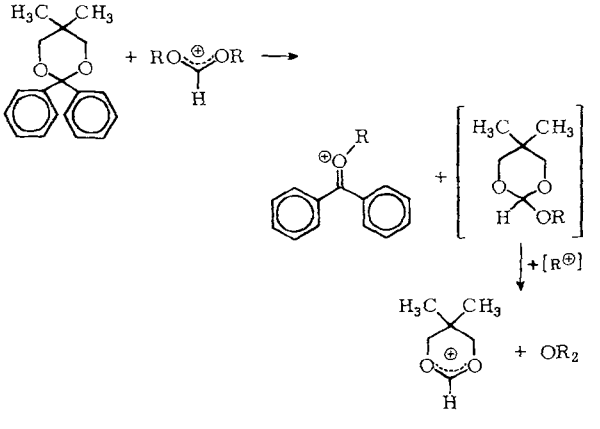
Ketal *(5)* R²	Ketal *(5)* R¹	Reagent	Yield of *(6)* (%)
CH_3	CH_3	$HC(OC_2H_5)_2^+SbCl_6^-$	29
C_6H_5	CH_3	$O(C_2H_5)_3^+SbCl_6^-$	47
C_6H_5	CH_3	$C_6H_5CH_2Br/AgBF_4$	35

[a] Only traces of 2-ethyl- or 2-*n*-pentyldioxolanylium salts could be detected by NMR spectroscopy.

[b] As well as 25% of the *p*-tolyl derivative (analysis by NMR spectroscopy).

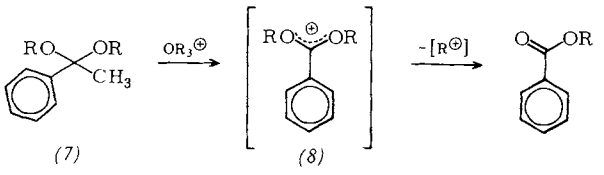
[c] As well as 45% of the phenyl derivative (analysis by NMR spectroscopy).

We have observed that ketals disproportionate under the influence of Lewis acids ($SbCl_5$ or BF_3) in CH_2Cl_2 or SO_2 even below room temperature, with intermolecular alkyl migration that leads to dialkoxycarbonium ions, *i.e.* carboxylic acid derivatives, and ethers of tertiary alcohols. Under the reaction conditions these ethers are converted into olefins, which are obtained as dimers or oligomers. When cyclic ketals, *e.g. (3)* or *(5)*, are used, the dialkoxycarbonium salts, *e.g. (4)* or *(6)*, are isolated in crystalline form. The disproportionation is also caused by the action of strong alkylating agents such as trialkyloxonium or dialkoxycarbonium salts [3] or alkyl halide-$AgBF_4$ mixtures [4] on ketals.



The yield of dialkoxycarbonium salt depends on the structure of the ketal. Reaction is particularly smooth with ketals of acetophenone, from which exclusively the methyl group is transferred. Yields are lower with the homologs containing larger alkyl groups. Removal of a secondary alkyl group, *e.g.* from 2-isopropyl-2-phenyldioxolane, can be effected only to a limited extent. Ketals of dialkyl ketones all give cyclic 2-alkyldialkoxycarbonium salts in only moderate yield. With ketals of unsymmetrical di-*n*-alkyl ketones the larger alkyl group is transferred preferentially. Benzophenone ketals are cleaved by alkylating agents into ketonic and alcoholic components [5], which can both react further with the alkylating agent.

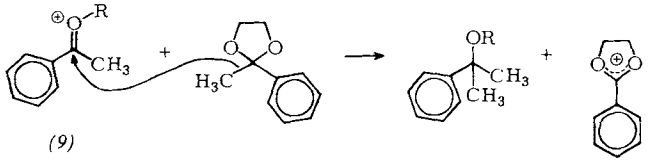
Open-chain ketals, *e.g. (7)*, also undergo disproportionation on reaction with trialkyloxonium salts; crystalline dialkoxy-



(7) (8)

carbonium salts such as *(8)* have not, however, yet been isolated since they react further as strong alkylating agents with ketals and ethers[3]; 20–30% yields of the dealkylation products are isolated, *i.e.* the carboxylic esters.

Ketonium salts, such as *(9a)* or *(9b)*, although not isolated, may be intermediates in the disproportionation of the ketals; they would react further with the excess of ketal undergoing alkyl fission[6].



(9) *(4)*

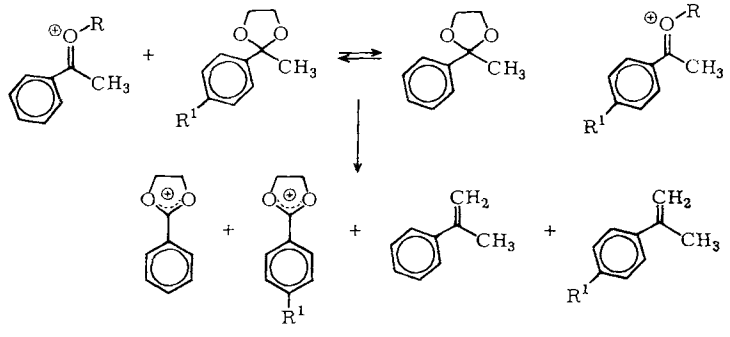
(a) R = $-CH_2-CH_2-OSbCl_5^{\ominus}$

(b) R = $-CH_2-CH_2-OC_2H_5$

(c) R = Alkyl

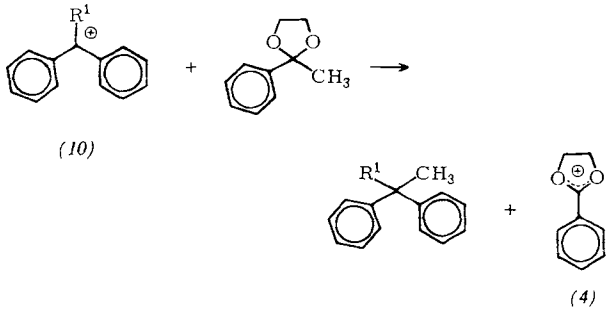
Dialkoxycarbonium salts may be obtained from ketals analogously by use of *O*-alkylketonium salts *(9c)*, which are obtainable in pure crystalline form by alkylation of ketones with dialkoxycarbonium salts[3].

The removal of the alkyl group can be regarded formally as a new type of electrophilic substitution on a saturated C atom, wherein carbonium ions constitute both the attacking and the leaving group. The weaker electrophile *(4)* is replaced by the stronger *(9)* with fission of a C–C bond.



If the ketonium salt and the ketal are derived from two different ketones, then generally both the starting materials yield a dialkoxycarbonium salt as well as an olefin. Alongside alkyl-transfer occur a series of alkoxy-transfers[7] leading to rapid exchange of functional groups[8].

Other stable carbonium ions, react like the alkoxycarbonium ions *(9)*, *e.g.* diphenylcarbonium ions *(10)* described by *Volz* and his co-workers[9] react with ketals with loss of alkyl[10].



(10) *(4)*

Alkyl fission, however, has not yet been achieved with triphenylcarbonium salts.

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[1] Read in part at the Westdeutsche Chemiedozenten-Tagung in Saarbrücken on April 11–14th, 1967.

[2] [a] *H. Meerwein, K. Bodenbenner, P. Borner, F. Kunert*, and *K. Wunderlich*, Liebigs Ann. Chem. *632*, 38 (1960); [b] *H. Meerwein* in *Houben-Weyl*: Methoden der organischen Chemie. Thieme-Verlag, Stuttgart 1965, Vol. VI/3, p. 329.

[3] *S. Kabuss*, Angew. Chem. *78*, 714 (1966); Angew. Chem. internat. Edit. *5*, 675 (1966).

[4] *H. Meerwein, V. Hederich*, and *K. Wunderlich*, Arch. Pharm. *291/63*, 541 (1958).

[5] Fission into ketonic and alcoholic components occurs also as competitor during the disproportionation. It is to be considered as dealkylation of the ketonium salt.

[6] *Meerwein et al.* [4,7] described the reaction of acetals, occuring with hydride transfer, that is analogous to disproportionation of ketones. These authors assume a direct transfer of the hydride to the alkyl group of the alkylating agent; however, it can be shown that this reaction is also a disproportionation, since in the reaction of 2-phenyldioxolane with triethyloxonium salt, apart from dioxolanylium salt *(4)*, derivatives of benzyl alcohol are formed. The reaction proceeds *via* alkoxycarbonium (aldehydium salts), which react with excess acetal with hydride removal.

[7] *H. Meerwein, V. Hederich, H. Morschel*, and *K. Wunderlich*, Liebigs Ann. Chem. *635*, 1 (1960).

[8] Such alkoxy-transfer occurs even at −40 °C, as may be shown by NMR spectroscopy. Alkyl fission is immeasurably slow at that temperature.

[9] *H. Volz*, Angew. Chem. *75*, 921 (1963); Angew. Chem. internat. Edit. *2*, 622 (1963); *H. Volz* and *W. D. Mayer*, Tetrahedron Letters *1966*, 5249.

[10] For information on the removal of alkyl groups by alkylcarbonium ions see *G. A. Olah* and *J. Lukas*, J. Amer. chem. Soc. *89*, 4739 (1967).

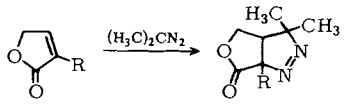
Synthesis of *gem*-Dimethylcyclopropanes by means of 2-Diazopropane

By *M. Franck-Neumann*[*]

Corey and *Jautelat*[1] recently reported the introduction of *gem*-dimethylcyclopropane units be means of diphenylsulfonium isopropylide. The action of 2-diazopropane[2] on electrophilic C=C double bonds is a further method for introduction of this group and we have studied its possibilities[3].

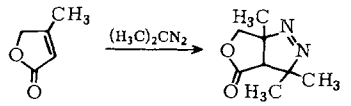
The butenolides[4] *(1a)* and *(1b)* react with 2-diazopropane at room temperature, yielding the expected[5] adducts *(2a)* (yield 90%; m.p. 74 °C, decomp.) and *(2b)* (yield 60%; m.p. 87 °C, decomp.). The diazo compound adds in the reverse direction to *(1c)*, yielding *(2c)* (yield 27%; m.p. 78 °C). The rate of reaction decreases rapidly on passing from *(1a)* to *(1c)*.

In their IR spectra the pyrazolines *(2a)* to *(2c)* show bands at 1775 cm^{-1} (γ-lactone) and 1555 cm^{-1} (azo group), and in the UV region they absorb at 322 nm (ε = 263), 327 nm (ε = 197), and 323 nm (ε = 190), respectively (in chloroform).



(1) *(2)*

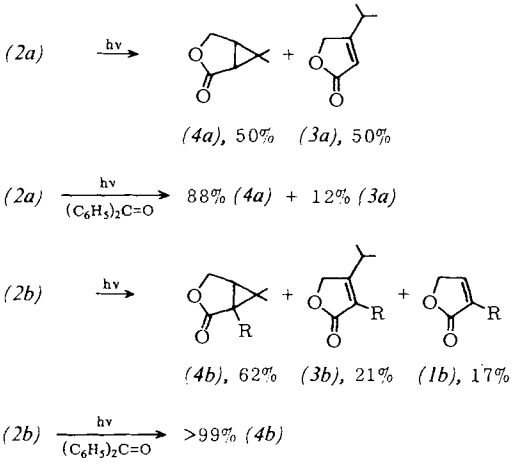
(a), R = H
(b), R = CH_3



(1c) *(2c)*

The NMR spectra (Table 1) are in agreement with the structures assigned.

In contrast to the relatively high thermal stability of the pyrazoline *(2c)*, compounds *(2a)* and *(2b)* decompose slowly from 70 °C upwards. Decomposition of *(2a)* in boiling benzene gives exclusively the 2-isopropylbutenolide *(3a)*, whereas a mixture of 80% of the butenolide *(3b)* with 20% of the cyclopropane derivative *(4b)* arises from *(2b)*. The yields of cyclopropane derivatives are higher on photolysis in benzene[6]. In this reaction *(4a)* and *(3a)* are obtained in a 1:1 ratio from *(2a)*, and a mixture of *(4b)* 62%, *(3b)* 21%, and *(1b)* 17% is formed from *(2b)*. Formation of *(1b)* is formally a 1,3-dipolar retrocycloaddition[7].



(4a), 50% *(3a)*, 50%

(2a) $\xrightarrow[(C_6H_5)_2C=O]{h\nu}$ 88% *(4a)* + 12% *(3a)*

(4b), 62% *(3b)*, 21% *(1b)*, 17%

(2b) $\xrightarrow[(C_6H_5)_2C=O]{h\nu}$ >99% *(4b)*

Table 1. NMR spectra of compounds *(2)*–*(4)* ($CDCl_3$, tetramethylsilane as internal standard, δ values in ppm). Unmodified signals are singlets; numerals in parentheses indicate the multiplicity.

	Methyl groups		Vinyl H	Intensity ratios
(2a)	1.40 1.51	2.76 (6) 4.30 (ABX) 5.67 (2)		3:3:1:2:1
(2b)	1.44 1.79	2.33 (4) 4.32 (ABX)		6:3:1:2
(2c)	1.47 1.57 1.62	2.40 4.41 (AB)		3:3:3:1:2
(3a)	1.22 [a] (2)	2.76 [a] (7) 4.87 (2)	5.84 (4)	6:1:2:1
(3b)	1.18 [a] (2) 1.83 (3)	2.99 [a] (7) 4.70 (4)		6:3:1:2
(4a)	1.17	1.80–2.25 4.00–4.55		3:1:1
(4b)	1.12 1.18 1.39	1.70 (2) 4.20 (ABX)		3:3:3:1:2

[a] J = 7 Hz.

We have now found that the proportion of cyclopropane to olefin is increased if the photolysis is sensitized by benzophenone. Also removal of nitrogen is about ten times faster than in absence of the sensitizer.

All the thermal and photochemical removals of nitrogen afford quantitative crude yields. The compositions assigned to the mixtures were determined by gas chromatography (polypropylene glycol column 190 °C). The structures of the products that were separated by preparative gas chromatography were supported by the following spectroscopic data:

(3a) shows, in its IR spectrum, the double band at 1750 and 1780 cm^{-1} characteritic of butenolides[8] and absorption by the double bond at 1635 cm^{-1}; *(3b)* absorbs at 1770 and 1680 cm^{-1}; *(4a)* and *(4b)* show only the strong bands at 1775 cm^{-1}; the protons in the three-membered ring give rise to a weak band at 3010 cm^{-1}. UV spectra in methanol: *(3a)*, λ_{max} = 209 nm (ε = 15600); *(3b)*, λ_{max} = 214 nm (ε = 15400); *(4a)*, λ_{max} = 207 nm (ε = 2800); *(4b)*, only end absorption.

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[1] *E. J. Corey* and *M. Jautelat*, J. Amer. chem. Soc. *89*, 3912 (1967).

[2] *H. Staudinger* and *A. Gaule*, Ber. dtsch. chem. Ges. *49*, 1897 (1916).

[3] This method has occasionally been used in the past, without isolation of the intermediate pyrazolines and without indication of its general possibilities: *P. C. Guha* and *D. K. Sankaran*, Ber. dtsch. chem. Ges. *70*, 1688 (1937); *S. Takei*, *T. Sugita*, and *Y. Inouye*, Liebigs Ann. Chem. *618*, 108 (1958); *H. M. Walborsky*, *T. Sugita*, *M. Ohno*, and *Y. Inouye*, J. Amer. chem. Soc. *82*, 5255 (1960).

[4] These known butenolides were prepared by a new, shorter synthesis: *M. Franck-Neumann* and *C. Berger*, Bull. Soc. chim. France, in press.

[5] *R. Huisgen*, *H. Stangl*, *H. J. Sturm*, and *H. Wagenhofer*, Angew. Chem. *73*, 170 (1961).

[6] 1% solutions were irradiated in a Pyrex glass apparatus with a mercury high-pressure lamp.

[7] Cf. *T. B. Van Auken* and *K. L. Rinehart Jr.*, J. Amer. chem. Soc. *84*, 3736 (1962).

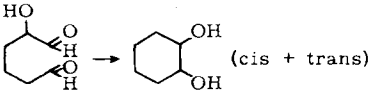
[8] *Y. Shyamsunder Rao*, Chem. Reviews *64*, 369 (1964).

1,6-C–C Linkage on Pressure-hydrogenation of α-Hydroxyadipaldehyde

By *H. Feichtinger* and *H. Noeske*[*]

Pressure-hydrogenation of aqueous solutions of α-hydroxyadipaldehyde *(1)* over Raney nickel at 85 °C and 100 atm gives 1,2,6-hexanetriol in 84% yield[1]. Almost quantitative yields can be obtained by using a continuous process[2] with a Ni–MgO solid-bed catalyst.

However, if a 20% aqueous solution of *(1)* is hydrogenated batchwise in an autoclave with magnetic stirring and in the presence of Ni–MgO catalyst[3] for 1.5 h at 105 °C and then for 4 h at 145 °C with a hydrogen pressure of 110 atm, subsequent filtration, evaporation, and distillation of the residue afford a fraction (some 20% of the total amount of product) that passes over at 76–86 °C/0.7 torr and solidifies in the receiver (softening point about 50 °C). After recrystallization from ether/petroleum ether, the above fraction melts at 63–77 °C. It was found to be a mixture of *cis*- and *trans*-1,2-



(1)

cyclohexanediol. In the hydrogenation of *(1)* under pressure the α-hydroxyl group had thus been eliminated and a ring had been formed by 1,6-C–C linkage.

The composition of the mixture was ascertained by oxidation with alkaline permanganate solution and detection of adipic acid by paper chromatography. The isomers were separated by way of the benzylidene derivative[4] of the *cis*-compound and were compared by IR spectroscopy with the same compounds obtained from pyrocatechol by hydrogenation over the same Ni–MgO catalyst. Finally the phenylurethane derivatives[5] of both isomers were prepared by means of phenyl isocyanate; they agreed in melting points and IR spectra with data recorded in the literature and found for the derivatives obtained by hydrogenation of pyrocatechol.

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[1] *H. Schulz* and *H. Wagner*, Angew. Chem. *62*, 117 (1950).

[2] *H.-W. Linden* and *H. Feichtinger*, German Pat. 1176117, Ruhrchemie AG; Chem. Zbl. *1965*, 5364.

[3] *H. Heckel*, *O. Roelen*, *W. Rottig*, and *K. Schenk*, German Pat. 897547, Ruhrchemie AG; Chem. Zbl. *1954*, 9434; Commercially available as Catalyst 55/5.

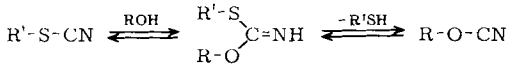
[4] *N. A. B. Wilson* and *J. Read*, J. chem. Soc. (London) *1935*, 1269.

[5] *R. Cornubert*, *A. Rio*, and *P. Sénéchal*, Bull. Soc. chim. France, Mém. *1955*, 46.

Cyanic Esters from Thiocyanates

By *W.-D. Habicher* and *R. Mayer* [*]

Iminothiocarbonates *(2)*, which are readily accessible from alcohols and thiocyanates *(1)* [1], can, as we have found, be converted into cyanic esters *(3)* [2] in good yield, with loss of a thiol, preferably in presence of a thiol-trapping agent.



(1) *(2)* *(3)*

R′ may be aliphatic, cycloaliphatic, arylaliphatic, or aromatic. Aliphatic and arylaliphatic groups are particularly suitable for use as R groups.

Examples: From ethyl thiocyanate *(1)*, R′ = C_2H_5, were obtained 76% yields of *n*-butyl *(3)*, R = *n*-C_4H_9, n_D^{25} = 1.4009, and 84% yields of *n*-pentyl *(3)*, R = *n*-C_5H_{11}, n_D^{25} = 1.4101, and isopentyl *(3)*, R = *iso*-C_5H_{11}, n_D^{25} = 1.4089.

General Procedure:

An iminothiocarbonate *(2)* (0.1 mole) is vigorously stirred in ether for 2–3 h at 0 °C in presence of a thiol-trapping agent (*e.g.* a mixture of 27 g of HgO and 20 g of anhydrous $MgSO_4$). Then the mixture is filtered, the solvent removed at 0 °C in a vacuum, and the residue distilled in a vacuum at a bath temperature not exceeding 30 °C. The cyanic esters *(3)* are condensed in a cold trap.

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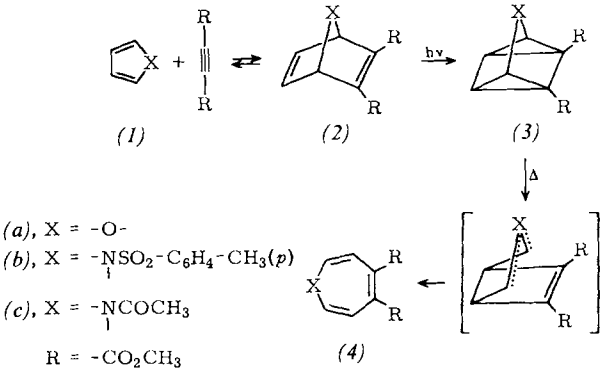
[1] *R. Mayer* and *W.-D. Habicher*, unpublished; *A. Knorr*, Ber. dtsch. chem. Ges. *49*, 1735 (1916).

[2] *E. Grigat* and *R. Pütter*, Angew. Chem. *79*, 219 (1967); Angew. Chem. internat. Edit. *6*, 206 (1967); *D. Martin*, Z. Chem. *7*, 123 (1967).

Synthesis and Pyrolysis of 3-Azaquadricyclane Derivatives. — A New Azepine Synthesis [1]

By *H. Prinzbach*, *R. Fuchs*, and *R. Kitzing* [*]

The oxepine synthesis that starts from furan and acetylene derivatives and consists of the Diels-Alder addition *(1a)* → *(2a)*, photochemical valence isomerization *(2a)* → *(3a)*, and the pyrolysis *(3a)* → *(4a)* has repeatedly proved its value [2]. We have prepared, by an analogous route, the first derivatives [*(3b)* and *(3c)*] of the thermally labile 3-azaquadricyclane system, and thence the azepines *(4b)* and *(4c)*.



(1) *(2)* *(3)*

(a), X = -O-
(b), X = -NSO$_2$-C$_6$H$_4$-CH$_3$(*p*)
(c), X = -NCOCH$_3$
R = -CO$_2$CH$_3$

(4)

(2b): M.p. 146 °C.
UV (CH_3CN): 288 nm (sh), ε = 1150 [a]; 227 nm, ε = 15900.
NMR ($CDCl_3$): τ (TMS = 10): 2.41 (2, D), *J* = 8.0 Hz; 2.74 (2, D); 2.96 (2, T), *J* = 1.5 Hz; 4.58 (2, T), *J* = 1.5 Hz; 6.28 (6, S); 7.59 (3, S).

(3b): M.p. 97 °C (isomerization).
UV (CH_3CN): 230 nm, ε = 11450 [a].
NMR ($CDCl_3$): τ (TMS = 10): 2.40 (2, D), *J* = 8.0 Hz; 2.75 (2, D), *J* = 8.0 Hz; 5.75 (2, D), *J* = 4.5 Hz; 6.45 (6 S); 7.30 (2, D), *J* = 4.5 Hz; 7.55 (3, S).

(4b): M.p. 111 °C.
UV (CH_3CN): 350 nm, ε = 810 [a]; 214 nm, ε = 23400.
NMR ($CDCl_3$): τ (TMS = 10): 2.17 (2, D), *J* = 8.0 Hz; 2.60 (2, D), *J* = 8.0 Hz; 4.00 (2, D), *J* = 7.5 Hz; 4.15 (2, D), *J* = 7.5 Hz; 6.22 (6, S); 7.55 (3 S).

(2c): B.p. 125–130 °C/10^{-3} torr; molecular ion at *m/e* = 251 [9].
UV (C_2H_5OH): 290 nm, ε = 1240.
NMR ($CDCl_3$) [b]: τ (TMS = 10): 2.77 (2, M); 4.21 (1, M), 4.36 (1, M); 6.19 (6, S); 8.07 (3, S).

(3c): M.p. 81 °C (isomerization).
UV (CH_3CN): 219 nm, ε = 12100.
NMR ($CDCl_3$) [b]: τ (TMS = 10): 5.39 (2, D), *J* = 4.5 Hz; 6.28 (6, S); 7.10 (2, S), *J* = 4.5 Hz; 7.70 (3, S).

(4c): Molecular ion at *m/e* = 251.
UV (CH_3CN): 355 nm, ε = 780; 226 nm, ε = 19700.
NMR ($CDCl_3$) [b]: τ (TMS = 10): 3.2–3.8 (br. M); 3.93 (2, D), *J* = 8.5 Hz; 6.10 (6, S); 7.79 (3, S).

[a] The weak maxima of the toluenesulfonyl group are not listed.

[b] Measured at *ca.* 36 °C. The spectrum shows the temperature-dependence expected from hindered rotation around the C–N bond.

Pyrrole derivatives containing a strong electron acceptor as *N*-substituent [*(1b)* and *(1c)*] react with dimethyl acetylenedicarboxylate, to afford the 7-azanorbornadienes *(2b)* and *(2c)* in 30–40% yield [3]. As in the UV spectra of 7-oxa and 7-methylene analogs [4], in the region 280–290 nm, maxima or shoulders are found, more or less pronounced according to the polarity of the medium, that may arise from interaction between the homoconjugated C=C double bonds.

Direct excitation of the electron transitions responsible for these absorptions by light of wavelength > 290 nm induces almost quantitative conversion of *(2)* into the tetracyclic amides *(3b)* and *(3c)*. These amides can be isolated in pure crystalline form and then characterized; isomerization to the azepines *(4b)* and *(4c)* occurs in solution at 20 °C at measurable rates [$t_{1/2}$ (40 °C, $CDCl_3$) *ca.* 30 min for *(3c)*, *ca.* 120 min for *(3b)*]. As in the case of the ether *(3a)*, the thermal "forbidden" [5] reversal *(3)* → *(2)* of the photo process cannot be detected (NMR). Further, the azepines *(4b)* and *(4c)* containing methoxycarbonyl substituents dimerize [6] in solution slowly even at 20 °C, *(4c)* faster than *(4b)*.

We have carried out numerous reactions, including cycloadditions and acid-catalyzed rearrangements [7], with the azaquadricyclane [*(3b)*, *(3c)*] and azepine derivatives [*(4b)*, *(4c)*]; these reactions, when considered together with the spectroscopic data, leave no doubt as to the correctness of the structures assigned [8].

Experimental:

An O_2-free ethereal solution of *(2b)* (500 mg) in anhydrous ether (200 ml) is irradiated at −30 to −40 °C (Pyrex filter, Philipps-HPK-125 lamp or Hanau-TQ-81 high-pressure lamp). The product *(3b)* is allowed to crystallize out slowly or is isolated (yield > 90%) after the solvent has been distilled off; *(4b)* is obtained pure (yield *ca.* 50%) when *(3b)* is heated for a short time in benzene (80 °C), and the whole is chromatographed on silica gel (benzene/CH_2Cl_2). The same conditions are used for *(4c)* except that pyrolysis is carried out in boiling ether.

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[1] Part XIV of the series "Photochemistry of Cyclohexadienes". – Part XIII: *H. Prinzbach, M. Argüelles, P. Vogel,* and *W. Eberbach*, Angew. Chem. *79*, 1103 (1967); Angew. Chem. internat. Edit. *6*, 1070 (1967).

[2] *H. Prinzbach, M. Argüelles,* and *E. Druckrey*, Angew. Chem. *78*, 1057 (1966); Angew. Chem. internat. Edit. *5*, 1039 (1966); *H. Prinzbach, P. Vogel,* and *W. Auge*, Chimia *21*, 469 (1967).

[3] *R. M. Acheson*, Adv. heterocyclic Chem. *1*, 133 (1963).

[4] *H. Prinzbach* and *J. Rivier*, Tetrahedron Letters *1967*, 3713.

[5] *R. B. Woodward* and *R. Hoffmann*, J. Amer. chem. Soc. *87*, 395 (1965).

[6] *G. Maier*, Angew. Chem. *79*, 446 (1967); Angew. Chem. internat. Edit. *6*, 402 (1967); *A. L. Johnson* and *H. E. Simmons*, J. Amer. chem. Soc. *89*, 3191 (1967).

[7] *W. Eberbach* and *H. Prinzbach*, Chimia *21*, 588 (1967); *H. Prinzbach, R. Fuchs,* and *R. Kitzing*, unpublished.

[8] Elemental analyses are available for all the products.

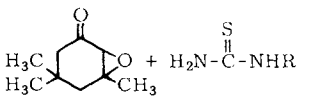
[9] We thank Dr. *B. Willhalm*, Firmenich & Co, Geneva, for the mass-spectrometric measurements.

2,4,5,6-Tetrahydro-5,5,7-trimethylbenzimidazole-2-thiones, a New Group of Benzimidazole Derivatives [1]

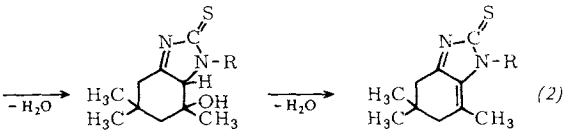
By *H.-D. Dell* [*]

In connection with investigations of dihydroisophorone we have attempted to convert the related epoxide *(1)* into the episulfide. Conversion of epoxy compounds into their S analogs can be effected with thiourea [2], such reactions being known also for cyclohexene epoxides [3].

However, warming equimolar amounts of *(1)* and thiourea in methanol (2 h, 70 °C) gives 2,4,5,6-tetrahydro-5,5,7-trimethylbenzimidazole-2-thione *(2)*, R = H, needles (from methanol), m.p. 189–190 °C (yield 70%).



(1)



(2)

Monosubstituted thioureas also undergo this reaction; *e.g.* *N*-phenylthiourea gives *(2)*, R = C_6H_5, crystals, m.p. 125 to 127 °C (from ethyl acetate); *N*-(1-naphthyl)thiourea gives *(2)*, R = 1-naphthyl, m.p. 178–180 °C. Use of thiosemicarbazide leads to an amino derivative *(2)*, R = NH_2, needles (from ethyl acetate), m.p. 163–164 °C. Reaction with dicyanodiamide or urea does not, however, afford the corresponding 2-imino or 2-oxo derivative.

The weakly acidic H atom of the NH group of *(2)*, R = H, can be replaced by Na when the compound is warmed with $NaNH_2$ in an inert solvent. The structure assigned accords with the IR spectrum and the chemical behavior. Compounds of this new type may be of interest as antimetabolites.

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[1] Part 5 of "Methyl-substituted Cyclohexane Derivatives". – Part 4: *K.-H. Boltze* and *H.-D. Dell*, Arzneimittelforsch., in press.

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Binding of the Substrate in Yeast Pyruvate Decarboxylase [1]

By *A. Schellenberger* and *G. Hübner* [*]

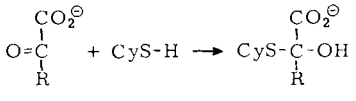
In order to study the function of the SH groups in yeast pyruvate decarboxylase (PDC; 2-keto acid carboxylase, 4.1.1.1), we have caused *N*-(*N*-acetyl-*p*-sulfamoylphenyl)-maleimide (ASPM) [2] to act on PDC or apo-PDC under the conditions set out in the Table. Inactivation of the enzyme in the presence of a large excess of the SH reagent is a first-order reaction in both cases.

Table 1. Half-reaction times for inactivation of apo-PDC and PDC by ASPM. Buffer: 0.1 M maleate, pH 6.6. Concentrations: ASPM 1.43×10^{-2} M; pyruvate 3.43×10^{-2} M; thiamine pyrophosphate (TPP) 3.57×10^{-3} M; Mg^{2+} 10^{-2} M.

Reactants	Half-reaction time (min)
Apo-PDC	2.5
Apo-PDC + TPP	2.5
Apo-PDC + Mg^{2+}	3.0
Apo-PDC + pyruvate	3.0
PDC	15
PDC + pyruvate	> 120

That the enzyme is protected by its substrate from attack by SH reagents was already known [3]. The results recorded in the Table show that the substrate is bound to an SH group of the enzyme before reaction with the coenzyme (TPP).

It might, however, also be the case that the SH groups involved in the enzyme action are protected by binding of the substrate to some other group in the active center before reaction with the relatively large ASPM molecule. We have therefore studied, as a model reaction, the reaction of pyruvate *(1)*, R = CH_3, and of trimethylpyruvate *(1)*, R = $C(CH_3)_3$, with cysteine, using spectroscopy in the region of the $n \rightarrow \pi^*$-transition at pH 7.4; we found that the extinction of a pyruvate solution at 314 nm is reversibly decreased by cysteine, but not that of other amino acids (glycine, alanine, serine). This result indicates formation of a hemiacetal *(2)* between pyruvate and cysteine.



(1) *(2)*

Stuart models show that for steric reasons trimethylpyruvate cannot form a hemiacetal. This explains why trimethylpyruvate is not decarboxylated by PDC and also why it does not act as a competitive inhibitor of the PDC reaction[4].

Apo–PDC reacts appreciably faster than holo-PDC with ASPM, neither the coenzyme nor Mg^{2+} ions protecting the apoenzyme from reaction with the SH reagent. We conclude from this, in agreement with earlier ideas derived from kinetic measurements[5], that the sites of binding for TPP and Mg^{2+} in the apoenzyme are at first free and relatively far removed from the site of binding of the substrate. Only on recombination to give the holoenzyme does a structural rearrangement of the protein components occur that draws the cysteine into the active center.

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[1] Part VII of Theory of Thiamine Pyrophosphate Activity. – Part VI: *A. Schellenberger, I. Heinroth*, and *G. Hübner*, Hoppe-Seylers Z. physiol. Chem. *348*, 506 (1967).

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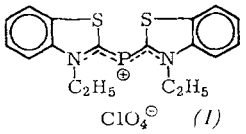
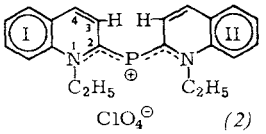
Crystal Structure of Bis-(1-ethyl-2-quinolyl)-phosphamethinecyanine Perchlorate

By *I. Kawada* and *R. Allmann*[*]

Some time ago the structure of 1-ethyl-2-[(1-ethylbenzothiazolin-2-ylidene)phosphino]benzothiazolium perchlorate *(1)* was determined[1], whereupon participation of the doubly bonded phosphorus in the π-electron system of the cyanine was established. On replacement of the benzothiazole by quinoline, steric causes (too close approach of the H atoms on C-3) should prevent formation of a planar cyanine cation *(2)*. This has in fact been confirmed by a structural study of 1-ethyl-2-[(1-ethyl-1,2-dihydroquinolin-2-ylidene)phosphino]-quinolium perchlorate *(2)*[2].



$ClO_4^{\ominus}$ *(1)*



$ClO_4^{\ominus}$ *(2)*

As the Figure shows, the two quinoline planes I and II are rotated by 40° and 24°, respectively, around the C–P bonds and out of the cyanine plane. The normals to planes I and II enclose an angle of 60°. Therefore resonance in the cyanine cation is hindered, which results in a noticeable lengthening of the C–P bonds: 1.81 and 1.77 Å as compared with 1.76 in *(1)* (but C–P = 1.83 Å in triphenylphosphine).

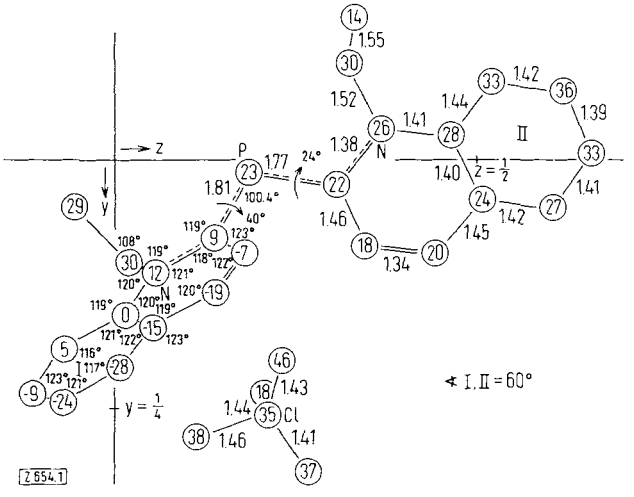


Fig. 1. *y,z*-Projection of a perchlorate anion and a phosphacyanine cation *(2)* with mean distances (Å) and bond angles. *x*-Coordinates in *a*/100 are given in the circles.

The slight asymmetry of *(2)* in the crystal indicates partial shift of the positive charge to side I of the cyanine cation. This is shown, not merely by the differences in the torsion angles and in the C–P bond lengths, but also in the shorter distance of the half-molecule I from the perchlorate anion; the only intermolecular atomic separations less than 3.4 Å are $N_I \cdots O$ 3.20 Å and $C\text{-}2_I \cdots O$ 3.26 Å.

In other respects the halves I and II are identical within the calculated standard deviations (σ = 0.01–0.02 Å for distances and 1–2° for angles). Therefore the distances and angles given in the Figure are the means of those determined for the two half-molecules. Attention is directed to the almost isolated double bond [(C-3) = (C-4) = 1.34 Å].

Crystallographic parameters for *(2)* are:

$a = 7.997 \pm 13$ Å	Space group $P2_1/c$
$b = 19.546 \pm 21$ Å	D_m (pycn.) = 1.36 ± 1 g cm^{-3}
$c = 14.157 \pm 28$ Å	$D_x = 1.34$ g cm^{-3}
$\beta = 93.67 \pm 0.16°$	$Z = 4$

The structure determination for *(2)* is based on 2560 independent reflections (of which 374 were unobservable) and was carried out in the same way as that of *(1)*. With isotropic individual temperature factors, the reliability factor between observed and calculated structure factors (excluding H atoms) was reduced to $R = 16.3\ \%$.

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Iron Derivatives of Five-membered Carbon-Nitrogen Heterocycles

By *F. Seel* and *V. Sperber*[*]

Dedicated to Professor B. Eistert on his 65th Birthday

By treating pyrazole *(1)*, imidazole *(2)*, and 1,2,4-triazole *(3)* with penta- or tetra-carbonyliron, mercury tetracarbonylferrate(II), ferrocene, or dicarbonylcyclopentadienyliron in the presence or absence of a solvent (benzene, toluene, or mesitylene) we have been able to prepare the almost colorless iron(II) derivatives of these nitrogen-heterocycles, namely, $Fe(N_2C_3H_3)_2$ from *(1)*, $Fe(N_2C_3H_3)_2 \cdot 0.5\ N_2C_3H_4$ from *(2)*, and $Fe(N_3C_2H_2)_2$ from *(3)*. In the case of imidazole, the synthesis can be effected even with iron powder. In the reaction of dicarbonylcyclopentadienyliron, cyclopentadiene and cyclopentene are by-products;

$$[C_5H_5Fe(CO)_2]_2 + 4\ N_2C_3H_4 \rightarrow 2\ Fe(N_2C_3H_3)_2 + C_5H_6 + C_5H_8 + 4\ CO$$

The deep brownish-red iron(III) derivative $Fe(N_2C_3H_3)_3$ is formed on reaction of dicarbonylcyclopentadienyliron chloride with *(1)*, together with dicarbonylcyclopentadienyliron which can be separated by extraction with toluene:

$$4\ C_5H_5Fe(CO)_2Cl + 10\ N_2C_3H_4 \rightarrow 2\ Fe(N_2C_3H_3)_3 + [C_5H_5Fe(CO)_2]_2 + 4\ CO + 4\ N_2C_3H_5Cl + 2\ C_5H_6$$

The iron(III) derivative of *(1)* is obtained in moderate yield by reaction of iron(III) chloride with the potassium salt in liquid ammonia. Also, reaction of the iron(II) compounds with silver salts of the heterocycles gives the iron(III) compounds:

$$Fe(N_2C_3H_3)_2 + AgN_2C_3H_3 \rightarrow Fe(N_2C_3H_3)_3 + Ag$$

The iron derivatives of the five-membered carbon-nitrogen heterocycles *(1)*, *(2)*, and *(3)* are clearly not aza analogs of ferrocene, but are coordination polymers. As such they dissolve in other substances only with decomposition. The iron(II) compounds are very sensitive to air, but the iron(III) compounds are not. A change in the type of chemical bonding is indicated in particular by the fact that the sandwich complex, π-cyclopentadienyl-π-pyrrolyliron ("azaferrocene")[1] can be converted into ferrocene by cyclopentadiene, whereas the iron(II) derivatives of the five-membered heterocycles *(1)*, *(2)*, and *(3)* with two or more nitrogen atoms do not undergo this reaction. Complexes of the type FeL_4I_2 [L = *(1)* or *(2)*], which were obtained from tetracarbonyliron(II) iodide, show that the coordination number of the metal atom is four in the iron(II) derivatives of *(1)* and *(2)* as well as in the poly-(1-pyrazolyl)iron(II) borates[2].

The behavior of pyrrole deviates to a remarkably large extent from that of heterocycles with two or more nitrogen atoms. It and its *N*-methyl derivative react with $Fe(CO)_4I_2$ to give coordination compounds of type FeL_2I_2 ($L = C_4H_4NH$ or $C_4H_4NCH_3$). Synthesis of the still unknown dipyrrolyliron(II) is apparently difficult because it can exist, if at all, only as an unstable sandwich complex ("diazaferrocene") and not as the more stable coordination polymer. In view of the stability of the coordination polymers $\{Fe(N_2C_3H_4)_{4/2}\}_G$ it is intelligible that the only pyrrole-iron compound isolated to date is $[Fe(NC_4H_4)_4]K_2$[3].

Complex compounds of the type $C_5H_5Fe(CO)_2L$ ($L = NC_4H_4$, $N_2C_3H_3$, or $N_3C_2H_2$) have been obtained by treating dicarbonylcyclopentadienyliron chloride with the potassium salts of all the five-membered nitrogen heterocycles in liquid ammonia. Of these, however, only the pyrrole derivative could be converted into the dumbbell complex $C_5H_5FeNC_4H_4$[4].

Experimental:

In order to prepare the iron(II) derivative of imidazole from ferrocene the two starting materials, mixed in the weight proportion 10:1, were warmed slowly to 250 °C in an highly evacuated sealed tube. An orange-colored solution resulted in the temperature region 90 °C [m.p. of *(2)*] to 120 °C. At 180 °C reaction begins, with lightening of the color of the melt and separation of a yellow crystalline precipitate. After 3 h the contents of the tube are allowed to solidify and then the excess of imidazole is sublimed off at 70 °C in a vacuum over a period of several hours, leaving a quantitative yield of $Fe(N_2C_3H_3)_2 \cdot 0.5\ N_2C_3H_4$ as yellowish-brown needles, 3 mm in length.

For preparation of the iron(III) derivative of pyrazole from dicarbonylcyclopentadienyliron chloride, the two components in the weight ratio 3:1 were dissolved in just sufficient toluene and boiled under reflux in an atmosphere of nitrogen. The solution changes from red to reddish-brown even before it boils, and a precipitate begins to separate. After 2 h the solvent is distilled off and the residual mixture is extracted with 50 ml of toluene per g of substance with exclusion of air. The brown residue is the desired product. It is washed with 0.05 N hydrochloric acid in the air.

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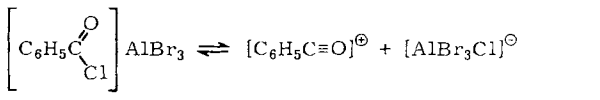
Identification of the Benzoylium Cation by IR Spectroscopy

By *H.-H. Perkampus* and *W. Weiss*[*]

In recent years numerous complexes between acid halides and Lewis acids have been studied by IR spectroscopy[1–3,5], and a new band around 2300 cm^{-1} was ascribed to an oxocarbonium ion. Repeated attempts were made to detect a corresponding band for the complex between a benzoyl halide and a Lewis acid[2,4]. Ionic complexes were obtained only from benzoyl fluoride and SbF_5 or AsF_5[3] and on treatment of methylbenzoyl chlorides with Lewis acids[2,5]. On the basis of conductivity measurements for the complex benzoyl chloride/$GaCl_3$ in the liquid state *Greenwood* and *Wade*[6] postulated an ionic structure $[C_6H_5CO]^{\oplus}[GaCl_4]^{\ominus}$, and *Oulevey*[7] demonstrated an exchange reaction between $AlCl_3$ and benzoyl chloride by means of radioactive chlorine, from which he deduced that the complex exists partly in an ionic form.

Our measurements were carried out with a cuvet described previously[8], wherein the substances can be measured directly as solids or as liquid films. Benzoyl chloride and $AlBr_3$ were placed in the cuvet at −196 °C and the spectrum was recorded from 2350 to 2100 cm^{-1} while the specimen was warmed cautiously. The substance film began to melt at about 0 °C, and at +7 °C a sharp band of low intensity appeared in the spectrum at 2209 cm^{-1}. The intensity of this band increased with rising temperature and reached a maximal value between 40 and 50 °C. After cooling, the bands had disappeared, but they reappeared on repeated increase in temperature. It is thus demonstrated that a temperature-dependent equilibrium between a coordinate and an ionic complex exists also in the system benzoyl chloride/$AlBr_3$.



Cation bands were also measured for the following solid systems (temperatures in parentheses are those up to which the samples were warmed; samples were later refrozen):

$CH_3COCl + AlBr_3 \rightarrow [CH_3CO]^{\oplus} + [AlBr_3Cl]^{\ominus}$: 2293 cm^{-1} (−28 °C)

$C_2H_5COCl + AlBr_3 \rightarrow [C_2H_5CO]^{\oplus} + [AlBr_3Cl]^{\ominus}$: 2264 cm^{-1} (−42 °C)

$C_2H_5COCl + GaCl_3 \rightarrow [C_2H_5CO]^{\oplus} + [GaCl_4]^{\ominus}$: 2264 cm^{-1} (−100 °C)

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Preparation of Octametaphosphates, $M^I_8[P_8O_{24}]$

By *U. Schülke* [*]

When lead tetrametaphosphate tetrahydrate, $Pb_2[P_4O_{12}]\cdot 4\,H_2O$ *(1)* is heated, one obtains a mixture of the hitherto unknown crystalline lead octametaphosphate $Pb_4[P_8O_{24}]$ *(2)* (70 %) and high-molecular crystalline lead polyphosphate *(3)* (30 %), as well as traces of lead mono-, di-, and triphosphate.

Quantitative evaluation of paper chromatograms of samples taken at various stages of the dehydration, as well as Guinier photographs, rate of water loss, and differential thermal analysis, show that, during the heating up and while the temperature is kept at 350 °C, dehydration and thermal rearrangement of *(1)* occur by the stages:

a) crystalline $Pb_2[P_4O_{12}]\cdot 2\,H_2O$;

b) ring-hydrolysis of the tetrametaphosphate anion by the residual crystal water, to give a mixture of lead mono-, di-, and tri-phosphate;

c) condensation of the hydrolysis products to *(3)* and anhydrous crystalline lead tetrametaphosphate *(4)*;

d) conversion of *(4)* into *(2)*.

The steps c) and d) occur simultaneously.

When $Pb(H_2PO_4)_2$ is heated, only a poor yield of *(2)* is formed, together with *(3)*. The appearance of the octameric compound in the dehydration products of $Pb(H_2PO_4)_2$ was observed previously by *Thilo* and *Grunze* [1] who, however, on the basis of the position of the octametaphosphate spot on a one-dimensional paper chromatogram, assumed that this material was a polyphosphate.

When the mixture formed by heating *(1)* is treated with alkali-metal sulfide or carbonate solutions, crystalline alkali-metal salts of octametaphosphoric acid are obtained, *e.g.* $Na_8[P_8O_{24}]\cdot 6\,H_2O$ *(5)*.

Preparation of (5):

5–10 g of compound *(1)*, prepared by mixing solutions of $Pb(NO_3)_2$ and $Na_4[P_4O_{12}]\cdot 4\,H_2O$ in water, is heated in a shallow dish, first at 110 °C for 30 min, and then at 350 °C for 30 min. 100 g of the dehydration product is made into a slurry in 200 ml of water and treated, with stirring, with a solution of 70 g of $Na_2S\cdot 9H_2O$ in 600 ml of water. After 15 min the precipitated PbS is filtered off, *ca.* 100 ml of ethanol is added to the filtrate with stirring, the precipitated sodium polyphosphate is removed, and the sodium octametaphosphate is caused to crystallize by addition of *ca.* 900 ml of ethanol and is then sucked off, washed with 50 % ethanol, and dried in the air. For further purification the sodium salt can be recrystallized by adding ethanol to its aqueous solution.

The cyclic nature of the octametaphosphate anion is shown by the following facts:

1. The ratio $M^I:P = 1:1$ in the crystalline Na, K, Ag, and Ca salts, which corresponds to the general formula $M^I_n(PO_3)_n$ for metaphosphates.

2. The acid-base titration curve of octametaphosphoric acid which, referred to one POH group, corresponds to the curve for a strong monobasic acid; weakly acidic end groups, such as are present in polyphosphates, were not found (a dilute aqueous solution of octametaphosphoric acid can be prepared by reaction of its sodium salt with Wofatit KPS in the H form).

3. The ^{31}P–NMR spectrum of the aqueous solution of *(5)* consists of only one signal; the chemical shift is 21.2 ± 1 ppm [2], referred to 85 % H_3PO_4, in the region of shifts observed for metaphosphates [3].

4. The position of the octametaphosphate spot in the two-dimensional paper chromatogram characterizes it as a member of the homologous series of metaphosphates with an anion that is larger than that of hexametaphosphate.

The ring size (the number of PO_3 groups per anion) was determined by the same method as was employed in the case of the recently isolated penta- and hexa-metaphosphates *i.e.* by alkaline ring fission in 0.2 N NaOH [4]; the cyclic anion of the octametaphosphate was in this way first cleaved to the octaphosphate with a chain-like anion, which was identified by paper chromatography.

Fission of the sixteen-membered cyclic anion is, however, so slow that most of the octaphosphate formed is degraded to low-molecular polyphosphates and trimetaphosphate before all the octametaphosphate is cleaved.

The octametaphosphates, thus first available in quantity, resemble the high-molecular polyphosphates more than they do the tri- or tetra-metaphosphates. For instance, in solution they show good ability for complex formation, similar to that of triphosphate and higher-molecular polyphosphates. However, in the resistance to nucleophilic reagents the octametaphosphates are the equal of the very stable hexametaphosphates [4,5].

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[2] I thank Dr. *G. Engelhardt* for measuring the NMR spectrum.

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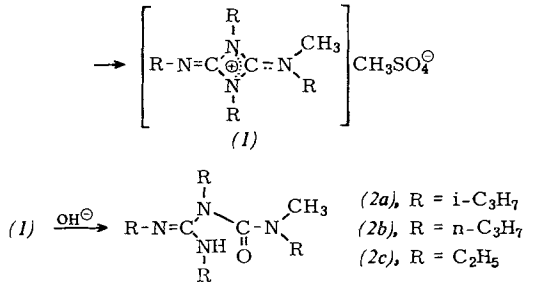
Dimerization of Carbodiimides[1]

By *K. Hartke* and *F. Rossbach*[*][2]

Aliphatic carbodiimides react readily with alkylating agents such as dimethyl sulfate. If equivalent amounts of the two compounds are mixed and kept at room temperature without a solvent being present, the ν-N=C=N stretching vibration of diisopropylcarbodiimide disappears in 5 days, of di-*n*-propylcarbodiimide in 30 h, and of diethylcarbodiimide in 16 h. NMR spectra indicate in each case reaction of two molar equivalents of carbodiimide with one of dimethyl sulfate to yield *N*-alkyl-*N*-methyl-1,3-dialkyl-2-alkylimino-1,3-diazetidine-4-iminium methyl sulfates *(1)*.

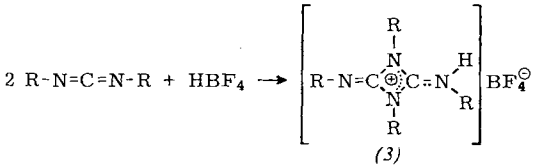


(1)

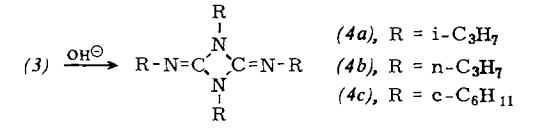
(2a), R = i-C_3H_7
(2b), R = n-C_3H_7
(2c), R = C_2H_5

The salts *(1)* are isolated as oils; they are soluble in water and on addition of an excess of aqueous sodium hydroxide are at once hydrolyzed to *N,N',N''*-trialkyl-*N*-(*N*-alkyl-*N*-methylcarbamoyl)guanidines *(2)*, which, being sparingly soluble, are then precipitated. Compound *(2a)* is crystalline, has m.p. 102–103 °C, is formed in 81 % yield, and has a molecular weight 286 (acidimetric); in the IR spectrum (KBr) νNH 2.99 μ, νCO 6.09 μ, νC=N 6.22 μ, and in the NMR spectrum ($CDCl_3$) doublets at 1.10 ppm [3 $C(CH_3)_3$] and 1.29 ppm [1 $C(CH_3)_2$], a singlet at 2.68 ppm (1 $N-CH_3$), and a broad singlet at 3.4 ppm (NH). The compounds *(2b)* and *(2c)* are liquid and have not yet been obtained analytically pure.

An analogous dimerization of aliphatic carbodiimides to salts of structure *(3)* is observed on admixture with 0.5 molar equivalent of anhydrous ethereal tetrafluoroboric acid[3] in anhydrous methylene chloride. IR spectroscopic studies showed that the reaction is complete within only a few minutes at room temperature.



(3)

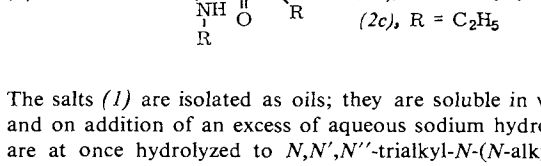


(4a), R = i-C_3H_7
(4b), R = n-C_3H_7
(4c), R = c-C_6H_{11}

The salts *(3)* were not isolated but were converted into the 1,3-dialkyl-2,4-bis(alkylimino)-1,3-diazetidines *(4)* by cautious neutralization with aqueous sodium hydroxide or by filtration through a column of basic Al_2O_3 [*(4a)*: m.p. 52 °C, yield 90 %. *(4b)*: b.p. 90 °C/0.05 torr, yield 70 %. *(4c)*: m.p. 122.5 °C, yield 95 %]. The structure *(4)* was proved by elemental analysis and spectroscopic data: *e.g.*, for *(4a)*: molecular weight 252 (acidimetric), 252 (mass spectrometric); IR (KBr) νC=N 5.96 μ; NMR (CCl_4) doublets at 1.12 ppm [2 $C(CH_3)_2$] and 1.29 ppm [2 $C(CH_3)_2$]. Dimeric aliphatic carbodiimides were previously almost unknown[4]. They are stable indefinitely at room temperature, but when warmed decompose partly into the monomers. Thus in the mass spectrum of *(4a)* one observes the molecular ion and fragments with mass numbers greater than that of the monomer only when the evaporation temperature is low. Moreover, some di-*n*-propylcarbodiimide is detectable by IR spectroscopy in the fresh distillate of *(4b)* but disappears after a few days.

Aromatic carbodiimides also dimerize, within a few minutes, on addition of 0.5 molar equivalent of anhydrous tetrafluoroboric acid in anhydrous methylene chloride; however, they afford in this reaction substituted quinazolinium salts of structure *(5)*, from which the 3-aryl-2-arylamino-4-aryliminoquinazolines *(6)* [*(6a)*, m.p. 181–185 °C[5], yield 85 %; *(6b)*, m.p. 246 °C, yield 82 %], are obtained by means of bases.

(5)



(6a), R = H
(6b), R = p-CH_3

The structure *(6)* was proved by IR, NMR, and mass spectral results. The compound *(6a)* was previously prepared by *McCoy* (1897) from chloro-*N,N'*-diphenylformamidinium chloride by means of aluminum chloride[6].

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[1] Part 9 of Carbodiimides. – Part 8: *K. Hartke*, Arch. Pharmaz. *300*, 766 (1967).

[2] We thank the Deutsche Forschungsgemeinschaft and the Verband der Chemischen Industrie for financial support of this work, and Dr. *Zahorszky*, Marburg, and Varian AG., Zürich, for measurement of the mass spectra.

[3] Preparation: *K. Hafner*, *A. Stephan*, and *C. Bernhard*, Liebigs Ann. Chem. *650*, 57 (1961); *U. Harder*, *E. Pfeil*, and *K.-F. Zenner*, Chem. Ber. *97*, 516 (1964).

[4] The only observation is by *F. Zetzsche* and *A. Fredrich*, Ber. dtsch. chem. Ges. *73*, 1114 (1940), who isolated a crystalline substance in low yield from the polymeric distillation residue of dibenzylcarbodiimide; on the basis of an N analysis and a not very accurate cryoscopic molecular-weight determination they ascribed to this product a 1,3-diazetidine structure.

[5] Compound *(6a)* melts partially at 171 °C, resolidifies, and remelts unsharply at 181–185 °C.

[6] *H. N. McCoy*, Ber. dtsch. chem. Ges. *30*, 1090 (1897); the structure was clarified by degradation [*H. N. McCoy*, *ibid. 30*, 1682 (1897)].

Preparation of Halogeno- and Acetato-organoplumbates(IV)[1]

By *F. Huber* and *E. Schönafinger*[*]

A large proportion of the covalent bond energy in the total free energy of the relevant system[2,3] is an important condition for the possibility of synthesis, and for the stability,

of lead(IV) compounds, which, in contrast to analogous compounds of other elements of the fourth Group, are almost all to be considered as intramolecular redox systems. Organolead(IV) halides, $R_{4-n}PbX_n$ ($X \neq F$), are thus more stable than the tetrahalides PbX_4.

We have now tried to prepare organosubstituted halogenoplumbates(IV) of the general formula $M^I_m[R_{4-n}Pb^{IV}X_{n+m}]$, since we wished to discover whether a corresponding stabilizing effect is to be seen among the organolead complex anions of which little was previously known. In view of the non-existence of purely inorganic hexabromo- and hexaiodoplumbates(IV), studies of the preparability of bromo- and iodo-organoplumbates(IV) were of particular interest.

For the series $M^I[R_3PbX_2]$ we mixed hot ethanolic solutions of triphenyllead chloride or bromide with the appropriate tetramethylammonium halide and, on cooling the solutions, obtained colorless crystalline precipitates.

$$(C_6H_5)_3PbX + (CH_3)_4NX \rightarrow [(CH_3)_4N][(C_6H_5)_3PbX_2] \quad (1)$$

(1a), X = Cl; m.p. 298 °C (decomp.)

(1b), X = Br; m.p. 277 °C (decomp.)

An analogous reaction with cesium bromide gave $Cs[(C_6H_5)_3PbBr_2]$, m.p. 209 °C (decomp.). Attempts to prepare the iodine compound failed; in these we isolated only starting materials.

Hills and *Henry*[4] mention briefly a product corresponding to *(1a)* but without characterizing its properties more closely. Compounds *(1a)* and *(1b)*, like the other compounds described here, are not sensitive to air or hydrolysis and are very difficultly soluble in the usual organic solvents. The solubility does not suffice for determination of exact molecular weights, but does suffice for conductivity measurements; *ca.* 10^{-3} M solutions in methanol at 20 °C have a conductivity about 100 times that of pure methanol [molar conductivity of *(1a)* $\mu_{20\,°C} = 122$ ohm^{-1} mole^{-1} cm^2], which we attribute to electrolytic dissociation of the compounds. In the solid state they may be built up, salt-like, of complex ions.

As example of compounds of type $M^I_2[R_3PbX_3]$ and as the as-yet sole alkyllead derivative, we were able to obtain the compound $[(CH_3)_4N]_2[(CH_3)_3PbCl_3]$ (decomp. 86 °C) by mixing solutions of trimethyllead chloride and tetramethylammonium chloride in ethanol at room temperature and extracting unchanged starting materials by ethyl acetate from the resulting precipitate. In all attempts to prepare other alkyl-substituted halogenoplumbates(IV) of this type, either the starting materials were recovered or, particularly on warming, the alkyl groups were removed with formation of halogenoplumbates(II).

Representatives of the series $M^I[R_2PbX_3]$ were provided by the colorless complex salts *(2)* precipitated when ethanolic solutions of diphenyllead dihalides or diacetate and of $(CH_3)_4NX$ (X = Cl, Br, or CH_3COO) were heated together:

$$(C_6H_5)_2PbX_2 + (CH_3)_4NX \rightarrow [(CH_3)_4N][(C_6H_5)_2PbX_3] \quad (2)$$

(2a), X = Cl; m.p. 301 °C (decomp.)

(2b), X = Br; m.p. 262 °C (decomp.)

(2c), X = CH_3COO; m.p. 223 °C (decomp.)

Under the same conditions cesium acetate and diphenyllead diacetate give the compound

$Cs[(C_6H_5)_2Pb(CH_3COO)_3]$, m.p. 274 °C (decomp.).

In the analogous reaction of cesium bromide with diphenyllead dibromide in ethanol the phenyl groups were removed quantitatively with formation of bromoplumbate(II). In anhydrous acetone, however, the compound

$Cs[(C_6H_5)_2PbBr_3]$, m.p. 223 °C (decomp.)

was obtained.

The reaction of iodides – which, like the other reactions, occurred independently of the molar ratio of starting materials used – led to the yellow salt

$[(CH_3)_4N]_2[(C_6H_5)_2PbI_4]$, m.p. 333 °C (decomp.)

which is an example of the type $M^I_2[R_2PbX_4]$.

Mixed compounds

$[(CH_3)_4N][(C_6H_5)_2PbX_{3-n}X'_n]$

were obtained from diphenyllead dihalides and $(CH_3)_4NX$ containing different halogens, n in the product formula depending on the exchange equilibrium. From a solution of diphenyllead dichloride and tetramethylammonium bromide (molar ratio 1:2) in ethanol there separated, *e.g.* after heating for 10 min, a product of formal composition

$[(CH_3)_4N][(C_6H_5)_2PbBr_{1.7}Cl_{1.3}]$

All attempts to convert dialkyllead dihalides by $(CH_3)_4NX$ or cesium halides into halogenodialkylplumbates(IV) resulted, after intermediate complex formation in solution, in quantitative elimination of the alkyl group R from the lead, and lead(II) compounds separated with evolution of gas, *e.g.*:

$$(CH_3)_2PbBr_2 + (CH_3)_4NBr \rightarrow [(CH_3)_4N][PbBr_3] + C_2H_6.$$

According to gas-chromatographic analyses the gas evolved consisted exclusively of dimerized alkyl groups only in the reactions of dimethyllead compounds (giving ethane). Removal of higher alkyl groups gave complex mixtures of alkanes and alkenes.

We have not yet been able to prepare compounds of type $M^I_m[RPbX_{3+m}]$. In place of the non-existent monorganolead trihalides we tried to combine phenyllead triacetate with $(CH_3)_4NX$ to give compounds with a halogenomonophenylplumbate(IV) anion; however, we isolated only lead(II) compounds, *e.g.* tetraethylammonium triiodoplumbate(II) from phenyllead triacetate and tetraethylammonium iodide.

The phenyl-substituted plumbates(IV) prepared are more stable than the unsubstituted analogs; the alkyl-substituted plumbates(IV) are less stable or cannot be isolated at all. In addition to the unexpectedly large effect of the group R, the influences of the anions and also of the cations and solvent on the stability are of not inconsiderable importance. An unfavorable summation of these factors can labilize a compound to such an extent that organic groups are cleaved from the lead and Pb(IV) is converted into Pb(II). This is a further example of the result of the "inert-pair" effect (cf.[3]), whose influence on the stability and chemistry of organometallic derivatives of the heavy elements of the third to the fifth Main Group has been little considered hitherto and which we are now investigating.

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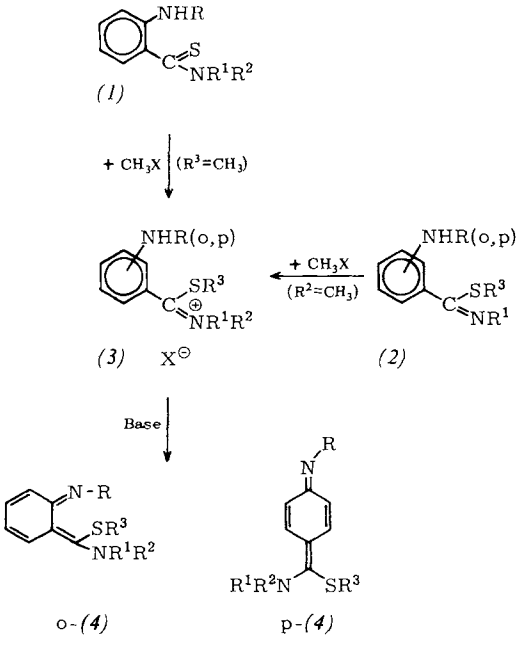
Quinone Methide Imines

By *R. Gompper* and *H.-D. Lehmann* [*]

Quinone methide imines cannot be prepared from aromatic amines and carbonium salts by processes analogous to those that have proved valuable for preparation of quinone methides [1] and quinodimethanes [2]. We have developed three methods for the synthesis of these compounds which, except for the stable *N*-phenylimine of fuchsone [3], have previously been only assumed [4], or proved by spectroscopy [5], to exist as intermediates; we here describe two of our methods.

1. *N,N*-Disubstituted thioanthranilamides *(1)* and corresponding *S,N*-disubstituted *o*- and *p*-aminothiobenzimidic esters *(2)* (so far we have used only 2-[*o*(*p*)-aminophenyl]-benzothiazole) react with methyl iodide or methyl *p*-toluenesulfonate (CH_3X), giving smoothly the salts *(3)*, whence HX can be removed by bases, *e.g.*, triethylamine, with formation of the stable quinone methide imines *(4)*.



(150 ml) is boiled under reflux for 2 days. The CS_2 is then distilled off, chloroform (200 ml) is added, and thereafter sodium carbonate solution is added gradually. The chloroform phase is separated, washed with water, and dried with calcium chloride. Distilling off the solvent leaves a yellow oil, which crystallizes when rubbed with a little acetone.

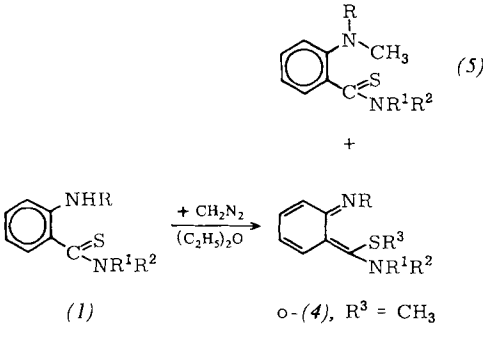
Preparation of N,N-Dialkyl-N-[o-(benzenesulfonylamino)-phenyl-α-(methylthio)benzylidene]ammonium Iodides (3), R = $SO_2C_6H_5$; R^1, R^2 = Alkyl:

0.1 mole of *(1)* is heated under reflux with 0.15 mole of methyl iodide in 100 ml of acetone for 15 min. Even during the boiling, the iodide separates in analytically pure form.

Preparation of N-(Benzenesulfonyl)-7-(dimethylamino)-7-(methylthio)-o-quinone methide imine (4), R = $SO_2C_6H_5$; R^1, R^2,R^3 = Methyl:

4.6 g of *(3)*, R^1, R^2, R^3 = CH_3, is suspended in 3 ml of anhydrous acetonitrile and treated with 0.7 g of *N*-ethyldiisopropylamine. Dissolution occurs with a yellow coloration. The mixture is covered with 1 ml of petroleum ether, and acetone is added to achieve homogeneity. The pale yellow, analytically pure *o*-quinone methide imine crystallizes out.

2. The action of diazomethane on *(1)*, R = $SO_2C_6H_5$, gives a mixture of *o-(4)* and *(5)*. The compound *o-(4)*, R = $SO_2C_6H_5$, R^3 = CH_3, R^1R^2N = morpholino, crystallizes from the ethereal solution in 76% yield and is easily separated from *(5)* (22%) in this way. The yield of *o-(4)* depends to a large extent on the nature of R^1 and R^2: from the pyrrolidide, $R^1 + R^2 = -(CH_2)_4-$, only 49% of *o-(4)* is obtained; from



Cpd.	R	R^1	R^2	R^3	M.p. (°C)	λ_{max} [a] (nm)	log ε	Yield (%)
o-(4)	$SO_2C_6H_5$	CH_3	CH_3	CH_3	172	377 [b]	—	90
	$SO_2C_6H_5$	$-(CH_2)_2-O-(CH_2)_2-$		CH_3	156	421	3.94	76(91)
	$SO_2C_6H_5$	$-(CH_2)_4-$		CH_3	173	—	—	49
	$SO_2C_6H_5$	$-(CH_2)_5-$		CH_3	185	—	—	29
	$SO_2C_6H_5$	CH_3	*o*-C_6H_4		249	467	3.53	56
	p-$SO_2C_6H_4CH_3$	CH_3	*o*-C_6H_4		237	470	3.68	60
	p-$SO_2C_6H_4Cl$	CH_3	*o*-C_6H_4		247	464	3.63	83
	2,4-$C_6H_3(NO_2)_2$	CH_3	*o*-C_6H_4		180 [c]	570	—	
	2,4,6-$C_6H_2(NO_2)_3$	CH_3	*o*-C_6H_4		225 [c]	452	4.3	100
p-(4)	$SO_2C_6H_5$	CH_3	*o*-C_6H_4		225	475	4.76	74
	p-$SO_2C_6H_4Cl$	CH_3	*o*-C_6H_4		237	474	4.5	65
	2,4-$C_6H_3(NO_2)_2$	CH_3	*o*-C_6H_4		—	565 [b]	—	
	2,4,6-$C_6H_2(NO_2)_3$	CH_3	*o*-C_6H_4		200 [c]	565	—	100

[a] In chloroform. — [b] In acetonitrile. — [c] With decomposition.

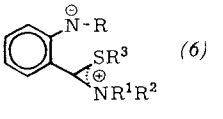
The starting materials *(1)* are accessible from *N*-substituted *o*- and *p*-aminobenzoyl chlorides or isatoic anhydrides by way of the amides which are then treated with P_2S_5. Compounds *(2)*, $R^1 + R^2$ = *o*-C_6H_4, can be prepared from the corresponding acid derivatives and *o*-aminothiophenol.

Preparation of N^1,N^1-Dialkyl-N^2-(benzenesulfonyl)thioanthranilamides (1), R = $SO_2C_6H_5$; R^1, R^2 = Alkyl:

A well-stirred suspension of N^1,N^1-dialkyl-N^2-(benzenesulfonyl)anthranilamide (0.1 mole) and P_4S_{10} (22.2 g) in CS_2

the piperidide, $R^1 + R^2 = -(CH_2)_5-$, only 29%; and from the dimethylamide, $R^1 = R^2 = CH_3$, none.

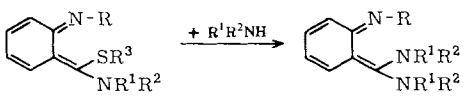
The quinone methide imines listed in the first Table are stable indefinitely if moisture is excluded. They show negative



(6)

solvatochromy, which indicates relatively great participation of the resonance structure *(6)* in the ground state.

Reaction of *o-(4)*, $R^3 = CH_3$, with secondary amines affords the *o*-quinone methide imines *(7)*.



o-(4) *(7)*

Cpd.	R	R^1	R^2	M.p. (°C)	λ_{max} (nm)	log ε	Yield (%)
(7)	$SO_2C_6H_5$	CH_3	CH_3	231	353	3.35	96
	$SO_2C_6H_5$	$-(CH_2)_2-O-(CH_2)_2-$		223	360	3.4	68
	$SO_2C_6H_5$	$-(CH_2)_4-$		219	—	—	32
	$SO_2C_6H_5$	$-(CH_2)_5-$		192	355	3.53	

The NMR spectra of *(7)*, $R^1 = R^2 = CH_3$, are temperature-dependent. For a solution in liquid SO_2 at −40 °C the signal due to the NCH_3 protons appears as a doublet (τ = 2.28 and 2.75), but at 37 °C as a singlet (τ = 2.48). The NCH_3 signal is also split (τ = 2.77 and 3.01) in the NMR spectrum of *o-(4)*, $R^1 = R^2 = CH_3$ (liquid SO_2, −40 °C). Most of the compounds *(4)* and *(7)* fluoresce strongly in the solid state.

When *o-(3)*, $R = C_6H_5$, is treated with K *tert*-butoxide in dimethylformamide a deep blue solution results. The *o*-quinone methide imine that is obviously formed could not be isolated but was proved to exist by cycloaddition of phenyl isocyanate and phenyl isothiocyanate.

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N,P-Organometalated Phosphine Imines from Aminophosphines

By *O. J. Scherer* and *G. Schieder* [*]

N-Organometalated phosphine imines can be prepared from alkyl- or aryl-phosphines and organometal azides [1]. On treatment with an excess of ammonia in ether at *ca.* −50 °C di-(*tert*-butyl)chlorophosphine [2] [b.p. 49–50 °C/5 torr; $J(^{31}PCCH)$ = 12.0 Hz] gives an 81 % yield of aminodi-(*tert*-butyl)phosphine *(1)* as a water-clear liquid that is sensitive to oxygen and to moisture and does not condense to give $\{[(CH_3)_3C]_2P\}_2NH$ when kept for four weeks in a closed vessel.

$$[(CH_3)_3C]_2P-Cl + x\ NH_3 \rightarrow [(CH_3)_3C]_2P-NH_2 + NH_4Cl$$
(1)

(1): b.p. 33–34 °C/2 torr; m.p. −1 to +1 °C; ^1H–NMR spectrum (Varian A-60, 60 MHz; 10 % solution in benzene; tetramethylsilane as external standard), $J(^{31}PCCH)$ = 11.0 Hz.

An etheral solution of *(1)* is smoothly metalated by *n*-butyllithium in hexane at 0 °C. Reaction of *N*-phosphinyllithium amide *(2)* with chlorotrimethyl-silane or -germane affords di-(*tert*-butyl)phosphinyltrimethylmetal amides *(3)*.

$$(1) + n\text{-}C_4H_9Li \xrightarrow{-\,n\text{-}C_4H_{10}} [(CH_3)_3C]_2P\text{-}NH\text{-}Li \quad (2)$$

$$\xrightarrow[-\,LiCl]{(CH_3)_3MCl} [(CH_3)_3C]_2P\text{-}NH\text{-}M(CH_3)_3 \quad (3)$$

(M = Si, Ge)

(3a): M = Si; b.p. 39–40 °C/1 torr; m.p. −4 to −2 °C; yield 80 %; ^1H–NMR spectrum, $J(^{31}PCCH)$ = 11.0, $J(^{31}PNSiCH)$ = 0.6 Hz.

(3b): M = Ge; b.p. 49–50 °C/1 torr; m.p. −6 to −4 °C; yield 72 %; ^1H–NMR spectrum, $J(^{31}PCCH)$ = 11.0, $J(^{31}PNGeCH)$ = 0.3 Hz.

Further metalation of compounds *(3)* [*(3a)* at room temperature; *(3b)* at −40 °C] in ether with *n*-butyllithium affords compounds *(4)* whose existence is proved by treatment with chlorotrimethylsilane or -germane.

$$(3) + n\text{-}C_4H_9Li \xrightarrow{-\,n\text{-}C_4H_{10}} [(CH_3)_3C]_2P\text{-}NLi\text{-}M(CH_3)_3 \quad (4)$$

$$\xrightarrow{+(CH_3)_3M'Cl} \left[\begin{array}{c} M'(CH_3)_3 \\ | \\ [(CH_3)_3C]_2P^{\oplus}\text{-}NLi\text{-}M(CH_3)_3\ Cl^{\ominus} \end{array}\right] \quad (5)$$

$$\xrightarrow{-\,LiCl} \begin{array}{c} M'(CH_3)_3 \\ | \\ [(CH_3)_3C]_2P{=}N\text{-}M(CH_3)_3 \end{array} \quad (6)$$

(6a): M = Si, M′ = Ge; sublimes at *ca.* 90 °C/0.1 torr; yield 87 %; ^1H–NMR spectrum, $J(^{31}PCCH)$ = 14.3, $J(^{31}PGeCH)$ = 4.4, $J(^{31}PNSiCH)$ = 0.4 Hz.

(6b): M = Ge, M′ = Si; sublimes at *ca.* 80 °C/0.1 torr; yield 75 %; ^1H–NMR spectrum, $J(^{31}PCCH)$ = 11.9, $J(^{31}PSiCH)$ = 2.2, $J(^{31}PNGeCH)$ = 0 Hz.

Although the ^1H–NMR spectrum of the phosphine imine *(6a)* with its P–Ge/N–Si bond before as well as after sublimation gives no indication of existence of the isomer *(6b)*, the compound *(6b)* slowly rearranges to *(6a)* during sublimation [the isomer mixture contains *ca.* 25 % of *(6a)* and 75 % of *(6b)* after the first sublimation; *ca.* 60 % of *(6a)* and 40 % of *(6b)* after a second sublimation; identified by ^1H–NMR spectroscopy].

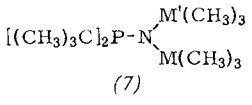
Heating at 120–130 °C for several hours is necessary for quantitative conversion of *(6b)* into *(6a)*. Keeping a benzene solution of the isomer mixture at room temperature for several days does not lead to enrichment of *(6a)*.

$$\begin{array}{c} Si(CH_3)_3 \\ | \\ [(CH_3)_3C]_2P{=}N\text{-}Ge(CH_3)_3 \end{array} \xrightarrow{\Delta} \begin{array}{c} Ge(CH_3)_3 \\ | \\ [(CH_3)_3C]_2P{=}N\text{-}Si(CH_3)_3 \end{array}$$
(6b) *(6a)*

The two phosphine imines *(6)* are readily soluble in ether, petroleum ether, and benzene; they react with CCl_4 [as does *(3)*]. Compounds *(3a)* and *(6a)* react to form $[(CH_3)_3C]_2P(Cl){=}N{-}Si(CH_3)_3$ (b.p. 42 °C/1 torr; m.p.

−13 °C; yield 90 %; ^{1}H–NMR spectrum: $J(^{31}PCCH)$ = 17.3, $J(^{31}PNSiCH)$ = 0.5 Hz; IR: P=N 1340 cm^{-1}). *(6a)* has a strong P=N band at 1320 cm^{-1} in its IR spectrum.

That the new class of *N,P*-organometalated phosphine imines *(6)* is formed by way of the intermediate addition product *(5)* and not by a rearrangement of *Michaelis-Arbuzov* type involving the intermediate *(7)* was proved by our experiments [*(4a)* M = Si + $(CH_3)_3GeCl$; *(4b)* M = Ge + $(CH_3)_3SiCl$]; if *(7)* had been formed, then the same



(7)

product or mixture of isomers would have resulted in the two cases.

Compound *(3)* exists exclusively in the aminophosphine form, this being proved by the IR spectrum (absence of a P=N band) and by oxidation with sulfur.

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CONFERENCE REPORTS

Second International Meeting on Fuel Cells

held in Brussels (Belgium) on June 19–23, 1967

Some 350 participants attended this Meeting which was arranged by the Belgian Research Organisation S.E.R.A.I. (Société d'Etudes de Recherches et d'Applications pour l'Industrie). They came from 22 countries and represented 190 firms and Institutes. This shows that fuel cells have not lost their fascination as direct converters of chemical into electrical energy. However, there has been no easing of the difficulties connected with direct electrochemical oxidation, particularly of organic fuels. The following report presents a selection from the total of 55 papers.

1. Studies of the Course of Reaction

In porous electrodes, conversion of the reactant gases takes place near the electrolyte meniscus that is formed in the pores of the electrode. However, there is as yet no general answer to the question whether the reaction route involves (i) adsorption on the dry pore walls, (ii) surface diffusion to those parts of the pores that are filled with electrolyte and subsequent charge transfer, or (iii) diffusion through an electrolyte film of about 1 μ thickness above the visible meniscus before adsorption and charge transfer. To clarify this problem, *F. G. Will* (General Electric Company, Schenectady, U.S.A.) had studied an enlarged model of a meniscus covered with an electrolyte film. He covered a plane horizontal platinum foil, 40 cm long (the pore wall), with an electrolyte layer of 0.5, 1, or 2 mm thickness (the enlarged electrolyte film). Hydrogen, as reactant gas, streamed over the sulfuric acid electrolyte. The reference electrodes were platinized platinum points dipping into the electrolyte layer at distances of 2 cm from one another. It was thus possible to measure, for each region, the potential and the change in concentration by means of the resistance between neighboring platinum points. The changes in resistance during the anodic oxidation were smaller by orders of magnitude than those calculated. The cause was found to be convection (which was demonstrated by means of pigment particles) resulting from gradients in the surface tension. Further, there was additional water transport through the gas phase; this was shown very impressively when the surface of the liquid was covered with Teflon foil, water transport being more strongly hindered than that of H_2. Mathematical derivation of the polarization curve at limiting current gave good agreement with experiment. Since the curves for half-immersed electrodes and for technical gas-diffusion electrodes showed the same characteristics, *Will* concluded that the model provides a good picture of the pore function, *i.e.* that a "film mechanism" is involved.

The effect of adsorption layers on electrode processes was discussed in many papers. For instance, on platinum electrodes oxidation of CO in alkaline solution is hindered by the oxygen adsorption layer formed from +800 mV (against the reversible H_2 electrode).

As *H. Binder*, *A. Köhling*, and *G. Sandstede* (Batelle-Institut, Frankfurt/M, Germany) showed, a sulfur film, in contrast to an oxygen film, is stable on platinum even in the region of the H_2 potential. Current curves, measured potentiodynamically, show oxidation of the sulfur film to SO_2 in aqueous potassium hydroxide at +450 mV (70 °C), in dilute sulfuric acid at +650 mV (70 °C), and in concentrated phosphoric acid at +550 mV (150 °C). When dipped into a solution containing H_2S, porous electrodes with Raney nickel as active component receive a defined sulfur film. A slow stream of reactant gas was passed over such electrodes at a gas pressure of 0.6 atm. The S sorbate had only negligible influence on the oxidation of ethylene in dilute sulfuric acid or on that of CO in alkaline solution, but the oxidation of CO in acid solution was accelerated; in experiments with a sulfur coverage of 1 with a CO:H_2O mixture = 1:1 in 44 N H_3PO_4 at 155 °C the oxidation current was increased by a factor as high as 5. However, with saturated hydrocarbons in acid or unsaturated hydrocarbons in alkali the reaction velocity was diminished approximately proportionally to the sulfur coverage. There is as yet no explanation for the different behavior of carbon monoxide and of saturated and unsaturated hydrocarbons.

The exchange current per unit area of electrode is often given as a measure of the utility of an electrocatalyst. *G. Richter* (Siemens AG, Erlangen, Germany) explained how the exchange current can be measured also for powder catalyst present in powder form in the electrolyte if care is taken to achieve good electrical contact between the particles and a lead electrode. The exchange current was calculated from the initial current-potential curve and referred to the amount of the catalyst. The specific surface in m^2/g and values proportional to the surface, such as the double layer capacity and the chemisorption capacity, have utility only for the same support material. According to the method of preparation and after-treatment, values of the chemisorption capacity of unsintered Raney nickel (at potentials between 0 and +10 mV) were found to lie between 0.3 to 0.54 A s/g and for the specific exchange current between 0.2 and 1.7 A/g; the corresponding values for platinum black were 0.8 A s/g and 8 A/g[1].

M. Bonnemay, G. Bronoel, E. Levart, and *G. Peslerbe* (Laboratoire d'Electrolyse du CNRS, Mendon-Bellevue, France) have studied the influence of the structure of catalytic metals on their activity. The distances between platinum atoms in the lattice were altered by applying a tension or a compression and the rate of oxidation of hydrogen was measured. At 50 mV overvoltage a four-fold greater current was observed at a platinum sample that was under mechanical tension than at one that was not under tension. It seemed appropriate to replace the external tension by an internal one and to disturb the structure by alloying with small concentrations of a foreign element. Structural hardening is achieved by adding 0.5 % of Si to platinum. Such a sample proved to be appreciably more active if quenched from 1000 °C than after slower cooling. However, addition of alloying elements has also an electronic influence.

2. Low-temperature and Medium-temperature Cells

An effective gas electrode was obtained by *H. P. Landi, W. A. Barber, J. D. Voorhies*, and *R. G. Haldeman* (American Cyanamid Company, Stamford, U.S.A.) from carbon coated with catalyst and with Teflon as binder. The peculiarity is the use of fibrous Teflon (5 wt.-%), which confers high mechanical strength combined with good flexibility on the electrode. The new structure has proved valuable as an H_2/O_2 as well as an air electrode. At 25 °C platinum was more active in the cathode than was palladium or palladium-silver. With 1.1 mg of Pt per cm^2 of electrode surface, in aqueous potassium hydroxide with air as oxidant, an electrode potential of −0.06 V was measured at 20 m A/cm^2, and one of −0.21 V at −100 mA/cm^2 (potentials against the Hg/HgO electrode).

To provide current for balloons, which are released in large numbers and periodically questioned by a satellite, *J. Lemaignen* and *Ph. Demange* (Compagnie Francaise Thomson Houston, Hotchkiss Brandt, France) developed hydrogen-oxygen batteries that are stated to give an average output of 80 mW for 6 months. Higher impact loading is made possible by a nickel-cadmium accumulator connected in parallel. Longer life is achieved by using exchange membrane cells with fluorinated cation-exchangers. Because of the extreme conditions of pressure (below 350 mbar) and temperature (down to −60 °C) the battery is built into a steel cylinder and is thermally insulated. A total weight of 1800 g is expected. The O_2 supply is contained in a 0.8-l pressure vessel which is made of fiber-glass reinforced resin to save weight. The corresponding H_2 vessel has a capacity of 1.6 l.

As explained by *A. Winsel* (Varta AG, Frankfurt/M., Germany), the Varta company constructs H_2/O_2 cells with DSK electrodes[1] containing Raney nickel as active component in the anode and, in the cathode, Raney silver or silver precipitated by a special process. Electrodes functioning on one side are used in 50 W batteries which are designed to operate at 50–60 °C. For higher performance, Janus electrodes are preferred that can be charged on both sides and are sealed after lamination with epoxide resin. A pressure electrolysis apparatus with valve electrodes is stated to compensate for gas losses from the cells on long storage. Further, gas production can be achieved by catalytic decomposition of hydrazine, boranate, or peroxide by using Janus electrodes that have inactive fine-pored covering layers and a catalytically active middle layer.

In their paper *P. Dubois* and *J. Jacquelin* (Compagnie Générale d'Electricité, Marcoussis, France) described a 1 kW battery for hydrogen and oxygen. The modules are constructed of 12 double-sided electrodes which are sintered from nickel and silver (33 wt.-%). The battery contains 32 modules. The stated performance is reached at a working temperature of 55 °C. The cells alone weigh 70 kg. They are not yet optimized. Attempts are under way to replace the 2 mm thick sinter electrodes by thinner ones; this should reduce the Ag content to a few percent.

H. J. R. Maget (General Electric Company, Lynn, U.S.A.) described air-operated cells with ion exchange membranes onto both sides of which electrodes containing noble metal are pressed. For the membrane material a polymer from sulfurized α,β,β-trifluorostyrene is used, which is appreciably more resistant to oxidation than the sulfurized styrene used previously. It is chemically stable at temperatures up to 70 to 90 °C. The cathode is made hydrophobic with 10 % Teflon; thus the water produced is in the form of droplets which are not carried away immediately in the stream of air. The air becomes heated on the electrode, so that circulation is favored by a chimney effect. The operational efficiency amounts to 50 %. The current density can reach 120 mA/cm^2. A fuel cell battery with a nominal performance of 300 W has been run for 8000 hours with an output of 15 W.

3. Cells with Dissolved Fuel

W. Vielstich (University, Bonn, Germany) divides catalysts for anodic oxidation of hydrazine into three groups. Raney metals give rise to a potential more negative than that of the hydrogen electrode and they afford a measurable current even at the hydrogen potential. Noble metals such as platinum set up the hydrogen potential, but silver, gold, and active charcoal lead to anodic currents only at very positive potentials. – Two mechanisms can be considered for the oxidation of hydrazine: according to one of them a mixed potential is set up, and according to the other there is elimination of H before passage of the current. An attempt to differentiate between the two possible mechanisms by analyzing the gases formed at a defined anodic current strength was unsuccessful. However, the disturbance of an O_2 cathode by hydrazine can be explained as due to formation of an O_2/N_2H_4 mixed electrode.

H. H. von Döhren, D. Sparbier, and *G. Wolf* (Varta AG, Kelkheim, Germany) reminded the audience that skeletal nickel is useless for acceleration of the oxidation of methanol below 80 °C. However, with platinum on carbonylnickel as carrier in 8 N KOH at 18 mA/cm^2 a cell potential of 0.4 V is obtained. A 55 W battery contains 15 cells, arranged in electrical series, with silver-catalyzed O_2 electrodes. Janus cathodes permit use of a higher O_2 pressure (about 1 atm) whereby the output can be increased. Whereas formaldehyde reacts very rapidly on this catalyst, the intermediate formate produced becomes enriched in the electrolyte during discharge and is converted only as the methanol concentration decreases.

M. Futterer, H. G. Plust, and *C. G. Telschow* (Brown Boveri & Cie, Baden, Switzerland) have also chosen platinum on porous nickel for anodes in methanol batteries, using, however, a hydrophobized charcoal-air electrode as cathode. The selectivity of this electrode for reduction of O_2 was so much improved that the self-discharge corresponds to a current of only 18–20 μA/cm^2. Prolonged output from 20 W methanol-air batteries is effected with 1 to 5 mA/cm^2. Thermal insulation of the batteries permits operation at external temperatures down to −30 °C.

4. Cells with Molten Carbonate as Electrolyte

If Al_2O_3 is heated with an excess of Li_2CO_3 at 650 °C, a molten electrolyte is formed with lithium aluminate as matrix, which according to *A. Salvadori, M. Louichon*, and *C. Lebras* (Gaz de France, La Plaine Saint Denis, France) has considerable advantages over the paste-form electrolytes used so far. Even at this high operating temperature natural gas cannot be oxidized directly but must first be reformed. Nickel is the active constituent of the anode. On the cathode side, copper oxide mixed with active silver prevents the undesirable increase in granule size.

[1] DSK electrodes are double skeleton catalyst electrodes.

The solubility of O_2 is interesting because of the chemical short-circuit that it may cause, even in molten electrolytes. *M. Schenke* and *G. H. J. Broers* (C.T.I.–T.N.O., Amsterdam, Netherlands) have determined the solubility by amperometric titration with solid Na_2SO_3. A concentration of 0.4×10^{-6}mole of oxygen per cm^3 was found in alkali carbonate mixtures at 700 °C under 1 atm pressure of oxygen. During studies of cathode corrosion the solubility of silver and of copper oxide was determined and also estimated by calculation. The solubility of the Ag^+ ion is about 4×10^{-5} g/cm^3 at 700 °C, which is in approximate agreement with the calculated value. The solubility of CuO is lower than that of Ag^+ but higher than its estimated value.

5. Fuel Cells with Reformer

W. Frie (Siemens A.G., Erlangen, Germany) has calculated the thermodynamic equilibria that can exist during the production of hydrogen by treatment of methanol with steam. The following components were taken into account: H_2, CH_4, CH_3OH, CH_2O, HCOOH, CO_2, CO, H_2O, $(CH_3)_2O$, and carbon. The selectivity of a catalyst can not be calculated thermodynamically. However, the curves reproduce the experimental findings satisfactorily even though methane and carbon are not taken into account.

M. Prigent, C. Dezael, and *O. Bloch* (Institut Francais du Pétrole, Rueil-Malmaison, France) have compared direct oxidation of methanol with oxidation after previous steam-reformation. Complete conversion of the methanol was achieved even at 200 °C with copper chromite and ferrite as catalyst. Owing to the low reaction temperature the CO content of the reformate is between 0.2 and 0.8 %. The authors believe it possible to attain an efficiency of 70 % for the reformer, of 60 % for the fuel cell, and thus of about 40 % for the complete set-up with a weight of 30 kg/kW. This should be compared with a direct methanol-oxidation cell which with a cell potential of 0.4 V has an efficiency of about 30 % and a weight of about 33 kg/kW. A comparison of the amounts of platinum used in the anodes also comes out in favor of the cell with the reformer.

F. L. Gray (Texas Instruments Inc., Dallas, Texas, U.S.A.) has studied steam reformation and partial oxidation as preliminary processes before introduction of the fuel gas into cells containing eutectic carbonate melts and oxide matrices. The new cells with double-sided cathodes produce 20 mW/cm^2. A 500 W battery is attached to a propane reformer. Partial oxidation of petroleum gas is to be tested in a 1 kW fuel cell apparatus. It seems possible to achieve a life of 1000 h for the battery. The starting up time from the cold amounts to 40 min, and the overall efficiency to 15 %.

[VB 99 IE]

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Rapid Chemical Separations for the Study of Short-lived Atomic Nuclei

By *G. Herrmann* [*]

Extremely neutron-rich atomic nuclei of about 40 elements may be obtained by nuclear fission. For examination of their properties these nuclides, whose half-lives amount to a few seconds, must be isolated by rapid chemical separations. To achieve this one may either speed up the usual methods of chemical analysis or utilize special nuclear-chemical effects.

The first method was illustrated by the following examples: Precipitation reactions are replaced by isotope- and ion-exchange on preformed precipitates, for instance, of halogen nuclides on silver halides or of alkali nuclides on salts of heteropolyacids. Solvent extractions may be accelerated by placing the extracting solvent on a finely divided powder through which the aqueous solution is then rapidly sucked; protactinium isotopes (in concentrated hydrochloric acid) can be separated in this way from a large excess of fission products when diisobutyl carbinol is used as solvent. Also, the formation of volatile hydrides of arsenic, selenium, antimony, and tellurium occurs very rapidly on addition of zinc to their acid solutions under suitable conditions – small volumes of concentrated hydrochloric acid and large amounts of fine zinc powder. Nuclear-chemical effects that can be used for rapid separations include β-recoil from solid surfaces,through which the materials produced from short-lived β-emitters leave a sample and are deposited on a foil; the yields admittedly depend more on the recoil energy than on the chemical properties. More specific are chemical reactions between recoil atoms and gaseous reactants when these yield volatile compounds, *e.g.* reaction of fission iodine with methane to give methyl iodide.

The applications of these procedures to the study of short-lived nuclides was illustrated by means of work carried out on neutron emitters present in fission products. After pulsed irradiation in the Mainz reactor, new neutron emitters of half-life down to 0.8 sec (^{140}I) were detected, and their contributions – as well as the contributions of known neutron emitters – to delayed neutron emission on fission of uranium-235 by thermal neutrons was measured [1].

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[1] *H. D. Schüssler, W. Grimm,* and *G. Herrmann,* Angew. Chem. *79*, 1018 (1967); Angew. Chem. internat. Edit. *6*, 998 (1967).

Recent Findings in the Organic Chemistry of Tin and Lead

By *W. P. Neumann* [*]

Recent development of the organic chemistry of tin is characterized by surprising possibilities of effecting reactions with compounds containing Sn–H, Sn–N, and Sn–O groups. Interest has centered more and more on the use of organotin compounds for syntheses in organic chemistry and on the study of reaction mechanisms [1].

The long Sn–H bond (1.70 Å) is not strongly polar but is readily polarizable, thus permitting three types of reaction: *Hydride transfer* is the first step in the smooth 1,4-addition that yields ketene *N*-stannylimines *(1)* (where Y is, *e.g.*, NR_2, OR, H, Cl, or NO_2), which react with numerous compounds of the type ROH, RX, and R–COX:

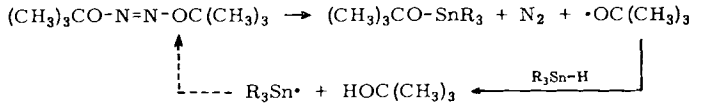
$$p\text{-Y}-C_6H_4-CH=C(CN)_2 + R_3Sn-H \rightarrow p\text{-Y}-C_6H_4-CH_2-C(CN)=C=N-SnR_3 \quad (1)$$

Many hydrostannations proceed by *radical mechanisms*. The Sn-H group is here disclosed as a very powerful radical trapping agent:

$$R'\text{-}CH=CH_2 + R_3Sn\cdot \longrightarrow R'\text{-}\dot{C}H\text{-}CH_2\text{-}SnR_3 \xrightarrow{R_3SnH} R_3Sn\cdot + R'\text{-}CH_2\text{-}CH_2\text{-}SnR_3$$

The hydrogen is eliminated as a *proton* in condensations with stannyl compounds $R_3Sn^{\delta\oplus}-X^{\delta\ominus}$, where advantageously $X = -N(C_2H_5)_2$.

The radical decomposition of diacyl peroxides is extremely powerfully induced by stannyl radicals. As shown by ^{18}O labeling, they attack the O–O bridge, the more readily the more the bridge is deprived of electrons by the influence of substituents. Radical decomposition of numerous azo compounds, R–N=N–X–R or R–X–N=N–X–R, is also powerfully induced, *e.g.*:



Here again electron deficiency on X is important. In every case investigated the mechanism is synchronous (S_R2).

Now experimental difficulties have been overcome, the organic chemistry of lead is developing rapidly[2]. On the basis of the observation that negative substituents, X, on lead can be readily replaced[2], sensitive organolead hydrides are no longer prepared in the pure state but are formed *in situ* by the following equilibria:

$$R_3Pb-CH_2-CH=CH_2 + R_3'SnH \rightleftarrows R_3'Sn-CH_2-CH=CH_2 + R_3PbH$$

$$(R_3Pb)_2O + 2\,R_3'SnH \rightleftarrows (R_3'Sn)_2O + 2\,R_3PbH$$

They are valuable for specific hydrogenations and are useful for additions to C=C, C≡C, SCN-, and OCN-groups (with conjugated systems 1,4-addition is possible), and also as catalysts for polyadditions.

N,N-Dialkylplumbylamines (*e.g.*, $R_3Pb-N(C_2H_5)_2$) can also undergo numerous 1,2- or 1,4-additions, *e.g.*, to isocyanates, nitriles, isocyanides, aldehydes, or carbodiimides. In this way –O–Pb– or new –N–Pb– groups are formed and further syntheses become readily accessible.

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[1] For a recent review see *W. P. Neumann*: Die Organische Chemie des Zinns. Enke Verlag, Stuttgart 1967.

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Nuclear Resonance Studies of Molecular Movements and Phase Changes in Solid Organic Substances

By *W. Müller-Warmuth* [*]

Toluene is an example of a system with several solid phases. Its properties can be continuously varied, by careful supercooling, over a wide range from the mobile to the highly viscous glassy phase. A crystalline phase also exists. Transition of the phases into one another can be followed by the temperature-dependence of the spin-lattice relaxation and by the second moments of the nuclear resonance curves.

Hindered rotation of the methyl group was studied for a number of solid ethers[1]. Many ethers are crystalline, some are glassy, and some exist in several phases side by side, depending on the thermal treatment. The marked narrowing of the ^1H–NMR lines that is observed on phase transition from the glassy to the crystalline state well below the melting point can be interpreted as isotropic movements of whole molecules.

Although rotation of the methyl groups normally leads to line narrowing and maxima in the relaxation rates only at elevated temperatures (usually above 77 °K), the second moment for all three xylenes was lower by a factor of 2 than that expected for a rigid lattice, even at very low temperatures (2 °K)[2]. Relaxation studies gave a similar surprising result[2]. With a working frequency of about 14 MHz, maxima in the spin-lattice relaxation occurred at 77 °K (*o*-xylene), 51 °K (*p*-xylene), and 16 °K (*m*-xylene). The values for the relaxation decreased only very slowly with decreasing temperatures. This behavior can be explained as due to reorientation processes of the methyl group by a tunnel effect. This mechanism is effective even at very low temperatures for the torsion ground state. In the relaxation, restrictions to energy transfer between various degrees of freedom in the organic solid can be noticed. A cosine law with two terms for the contributions with six-fold and three-fold symmetry serves as potential function. The potential barriers lie between 0.2 and 2.3 kcal/mole.

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[1] *K. Grude, J. Haupt*, and *W. Müller-Warmuth*, Z. Naturforsch. *21a*, 1232 (1966).

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Investigation of Proton-Transfer Processes by Electrochemical Relaxation Techniques

By *H. W. Nürnberg* [*]

The dissociation and recombination of carboxylic acids in aqueous solution is an important example of proton-transfer processes that are of significance in many chemical and biochemical reactions. The rate constants of these very fast reactions ($\tau_{1/2} \approx 10^{-6}$–$10^{-8}$ sec) can, for example, be determined by suitable voltammetric techniques when the equilibrium

$$HA \underset{k_r}{\overset{k_d}{\rightleftharpoons}} H^{\oplus} + A^{\ominus}$$

is displaced by means of the coupled electrode process of hydrogen evolution at mercury

$$H^{\oplus} + e^{\ominus} \rightarrow {}^1/_2\,H_2$$

and the velocity is measured *via* the current passing the electrode or a component of this current.

The rate constants k_d and k_r can be determined from the limiting current values that are obtained from the resulting current-voltage curve (polarogram) provided that the current is measured so fast ($t_1 \approx 30$–1 μsec) that it is not merely the rate of diffusion of the reaction components that determines the value of the current. The method of High Level Faradaic Rectification[1] enabled satisfactory measurements to be made for the first time in the μsec range and thus made possible the determination of kinetic data for 17 structurally different carboxylic acids[2]. The results are corrected for the influence of double layer effects at the electrode[3] and are therefore the true values in 1 M lithium halide solution.

On the basis of the results obtained, the following conclusions may be drawn: In many cases the carboxylic acids behave normally, *i.e.* recombination is diffusion controlled in each case with the same k_r value, and k_d is proportional to the equilibrium constant K_c. The order of the values of k_d and K_c is in general agreement with the extent of inductive and mesomeric effects arising from the structure of the respective acid.

Deviations from normal behavior exist (i) in the case of α- and *ortho*-hydroxy acids because of the tendency toward formation of intramolecular hydrogen bonds with the carboxyl group in the acid anion and (ii) in the case of acids having an alkyl group in the γ or the *ortho* position. These hydrophobic groups render the structure of the water in their neighborhood more rigid and thus make more difficult the reorientation of the water molecules to form hydrogen-bond systems, between the acid anion and the hydrated proton ($H_9O_4^{\oplus}$), that are suitable for proton transfer. In 1 M lithium halide solution, the value of $k_r = 3.7 \times 10^{10}$ indicates that this intermolecular hydrogen-bond system extends on average over 13.5 Å, *i.e.* over about five water molecules.

In general, these results confirm the view first put forward by *Eigen*[4] that an intermolecular hydrogen-bond system extending over several water molecules is of decisive importance for proton transfer in the course of dissociation and recombination. This hydrogen-bond system also plays an important role in the reduction of $H^{\oplus}$ ions at an electrode, *i.e.* in the transfer of a proton to the electrode surface immediately preceding the rate-determining charge-transfer step.

The linear $k_d - K_c$ relationship that is characteristic of normal behavior corresponds to a linear entropy relationship since the measurements were made within a temperature range (*ca.* 20 °C) where $-\log K_c$ goes through a flattened maximum where $\Delta H \approx 0$ and $\Delta H_d^{\ddagger} \approx H_r^{\ddagger}$.

The significance of the entropy, and consequently of the orientation of the solvent molecules in the initial, transition, and final states of dissociation, is thus clearly emphasized. In general, the more hydrophilic an acid is (*i.e.* the lower the decrease in entropy of the system acid molecule plus surrounding solvent molecules on dissociation), the more rapidly and completely will it dissociate. The influence of inductive and mesomeric effects arising from the structure of the respective acid corresponds to this entropy relationship and is in fact its cause.

Lecture at Bonn on June 20, 1967 [VB 100 IE]
German version: Angew. Chem. *80*, 84 (1968)

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[1] *G. C. Barker* and *H. W. Nürnberg*, Naturwissenschaften *51*, 191 (1964).
[2] *H. W. Nürnberg*, Fortschr. chem. Forsch. *8*, 241 (1967).
[3] *H. W. Nürnberg*, Disc. Faraday Soc. *39*, 136, 160 (1965).
[4] *M. Eigen*, Z. physik. Chem. NF. *1*, 154 (1954).

SELECTED ABSTRACTS

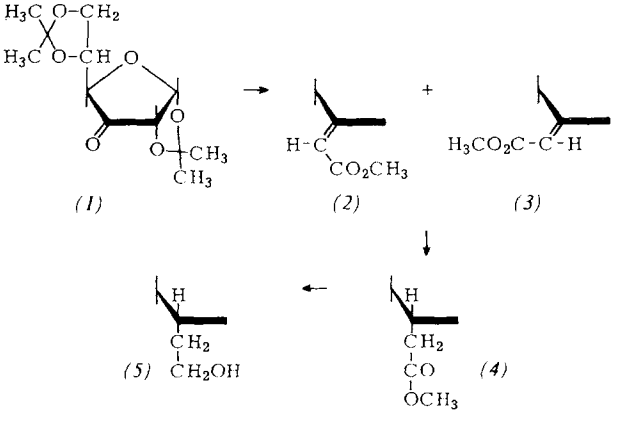
Tris(triphenylphosphine)cobalt dihydride, $H_2Co(P(C_6H_5)_3)_3$, *(1)*, a complex that binds molecular nitrogen, has been prepared by *A. Misono, Y. Uchida, T. Saito,* and *K. M. Song*, by the reaction of Co(III) acetylacetonate, triphenylphosphine, and triisobutyl-aluminum in ether at 10 °C in the presence of H_2; yellow crystals, 50 % yield. The complex is very sensitive to air and decomposes at 77 °C under vacuum, with liberation of H_2 and benzene. Under nitrogen, the color of the benzene solution changes from brown to red, and orange crystals of $N_2Co(P(C_6H_5)_3)_3$ can be precipitated with petroleum ether. *(1)* takes up CO in exchange for hydrogen, and hydrogenates ethylene at room temperature. / J. chem. Soc. (London) C *1967*, 419 / –Ma. [Rd 729 IE]

7-, 8-, and 9-membered silacyclic hydroxy and oxo compounds containing functional groups were synthesized for the first time by *R. A. Benkeser* and *R. F. Cunico*. Pyrolysis (400–500 °C) of dimethylbis(3-carbomethoxypropyl)silane in the presence of $ThCl_4$ gave 1,1-dimethylsilacyclooctan-5-one (2,4-dinitrophenylhydrazone: m.p. 134.5–135 °C). Acyloin ring closure of dimethylbis(3-carbomethoxypropyl)silane with sodium in toluene gave a mixture of 1,1-dimethyl-6-hydroxysilacyclononan-5-one and 1,1-dimethylsilacyclononan-5-ol (yield 47 %).The acyloin ring closure of dimethylbis(2-carbomethoxyethyl)silane gave 1,1-dimethyl-5-hydroxysilacycloheptan-4-one (yield 28 %), which yielded 1,1-dimethylsilacycloheptan-4-one on reduction (treatment with propanethiol, $ZnCl_2$, and HCl gas in benzene, then with $HgCl_2$–$CdCO_3$ in aqueous acetone). / J. org. Chemistry *32*, 395 (1967) / –Ma. [Rd 686 IE]

Xanthine oxidase from milk is catalytically active even in anhydrous organic solvents. *F. R. Dastoli* and *S. Price* measured the oxidation of crotonaldehyde by methylene blue, which is catalyzed by the xanthine oxidase, in a series of solvents in which the salt-free lyophilized enzyme was completely insoluble. The reaction rates (V_{max}) were higher than 10 % of the rate in water (for 0.05 M potassium phosphate; pH= 7.5); large differences in the Michaelis constants for crotonaldehyde were found (water: K_M = 3 mM; acetone: K_M = 1; *o*-dichlorobenzene: 8; furan: 8; benzene: 17; thiophene: 20; pyridine: 70; toluene: 120). / Arch. Biochem. Biophysics *118*, 163 (1967) / –Hö. [Rd 709 IE]

The conversion of phenylalanine into lignin-forming glucosides has been observed by *K. Freudenberg* and *J. Torres-Serres* following the administration of the ^{14}C-labeled compound to young spruce branches. Gluco-*p*-coumaryl alcohol, coniferin, and syringin were formed in a few days. Two other labeled compounds were presumably glucosides of piceatannol. / Liebigs Ann. Chem. *703*, 225 (1967) / –Ma. [Rd 722 IE]

A new route to branched sugars by a modified Wittig reaction with ketoses is reported by *A. Rosenthal* and *L. (Benzing) Nguyen*. When *e.g.* 1,2;5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose *(1)* in DMF at 0 °C is made to react with an ice-cold solution of trimethyl phosphonoacetate and K *tert*-butoxide in DMF (20 hours, 20 °C), followed by



reduction of the sugars *(2)* and *(3)* to the methoxycarbonylmethyl derivative *(4)* and reduction of *(4)* with $LiAlH_4$, the product obtained is 3-deoxy-3-*C*-(2-hydroxyethyl)-1,2;5,6-di-*O*-isopropylidene-α-D-allofuranose *(5)*. / Tetrahedron Letters *1967*, 2393 / –Ma. [Rd 724 IE]

Insertion of dihalogenocarbenes into Si-Hg and Ge-Hg bonds, according to *D. Seyferth, R. J. Cross,* and *B. Prokai,* occurs in the reaction of bromodichloromethyl- (or dibromochloromethyl)phenylmercury with bis(trimethylsilyl)- or bis(trimethylgermyl)mercury (molar ratios 2:1; in benzene at 65–75 °C; 70 min). The principal products are trihalogenovinyltrimethylsilane or -germane, which are obtained in yields of 43 or 63 % respectively (filtration; gas-liquid partition chromatography). A plausible reaction sequence is given, but it is not yet certain whether the rate-determining step is a bimolecular reaction between the two Hg compounds or the decomposition of $C_6H_5HgCCl_2Br$.

$$((H_3C)_3Si)_2Hg + H_5C_6Hg{-}CCl_2Br \xrightarrow[-H_5C_6HgBr]{} (H_3C)_3Si{-}Hg{-}CCl_2{-}Si(CH_3)_3$$

$$(H_3C)_3Si{-}Hg{-}CCl_2{-}Si(CH_3)_3 \xrightarrow{+H_5C_6HgCCl_2Br} (H_3C)_3Si{-}Hg{-}CCl_2{-}CCl_2{-}Si(CH_3)_3 \longrightarrow$$

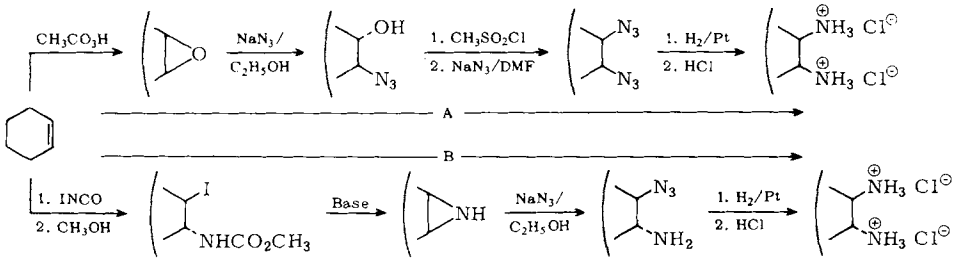
$$(H_3C)_3SiHgCl + (H_3C)_3Si{-}CCl{=}CCl_2$$

$$\downarrow$$

$$(H_3C)_3SiCl + Hg$$

/ J. organometallic Chem. *7*, P 20 (1967) / –Jg. [Rd 744 IE]

A method for the stereospecific synthesis of vicinal diamines has been developed by *G. Swift* and *D. Swern* using sterically pure compounds in stereospecific reactions that proceed in good yields. Routes A and B, which lead to the stereoisomers, can be illustrated for cyclohexene:



This method represents an important advance, particularly in the stereospecific synthesis of aliphatic vicinal diamines. *meso*-3,4-Diaminohexane dihydrochloride (route B) and *threo*-3,4-diaminohexane dihydrochloride were obtained from *trans*-3-hexene in yields of 72 and 35 % respectively. Since both *cis*- and *trans*-4-methyl-2-pentene could be used in the pure state, it was possible to check that all the reactions of routes A and B proceed smoothly and specifically; of the four products the pairs obtained by opposite routes are identical in all their properties (yield: 62–71 % by route A, 59–60 % by route B). / J. org. Chemistry *32*, 511 (1967) / –Jg. [Rd 747 IE]

A precursor of the biosynthesis of insulin has been isolated by *D. F. Steiner* and *P. E. Oyer* from incubates with human tumor tissue (tumor of the Langerhans' islets). They detected the incorporation of [^{3}H]-leucine and [^{3}H]-phenylalanine into insulin and a high molecular weight protein. The latter has a molecular weight of about 10800 (insulin 6000) and an N-terminal phenylalanine (as does the B chain of insulin), and exhibits immunological relationship to insulin. Unlike insulin, however, the protein is not split into two chains by sulfitolysis. Treatment of this high molecular weight protein with small quantities of trypsin yields a product that behaves chemically and immunologically like insulin. This observation supports the hypothesis that the two polypeptide chains of insulin are synthesized as a single chain. The proteolytic attack would then take place after the configuration of insulin has been formed. / Proc. nat. Acad. Sci. USA *57*, 473 (1967) / –Scha. [Rd 726 IE]

The tricyanovinylation of aromatic compounds without electropositive substituents, according to *R. Henderson* and *W. A. Sheppard,* can be achieved with tetracyanoethylene (TCNE) if the latter is made more electrophilic by complex formation with $AlCl_3$. Benzene, toluene, fluorobenzene, and naphthalene react in this way (see table), but durol (sterically hindered) and chlorobenzene do not. The benzene derivative, for example, is obtained by heating of a deep red-brown TCNE/$AlCl_3$ solution (molar ratio 1:1) in benzene for 1 hour, chromatographic separation on Al_2O_3, recrystallization from benzene or acetonitrile, and sublimation.

Ar	Ar–C(CN)=C(CN)$_2$	
	m.p. (°C)	yield (%)
C_6H_5	98.3–99.2	35
p-CH_3–C_6H_4	115.5–117	23
p-F–C_6H_4	122–123	17
β-naphthyl	174–178	20

/ J. org. Chemistry *32*, 858 (1967) / –Jg. [Rd 749 IE]

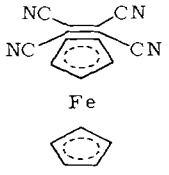
Two L-asparaginases (L-asparagine amidohydrolase, EC 3.5.1.1), of which only one exhibits antitumor activity, have been isolated by *H. A. Campbell et al.* from *Escherichia coli* B. L-Asparaginase has been known for some time as the effective antitumor agent in guinea-pig serum, while this enzyme from yeast or *Bacillus coagulus* is ineffective. The two new enzymes differ in their solubility properties, their chromatographic behavior, and their activity as a function of pH. The authors purified the antitumor fraction by a factor of 90; a glutaminase activity of 2 % appears to be a characteristic of the enzyme. / Biochemistry *6*, 721 (1967) / –Scha. [Rd 725 IE]

The vapor pressure above the calcium carbide phase has been determined by *R. H. Flowers* and *F. C. W. Pummery* between 1250 and 1950 °K for equilibrium conditions by the Knudsen effusion method:

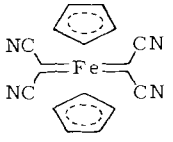
$$4.575 \log p = (-49000 \pm 950)/T + (13.3 \pm 0.6).$$

Pure calcium carbide, $CaC_{2.05 \pm 0.03}$, was prepared from graphite and calcium (purity: 99.9 %; impurities Mg and Al) in a helium atmosphere. The gas phase consists almost entirely of monoatomic Ca (target quantities: 1 to 20 μg); carbon does not vaporize in appreciable quantities. In the range CaC_2 to $CaC_{3.5}$, the vapor pressure is independent of the excess of carbon, *i.e.* an independent C phase is present for Ca:C > 1:2. Since the heat of vaporization of Ca (L_{298} = 42.4 ± 0.4 kcal mole^{-1}) and the specific heat of CaC_2 are well known, the standard heat of formation of CaC_2, $-(\Delta H^0_{298} - L_{298}) = -13.1 \pm 1.5$ kcal mole^{-1} (SrC_2: −20.2 ± 3, BaC_2: −19.5 ± 3) can be calculated very accurately from the average of the enthalpies of formation (according to the 2nd and 3rd laws), $\Delta H^0_{298} = 55.5 \pm 1.5$ kcal mole^{-1} for the reaction CaC_2 (solid) → Ca(gas) + 2 C (solid). / J. inorg. nuclear Chem. *29*, 311 (1967) / –Jg. [Rd 727 IE]

The bonding in the ferrocene-tetracyanoethylene (TCNE) adduct (1:1) has been elucidated by *R. L. Collins* and *R. Pettit* by Mössbauer spectroscopy of the ^{57}Fe nucleus (10 mCi source; ^{57}Co in Cu). Since 1962, both the ferrocenium tetraethylide and the charge-transfer structures had been considered possible. The spectra of free ferrocene and of the TCNE adduct at 77 °K are extremely similar (isomeric shift: + 0.475 ± 0.01 and 0.465 ± 0.01 mm/s, in relation to iron; quadrupole splitting: 2.400 ± 0.02 and 2.397 ± 0.02 mm/s; Karyagin effect: 1.14:2 and 0.81: 1), whereas ferrocenium dichlorodicyano-*p*-benzosemiquinoide, which is known to be a ferrocenium salt, has a quite different structure.



(1)



(2)

The Fe nucleus is therefore only slightly influenced by the TCNE. A symmetrical and salt-like structure *(2)* can therefore be ruled out in favor of a charge-transfer structure *(1)*, in which the TCNE interacts "from the outside" with only one benzenoid ring. / J. inorg. nuclear Chem. *29*, 503 (1967) / –Jg. [Rd 728 IE]

The ion-exchange properties of a titanium hexacyanoferrate(II) complex having the approximate composition $[(TiO_2)(OH)HFe(CN)_6 \cdot 4H_2O]_n$ have been examined by *K. H. Lieser, J. Bastian, A. B. H. Hecker,* and *W. Hild.* The gel-like product, which can be dried (after which it still contains a total of 21 % of H_2O) and sieved (grain sizes 0.1 to > 1 mm) and is insoluble in water, is obtained by precipitation from 0.5 M $TiCl_4$ + 2 M HCl solution with a 0.4 M acid solution of $K_4[Fe(CN)_6]$ or hexacyanoiron(II). Properties: in contact with H_2O, pH ≈ 3; exchange capacity 1.4 to 1.5 m-eqt/g (theoretical 2.3 m-eqt/g, *i.e.* a maximum of 1 exchangeable proton per $Fe(CN)_6$ unit); specific area 185 m^2/g; stable in 2 M HCl, decomposes slowly in 5 M HCl; above pH = 4 (titration with NaOH), decomposes into $Na_4[Fe(CN)_6]$ + titanium dioxide gel. The selectivity for Cs is very high; the selectivities for the alkali and alkaline earth metals at concentrations of 10^{-8} to 1 mole/l decrease in the order Cs > Rb > K > NH_4 > Na > Li and Ba > Sr > Ca > Mg > Be. Separation factors for some 1:1 solutions at pH = 2.1 to 2.4: Cs/Rb = 5.5, Cs/NH_4 = 42.8, Cs/Li = 23; K/NH_4 = 9.4; Na/Li = 12; Ba/Sr = 4.7, Ba/Be = 27; Sr/Ca = 1.2, Sr/Mg = 9.3. The exchange proceeds rapidly ($\tau_{1/2}$ ≈ 2 min); and is followed by two slower processes having $\tau_{1/2}$ ≈ 10 min and 20 h, respectively. In the pH range between 2.5 and 0, the partition coefficients change by factors of 10 to 1000. / J. inorg. nuclear Chem. *29*, 815, 872 (1967) / –Jg. [Rd 740 IE]

A new process for the synthesis of aminals and enamines has been found by *H. V. Hirsch* in the reaction of tris(dimethylamino)- trispiperidino-, or tris-(1-pyrrolidinyl)arsine with aldehydes or ketones. Aminals are formed if there is no vicinal hydrogen present (eq. (a)); otherwise, dialkylamine is eliminated to form enamines (eq. (b)).

$$2\ As(N(CH_3)_2)_3 + 3\ R{-}CO{-}R' \xrightarrow[-As_2O_3]{} 3\ R{-}C(N(CH_3)_2)_2{-}R' \qquad (a)$$

$$2\ As(N(CH_3)_2)_3 + 3\ R_2CH{-}CO{-}R' \xrightarrow[-As_2O_3]{-3\ HN(CH_3)_2} 3\ R_2C{=}CR{-}N(CH_3)_2 \qquad (b)$$

Examples of compounds prepared are:

Aminals	B.p. (°C/mm)	Yield (%)
ω,ω-Bis(dimethylamino)toluene	51/2	73
Bis(dimethylamino)methane	77	84
Enamines		
1-Piperidinocyclohexene	70/2	75
α-(1-Pyrrolidinyl)styrene	75/1	25
4-Dimethylamino-*N*-methyl-Δ^3-piperideine	76/10	83

/ Chem. Ber. *100*, 1289 (1967) / –Jg. [Rd 745 IE]

All the fluorotelluric acids $TeF_n(OH)_{6-n}$ have been prepared by *L. Kolditz* and *I. Fritz*, those with $n = 1$ to 4 were obtained from telluric acid and hydrofluoric acid, while pentafluorotelluric acid, was obtained from barium tellurate and fluorosulfuric acid. The solid mixture of fluorotelluric acids can be resolved by paper or column chromatography at 0 °C on cellulose (eluent: 75 ml of propanol + 25 ml of H_2O + 5 g trichloroacetic acid), the R_f values being as follows:

$n = 5$	$n = 4$	$n = 3$	$n = 2$	$n = 1$	$n = 0$
0.980	0.854	0.745	0.577	0.365	0.264

The main products, di- and tetrafluorotelluric acids, are more strongly acidic than $Te(OH)_6$; they are monobasic to weak bases (*e.g.* pyridine, quinoline) and dibasic to strong bases. The reaction of $Te(OH)_6$ with KF in aqueous solution without further acidification yields a product $Te(OH)_6 \cdot 2KF$, which is stable even in contact with the solution. Since (a) the IR spectrum does not contain H_2O bands, (b) all the fluorine can be titrated with $ZrOCl_2$, and (c) a mixture of $Te(OH)_6$ + KF can be ruled out by X-ray analysis, the product is evidently a complex in which the coordination number of Te is increased. / Z. anorg. allg. Chem. *349*, 175, 184 (1967) / –Jg. [Rd 741 IE]

The fluorination of cyanogen chloride, according to *J. B. Hynes, B. C. Bishop,* and *L. A. Bigelow*, leads under mild conditions to interesting fluorination products containing both Cl and N. In the direct process, ClCN diluted with N_2 was injected into pure F_2 at 94 °C (F:ClCN:N_2 = 5.3:1:10); in the indirect process a Cl_2-ClCN mixture (1:6 to 2:1) was condensed on an excess of AgF_2 at –196 °C, and the autoclave was brought to room temperature over a period of 20 hours. In both cases the mixture was resolved by rectification and gas chromatography.

CF_3NClF	b.p. –32.8 °C; colorless stable gas; first "organic" compound having the formula RNClF; typical mass-spectrometric component: ClN^+
$CClF_2NF_2$	a little; colorless stable gas; typical mass-spectrometric components: CF^+, Cl^+, CF_2^+, CF_3N^+, $CClF_2^+$, CF_4N^+
$CF_3N{=}NCClF_2$	b.p.5.8 °C; yellow liquid; heat of dilution = 5.86 kcal $mole^{-1}$ Trouton const. = 21.0 cal deg^{-1} $mole^{-1}$
CF_3NCl_2	b.p. 14.9 °C; heat of dilution = 6.1 kcal $mole^{-1}$; very stable to dilute alkali; photolyzes to $CF_3N = NCF_3$

/ Inorg. Chem. *6*, 417 (1967) / –Jg. [Rd 746 IE]

Neuere Methoden der Präparativen Organischen Chemie. (New methods of preparative organic chemistry). Edited by *W. Foerst*. Verlag Chemie, Weinheim/Bergstr., Vol. IV. 1066. viii, 304 pp. 2 figures, 44 tables, bound DM 38.–; Vol. V 1967, viii, 280 pp., numerous figures and tables, bound DM 38.–.

After the appearance of the first volume in 1944, "Neuere Methoden" made its mark within a short time, and was used, not only as a convenient and very useful source of information to the chemist engaged in preparative work, but also by advanced students preparing for examinations. This tradition was carried on in 1960 by the second and third volumes [1], and the present review deals with Volumes IV and V. Like the earlier volumes, they contain a selection of articles from recent volumes of Angewandte Chemie, and deal exclusively with important and recent methods of preparative organic chemistry.

Volume IV: α-Additions to isonitriles, triple additions, and four-component condensations (*I. Ugi* 1962 [2], revised 1965); the text has been rearranged, the nomenclature has been partly improved, and nsiderable supplementary material has been added in places. Isonitrile syntheses (*I. Ugi et al.* 1965, revised 1965). Reactions of sodium hydrazide with organic compounds (*Th. Kaufmann et al.* 1964, revised 1965); a number of new findings and numerous procedures have been added. Ethynation reactions (*W. Ried* 1964, revised 1965); Parts I and II have been combined, and supplementary material has been added in places. Syntheses with nascent quinones (*H. W. Wanzlick* 1964), cyclization of dialdehydes with nitromethane (*F. W. Lichtenthaler* 1964, revised 1965). Use of complex boron hydrides and of diborane in organic chemistry (*E. Schenker* 1961, revised 1965). This article has been completely rearranged, and now contains 1700 references instead of 865 and 49 procedures instead of 22. This contribution is a most valuable review of this extremely important and rapidly developing method.

Volume V: New reactions of alkylidenephosphoranes and their preparative uses (*H. J. Bestmann* 1965); the three parts, which were originally published separately, have been combined. Syntheses with heterocyclic amides (azolides) (*H. A. Staab* and *W. Rohr* 1962, revised 1966); many results from recent years and 11 procedures have been added. Organic syntheses with imides of sulfur dioxide (*G. Kresze* and *W. Wucherpfenning* 1967). Syntheses of naturally occurring fatty acids by sterically controlled olefination of carbonyl compounds (*L. D. Bergelson* and *M. M. Schemjakin* 1964, revised 1965). Syntheses with *s*-triazine (*Ch. Grundmann* 1963, revised 1965). Silylation as an aid in organic synthesis (*L. Birkhofer* and *A. Ritter* 1965, revised 1965). Organosodium and organopotassium compounds (*M. Schlosser* 1964, revised 1965); Parts I and II have been modified and combined, and some of the procedures have been revised.

All the contributions now contain very useful procedures, either in the body of the text or at the end, which may be used directly. Each volume again contains an index of reactions and compounds. The articles are very readable, since they are clear and not too long. The authors have spared no effort to present their own fields in a convenient form. The formulas and the presentation are very good, and printing errors are rare (*e.g.* IV, p. 172). The printed area of Angewandte Chemie has been halved horizontally. Those who regret that this again makes the books wider than they are high (21×18.5cm), so that they spoil the appearance of the row of books on the shelf, can console themselves with the modest price that can be achieved in this way.

Many may think that an important preparative method would be better described in a detailed monograph or handbook. However, there are many points in favor of the publication and continuation of this series. These are not subjects that can already be found in specialized books, but new developments, which ought to be made known as soon as possible. In this way, many interesting points can be presented for which a complete and final description is not as yet worth while.

Readers of Angewandte Chemie may think that they have no need for these volumes, but a given preparation will be easier to find in Neuere Methoden than in Angewandte Chemie, and in addition will contain more recent information.

Another advantage is the collection of unrelated topics. The study of these volumes must be recommended to every chemist and postgraduate student. They provide a broad view of progress in preparative organic chemistry, and are also excellently suited for revision by subscribers to Angewandte Chemie before examinations. *H. Musso* [NB 685 IE]

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[1] Cf. Angew. Chem. *76*, 511 (1964).

[2] Year in which the article appeared in Angewandte Chemie.

Mikromethoden für das klinisch-chemische und biochemische Laboratorium (Micromethods for the Clinical Chemistry and Biochemistry Laboratory). By *H. Mattenheimer*. Verlag Walter de Gruyter & Co., Berlin 1966. 2nd Edit., x, 223 pp., 35 figures, plastic cover DM 30.

The publication of a second revised and enarged edition of "Mikromethoden" is very welcome. The micromethods, developed more than 30 years ago by *K. Linderstrøm-Lang* and *H. Holten*, are finding increasing application in clinical chemistry and biochemistry laboratories wherever it is necessary to investigate small quantities of material. The book describes apparatus and general procedures, then deals with special procedures for chemical and enzymatic determinations, determinations of enzyme activities in the biological fluids and in tissue samples, and finally with ultramicro methods for the determination of enzymes. The methods described are nearly all colorimetric, with the emphasis on "optical tests" for the determination of metabolites and enzyme activities.

The book is a valuable aid in the laboratory, particularly for technical personel. The reviewer would recommend that a subject index be compiled for later editions, and that the simplified method given in the appendix for the clinical-chemical determination of glucose in blood should be omitted, since it does not stand up to critical examination.

B. Hess [NB 584 IE]

Der Arbeitnehmer als Erfinder. Seine Rechte und Pflichten. (The Employee as Inventor. His Rights and Obligations.) By *O. Röpke*. W. Kohlhammer Verlag, Stuttgart-Berlin-Köln-Mainz 1966. 1st Edit., 176 pp., paperback, DM 16.80.

The author has succeeded in providing an ex remely clear explanation of the rights and obligations of the employee (and employer) as they are to be found in legislation and general guiding principles concerning employees' inventions. It must, however, be pointed out that, in particular, the problems of industrial law will cause much difficulty to the employee-inventor, who generally has little experience in such matters, and he may easily be led to false conclusions. The book deals with inventions made in the course of employment, and with free-lance inventions, in the light of important decisions made by the German Federal Supreme Court and the recommendations of the Arbitration Committee for Employees' Inventions. The guiding principles for the remuneration of such inventions are also considered. Further, a summary is given concerning patent and utility model appli-

cations for free-lance inventions, the utilization of these protective rights, and the general treatment of employees' suggestions. The book closes with a section on tax concessions for the remuneration of employees' inventions, for income from free-lance inventions, and for bonuses for suggested improvements. In the voluminous appendix, the relevant legislation, ordinances, and guiding principles are given and various forms are also reproduced. The book can also be recommended to employers and to those whose profession it is to advise inventors. *V. Vossius* [NB 628 IE]

The Chemistry of Technetium and Rhenium. By *R. D. Peacock*. Topics in Inorganic and General Chemistry, Monograph 6. Edited by *P. L. Robinson*. Elsevier Publishing Company, Amsterdam-London-New York 1965. 1st. Edit. ix, 137 pp., 14 Figures, 29 Tables. 55s; 27.50 Dfl.

The main purpose of the monograph, which is a review of the present knowledge of rhenium and technetium, is to be found in the comparison of the chemistry of these homologous elements. The author not only describes the various classes of compounds but explains the material in the light of modern transition-metal chemistry. Understandably, the greater part of the book is devoted to the chemistry of rhenium. The literature is covered up to the middle of 1965; however, various omissions have been made, even in the better documented chemistry of technetium. For example, one searches in vain for information concerning the technically and scientifically remarkable inhibition of corrosion exhibited by pertechnate ions. Nevertheless, the book assists the reader in gaining a deeper understanding of the chemistry of these transition elements and will prove stimulating reading for chemists interested in inorganic and radiochemistry.

K. Schwochau [NB 620 IE]

Introduction to Nuclear Chemistry. By *D. J. Carswell*, Elsevier Publishing Co., Amsterdam-London-New York 1967, 1st Edit., ix, 279 pp., 69 figures, 23 tables, Dfl. 32.50.

This book is based on lectures which the author gave over the course of many years at the University of New South Wales in Australia. It deals with the structure of the atom and of the nucleus, the laws of radioactive decay, nuclear reactions, types of decay, the use of physical nuclear methods in chemistry, such as the Mössbauer effect and nuclear magnetic resonance, detectors and their mode of action, radiation chemistry, mass spectrometry, isotope separation, neutron sources, accelerators, the actide elements, and the application of radioisotopes in industry and research. The concluding chapter lists 16 simple experiments which, without substantial outlay of time or money, provide an experimental insight into radiochemistry and nuclear chemistry.

The book is very simply written. Mathematical and abstract treatment is largely avoided, sometimes with adverse effects. For example, the reviewer thinks it unlikely that the description of isotope dilution analysis can really be understood. In a demanding chapter, in which several electronic circuits are described and in which the mode of action of a diode or triode is compared with that of a transistor by means of a circuit diagram, the statement of Ohm's law is too trivial. In the chapter "Actinides" the description of the stability of the individual actinide valences appears to need revision, as well as a better presentation.

Despite these drawbacks, the book should be particularly suitable for students who wish to acquire some overall knowledge of nuclear chemistry and who have no opportunity to attend lectures on nuclear and radiochemistry. A big help in understanding the subject matter is the short summary given at the end of each chapter. On the other hand, the price of about £ 3.0.0 seems a little high for this introductory book. *C. Keller* [NB 649 IE]

Nobel Lectures Chemistry 1901–1921 and 1922–1941. Issued by the Nobel Foundation, Elsevier Publishing Company, Amsterdam-London-New York, 1966. Volume 1901–1921, xii, 409 pp., several illustrations, Dfl 80.–; Volume 1922–1941: 53 pp. several illustrations, Dfl. 80.–.

The first Nobel prizes were awarded in 1901. They were, and in a certain sense still are, a present from the nineteenth century to the twentieth, for *Alfred Nobel* died in 1896. It must have been particularly difficult at the time to find among the many eminent chemists the one who deserved to be the first awarded this great distinction. *Cannizzaro*, *Gibbs*, *Thomsen* and *Berthelot*, *Arrhenius*, *Ostwald* and *A. von Bayer*, *Emil Fischer*, and *Moissan* were considered, and some of them received the prizes in later years. The majority of the votes (11 of 20) went to *van't Hoff* in 1901. It is a pleasure to read his Nobel lecture today, more than 65 years later. *van't Hoff* deals with osmotic pressure and chemical equilibria and it is of interest to note that neither here nor in the motivation for awarding the prizes is there an indication of the discovery of the asymmetric carbon atom. This work is mentioned only in the eulogy – in one sentence. One becomes acutely aware of the fact that the material that we learn today in the first few semesters as something self-evident was by no means self-evident at the beginning of the century.

In 1902 *Emil Fischer* received the prize for his fundamental work on sugars and purines, and in 1903 it was *Arrhenius*' turn for his theory of electrolytic dissociation (who can envisage the time when talk of the *theory* of electrolytic dissociation was the order of the day?). In 1904 *Ramsay* was honored for his discovery of the inert gases, in 1906 *Moissan* for his discovery of fluorine, in 1907 *Buchner* for his demonstration of cell-free fermentation. Self-evident truths today, but were they 60 years ago?

Anyone with a sense of history will find his money well spent on the two volumes of Nobel lectures that have now been issued by Elsevier. The reader will encounter many important men who have shaped our modern thinking, but will meet them in a way different from that in textbooks. One could say he will meet them on a more personal level.

H. Grünewald [NB 643 IE]

Biological Chemistry. By *H. R. Mahler* and *E. H. Cordes*. Harper and Row (Publishers) New York-London 1966. 1st Edit., xv, 872 pp., numerous figures and tables, 63 s.

The outstanding contribution made by American workers to biochemistry during recent years is very largely the result of this subject gaining a firm place a long time ago in both medical and natural science faculties of American universities. In chemistry, as in medicine and biology, biochemistry has become a pillar of a modern syllabus admittedly with different aims. While biochemistry (physiological chemistry) in the field of medicine is characterized by the functions and pathology of organs, in chemistry it is the fundamental set of chemical and physicochemical principles of the life-determining processes. Although all aspects of biochemistry are interdependent, they can be developed better independently of one another if the curriculum is adapted to achieve this aim in the optimum manner. It is clear that a rapid advance in one section will promote a similar speeding up in another. This subdivided responsibility somewhat resembles a technique applied for difficult ascents during mountain climbing. Two ropes are needed for climbing overhanging rocks. One is used to pull while it runs through the hook fixed above the climbers, and the second is carried loosely. After the fixing of the next hook, the second rope in turn takes up the pull. The above general remarks seemed necessary in order to characterize the place and importance of this new work. The book has been written for chemists by chemists. The authors have done splendidly, and in many respects have achieved a breakthrough for biochemistry in the part it occupies in chemical teaching. The book reproduces fairly accurately

the two-semester course of lectures given at Indiana University for graduate students. Since a thorough background in organic and physical chemistry is assumed, certain traditional sections of biochemistry textbooks have been eliminated. For example, there is no chapter on carbohydrate chemistry. The structure of coenzymes is likewise discussed only as far as its function in enzymatic reactions makes this necessary. The difficult problem of protein and nucleic acid structure, relegated to the later chapters in most textbooks, is placed right at the beginning. It is characterized by a thoroughness and breadth normally found only in large reference books and survey articles. Two similarly detailed chapters on the thermodynamics and kinetics of enzyme reactions follow to provide the prerequisite basis for the discussion of the mechanism of enzyme action (in a separate chapter). Enzyme action here signifies the catalytic action of protein, not the chemical principles of coenzyme activity. The latter is dealt with in detail for each coenzyme in the next chapter.

The first half of the book, which is devoted to theoretical principles and general aspects, concludes with a chapter about the structure of cells and the organization of enzymatic activities in cell fractions and particles. The second half deals with the dynamics of the chemical events in the cell. A sequence of chapters of conventional nature is found: carbohydrate metabolism, amino acids, nucleic acids, oxidation of fatty acids, and decomposition of complex lipids, and also chapters on the tricarboxylic acid cycle, biological oxidation, an extensive chapter on photosynthesis, and finally two chapters on biosynthesis (lipids and proteins).

As is to be expected in a first edition, some aspects are unbalanced. This is often due to the fact that in some fields there are gaps in the literature references. It will be possible to make the necessary improvements in the new editions, which will no doubt soon be forthcoming. In particular, reference may be made to the chapter "Quaternary structure of proteins", which has in no way been given the detailed treatment that is devoted later to the model of allosterism as a controlling principle in enzyme activity. Many decisive facts, such as the relationship between the number of subunits and the number of coenzyme binding sites, particularly in dehydrogenases, have been omitted entirely. The spontaneous association of subunits to form typical structures and active complexes likewise depends on the interactions determining the structure of higher order, and characterizing the allosteric transformations. The literature references attached to each chapter are most welcome, survey articles and papers to which special progress can be attributed being listed separately. The German reader will note that original work from German periodicals is rarely mentioned, and, when it is, with mutilated names. The subject of biochemistry in natural science faculties will receive a strong impetus through this work, and it is hoped that the book will achieve the widest possible distribution. *K. Wallenfels* [NB 639 IE]

Organic Compounds with Nitrogen-Nitrogen Bonds. By *C. G. Overberger, J.-P. Anselme*, and *J. G. Lombardino*. From the Series "Modern Concepts in Chemistry". The Ronald Press Company, New York 1966. 1st Edit., vi, 115 pp., $ 7.00.

The authors of the present work have succeeded admirably in presenting a concise survey of the vast field of compounds with NN bonds. In addition to the subject and author index, the book contains a theoretical introduction and chapters on the following topics: Hydrazines, azomethines having NN bonds (hydrazones, azines, osazones), azo compounds, diazo compounds (aromatic diazonium salts, diazoalkanes, diazirines), hydrazides, *N*-nitrosamines (*N*-nitramines), azides (tetrazenes, triazenes). Each chapter is carefully subdivided and completed by a literature register in which particular emphasis is placed upon review articles and surveys. The literature is covered up to 1965.

It is only to be expected that in 115 pages the information given is in a concentrated form and that a somewhat subjective choice of material has been made. Nevertheless, the authors have made such a good selection that the reader has no difficulty in obtaining a good idea of the preparation and reactions of these compounds and, particularly, of the work carried out with them during the last decade.

E. Fahr [NB 619 IE]

The Encyclopedia of Chemistry. Edited by *G. L. Clark* and *G. G. Hawley*. Reinhold Publishing Corporation, New York 1966. 2nd Edit., xxi, 1144 pp., numerous illustrations, $ 25.00.

The appearance of a second edition of an "Encyclopedia" exceeding 1000 pages within nine years can be described as an achievement. It may be expected that work has meanwhile been carried on to eliminate out-of-date information, to collect together scattered pieces of information, and to cut down verbosity. Unfortunately, these expectations have not been entirely fulfilled.

A cursory glance through the volume gives an excellent impression. There is hardly a subject that is not discussed (admittedly some entries, such as Carbene, Cobalamine, and Tacticity, are absent the printing is pleasant, the illustrations are large and clear. Careful reading of the text, however, reveal that the quality of the articles varies. Side by side with good, modern, and clearly written contributions (*e.g.* on crystal field theory and nuclear reactors), there are others which provide out-of-date information, engage in long, pointless argument, or are poorly coordinated. For example, information about nucleic acids is contained in three different places. Four authors are named, and there is no indication that they had previously agreed on who is to say or write what.

On the library shelf the book will often be useful and sometimes annoying. There is a long way to go before the editors and the authors achieve a true encyclopedia.

H. Grünewald [NB 645 IE]

Interpretation of Mass Spectra. By *F. W. McLafferty*. W. A. Benjamin, Inc., New York-Amsterdam 1966. 1st ed., xvii, 229 pp., several figures, bound $ 9.00.

The ever-increasing importance of mass spectrometry in science and industry has made it necessary to systematize the interpretation of mass spectra, *i.e.* to classify them according to significant aspects. While the hitherto published books confine themselves to the decomposition mechanisms of classes of organic compounds, the author of this treatise attempts to instruct the reader in the interpretation of mass spectra by the use of spectra of unknown organic substances. Problems of instrumentation are therefore merely touched on in the introduction.

The elucidation of reactions leading to molecular fragmentation and hence conclusions regarding the type and structure of a compound form the predominant content of the interpretation of mass spectra. Certain fundamental rules are set up for the treatment of decomposition mechanisms and the reactions are classified in few general groups. Although certain simplifications are necessary, this systematization does represent an aid for evaluating mass spectra.

The method with which the author introduces the student and scientist to the problems of the interpretation of mass spectra is interesting. Progress from initially simple decomposition mechanisms to ever more complicated ones enables the student to test his understanding on unknown spectra and to compare his solution with that given in the final chapter. One advantage of this method is that it also provides practice in interpretation. *H. Krone* [NB 635 IE]

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The Structure and the Function of Gangliosides[**]

BY H. WIEGANDT[*]

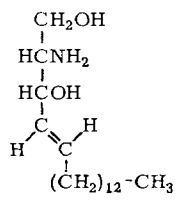
Dedicated to the memory of Richard Kuhn

Gangliosides are found in the brain and other organs, and are composed of sphingosine, fatty acids, hexoses, and sialic acid. Types of gangliosides differ in the fatty acids and the sugar residues. The carbohydrate residue in the quantitatively predominating brain gangliosides is ganglio-N-tetraose, a tetrasaccharide. In these gangliosides, this residue combines with one or more molecules of sialic acid. The oligosaccharide part is a carrier of serologic properties. Gangliosides are characteristic lipid components of some neuronal membranes in the central nervous system, and can be localized on the synaptic apparatus of nerve cells in the cerebral cortex. Their site of occurrence and physiological action point to their participation in the transmission of impulses. It was in the brains of the mentally ill that gangliosides were first discovered, and indeed their pathologic accumulation can possibly be attributed to congenital defect of enzymes involved in their synthesis or metabolism. Gangliosides are produced from their components by acceptor-specific transferases.

1. Introduction

Work began on a new type of acidic lipids having a high carbohydrate content when *Klenk*[1] characterized a substance he isolated from the brains of patients suffering from amaurotic familial idiocy and Nieman-Pick disease, the existence of these lipids having earlier been detected by *Landsteiner* and *Levene*[2] and by *Thierfelder* and *Walz*[3] on account of the formation of characteristic dyes by these compounds with *p*-dimethylaminobenzaldehyde and orcinol. *Blix*[4] found in 1938 that these lipids regularly occur also in the normal brain. *Klenk* suspected that "Substance X" was localized in ganglial cells, and therefore named it ganglioside[5].

The identification of gangliosides as sphingolipids[*] and the determination of their constituents date back to the fundamental work of *Klenk et al.* Gangliosides are composed of sphingosine *(1)* [(2*S*:3*R*)-2-amino-*trans*-4-octadecene-1,3-diol], fatty acids, hexoses, and a sialic acid, *i.e.* an *N*-acylated or an *O*-acylated neuraminic acid *(2)* (5-amino-3,5-didesoxy-D-*glycero*-β-D-*galacto*-nonulosonic acid), mostly *N*-acetyl- or *N*-glycolylneuraminic acid (NANA or NGNA).



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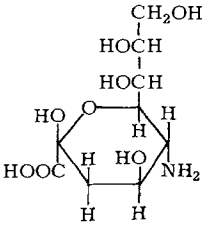


(2)

[*] Doz. Dr. H. Wiegandt
Physiologisch-chemisches Institut der Universität
355 Marburg, Deutschhausstrasse 1–2 (Germany)

[**] Abbreviations: Glc = glucose; Gal = galactose; GlcNAc = *N*-acetylglucosamine; GalNAc = *N*-acetylgalactosamine; NANA *N*-acetylneuramic acid; NGNA = *N*-glycolylneuramic acid; Lact = lactose; Sph = sphingosine; Cer = ceramide. The abbreviations for oligosaccharides are listed in Table 1 (for the nomenclature, see Section 3.1 and [6]).

[1] *E. Klenk*, Hoppe-Seylers Z. physiol. Chem. *235*, 24 (1935).

[2] *K. Landsteiner* and *P. A. Levene*, J. Immunology *10*, 731 (1925).

[3] *H. Thierfelder* and *E. Walz*, Hoppe-Seylers Z. physiol. Chem. *166*, 217 (1927).

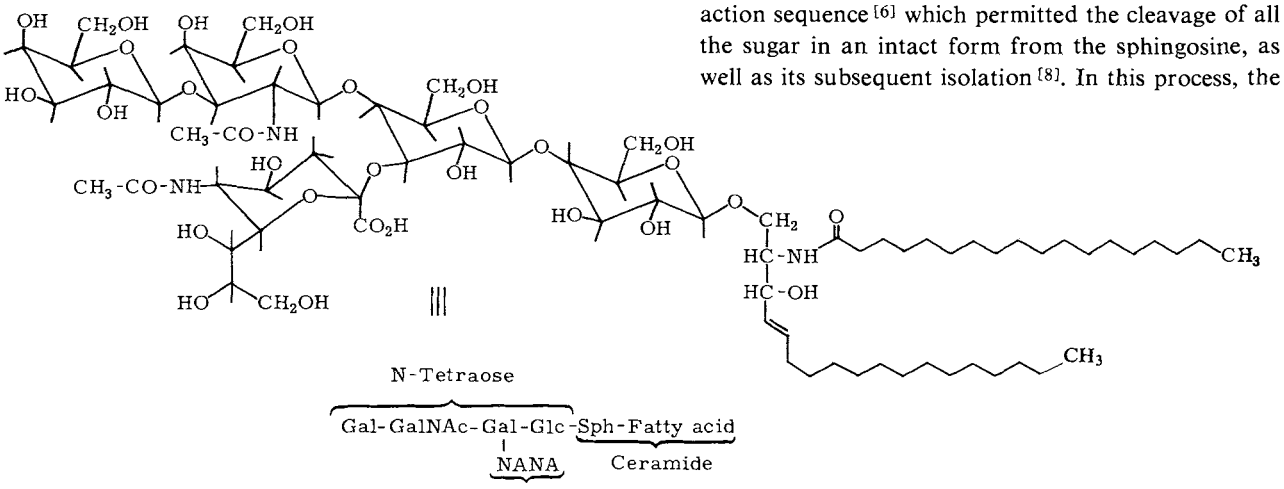
[4] *G. Blix*, Scand. Arch. Physiol. *80*, 466 (1938).

[5] *E. Klenk*, Hoppe-Seylers Z. physiol. Chem. *273*, 76 (1942).

[*] Sphingolipids are fatty substances containing sphingosine as the basic component.

2. Structure of Gangliosides

Gangliosides were isolated and obtained in the pure form by the use of chromatographic methods. The elucidation of the chemical structure of the ganglioside $G_{GNT}1$ *(3)* (see below) isolated from the brain was attempted first, as this compound was available



N-Tetraose

Gal-GalNAc-Gal-Glc-Sph-Fatty acid

NANA Ceramide

Sialic acid = *N*-acetylneuraminic acid

$G_{GNT}1$ *(3)*

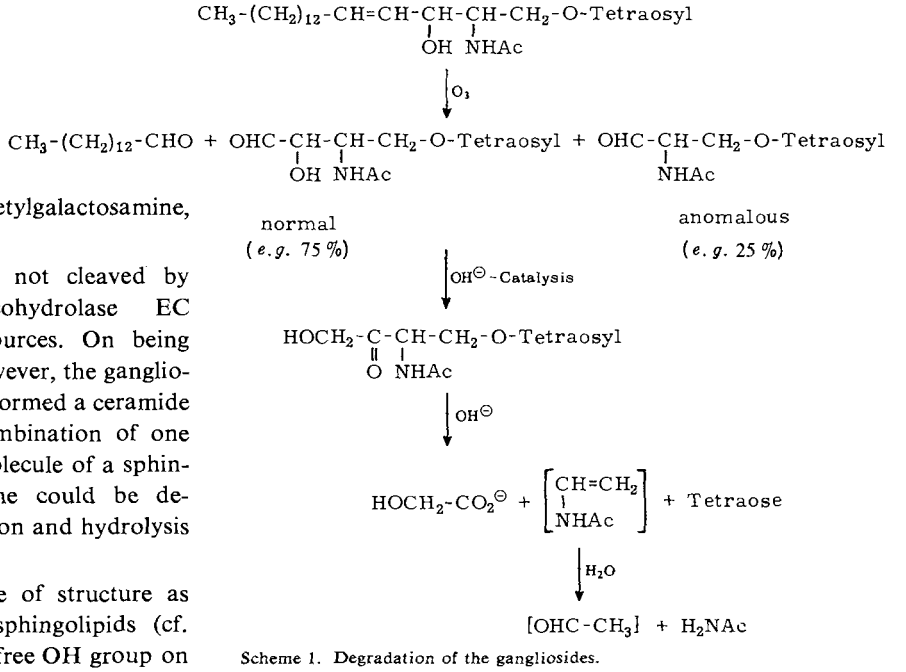
in the pure state in a sufficiently large amount. After exhaustive hydrolysis, quantitative analysis revealed a molecular ratio of 1:1:1:2:1:1 between sphingosine, fatty acid, glucose, galactose, *N*-acetylgalactosamine, and *N*-acetylneuraminic acid.

The sugar-sialic acid linkage was not cleaved by neuraminidase (neuraminate-glycohydrolase EC 3.2.1.18) samples from various sources. On being heated with dilute mineral acids, however, the ganglioside $G_{GNT}1$ lost its sialic acid and formed a ceramide tetrasaccharide. (Ceramide is a combination of one molecule of a fatty acid and one molecule of a sphingosine base.) 3-*O*-Methylsphingosine could be detected after the exhaustive methylation and hydrolysis of ceramide tetrasaccharide.

Gangliosides exhibit the same type of structure as that characteristic of other glycosphingolipids (cf. Table 2): a sphingosine base with a free OH group on C_3 carries a fatty acid molecule linked by an amide to the 2-amino group. A carbohydrate is linked by a glycoside to the OH group on the C_1 atom of the ceramide. The sialic acid characteristic of the gangliosides is bound to the sugar residue by a ketoside linkage. In a strongly acidic medium, the Des-NANA-$G_{GNT}1$ is further cleaved, giving rise to several free and still ceramide-bound sugars.

In the degradation of gangliosides with glacial acetic acid/acetic anhydride and catalytic amounts of conc. sulfuric acid [6] however, sialic acid is cleaved from the ganglioside only partially (but the ceramide is liberated), so that one obtains free oligosaccharides in which the linkage to the sialic acid remains intact.

The elucidation of the structure of gangliosides made a big step forward after the introduction of a new reaction sequence [6] which permitted the cleavage of all the sugar in an intact form from the sphingosine, as well as its subsequent isolation [8]. In this process, the C=C double bond in the sphingosine is split oxidatively with *e.g.* ozone, periodate and OsO_4 [9], or *m*-chloroperbenzoic acid [10]. The resulting substances can be fragmented by treatment with a weak base in such a way that the sugar residue is liberated [*]. The route shown in Scheme 1 has been proposed [7] for this reaction sequence.



Scheme 1. Degradation of the gangliosides.

[6] *R. Kuhn* and *H. Wiegandt*, Chem. Ber. *96*, 866 (1963).

[7] *H. Wiegandt*, Lecture at the 7th International Congress Biochemistry (Tokyo) 1967.

[8] *H. Wiegandt* and *G. Baschang*, Z. Naturforsch. *20b*, 164 (1965).

[9] *S. Hakamori*, J. Lipid Res. *7*, 789 (1966).

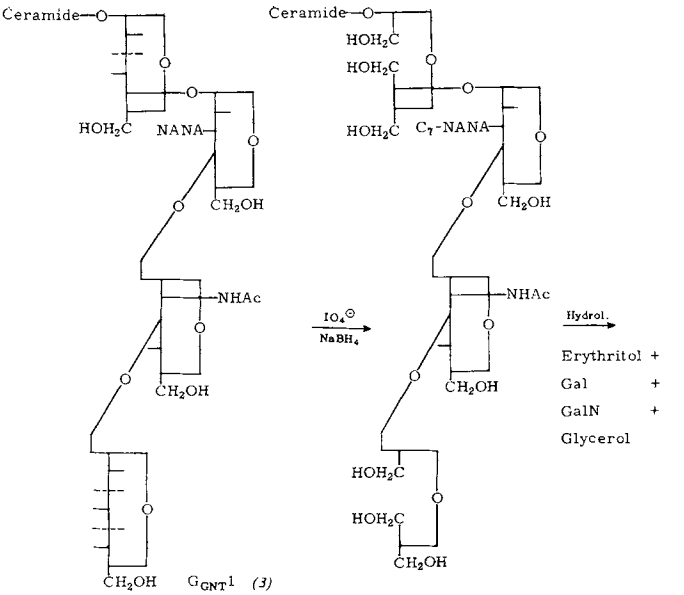
[10] *H. Wiegandt*, unpublished.

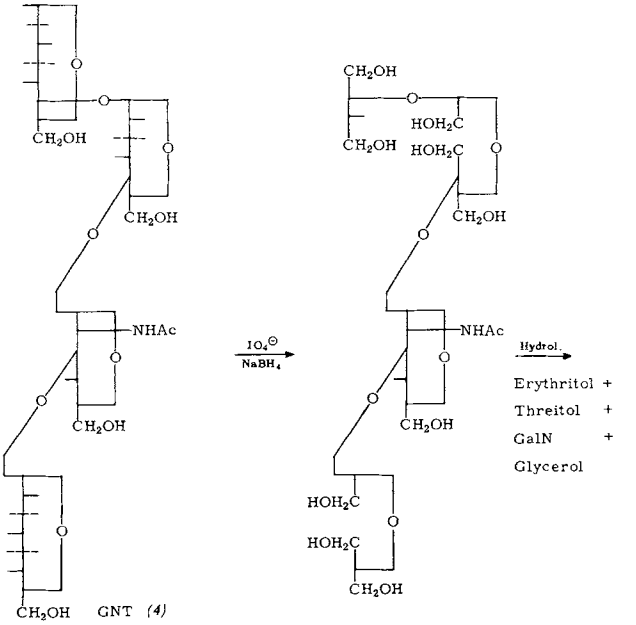
[*] When $OsO_4/IO_4^{\ominus}$ or *m*-chloroperbenzoic acid is used, the carbohydrate moiety should first be protected by peracetylation. The *O*-acetyl groups are cleaved off in the alkaline fragmentation.

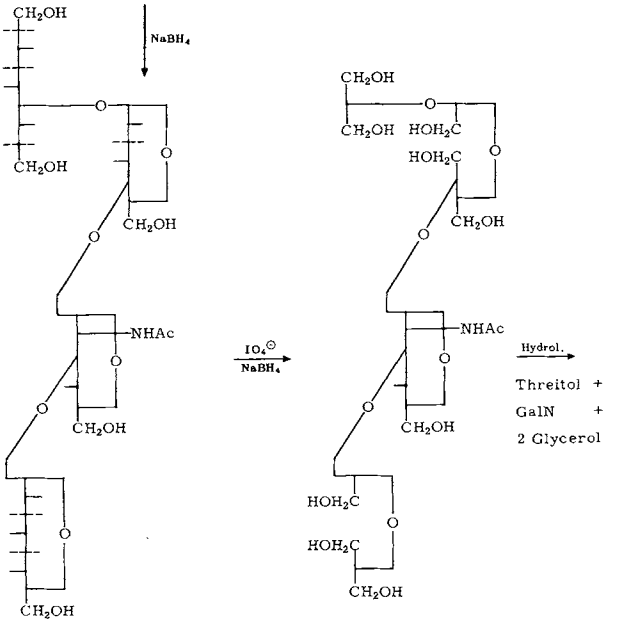
This method has been used to obtain the sialic acid-containing sugar residue from the neuraminidase-resistant ganglioside $G_{GNT}1$. The cleaving-off of sialic acid by careful acidic hydrolysis with 0.1 N H_2SO_4 at 80 °C gave the base sugar ganglio-*N*-tetraose. Further partial hydrolysis with the same medium at 100 °C permitted the isolation and characterization of two trisaccharides GNTrI and GNTrII and all three possible disaccharides GNBI, GNBII, and Lact.

The known nitrogen-containing tetrasaccharides can be easily separated paper chromatographically. Paper chromatographic "fingerprinting" of the products formed in the partial hydrolysis or the alkaline degradation represents another method of characterizing these saccharides on the microscale [19].

Ganglio-*N*-tetraose, GNT *(4)*, and $G_{GNT}1$ were cleaved with periodate, and the aldehydic fragments were reduced with $NaBH_4$. The comparison of the results showed that the sialic acid (here NANA), which cannot be cleaved off enzymatically, is linked to the C_3 of the second sugar residue of GNT.







3. Determination of the Components of Gangliosides

The differences between the gangliosides lie mainly in their carbohydrate moiety, but the sphingosine bases and the fatty acids may also vary. The gangliosides so far prepared in the pure state are uniform only as regards their sugar residue, and yet it is this residue that is essentially responsible for the differences in the chromatographic, chemical, and physiological properties.

Apart from sphingosine *(1)*, such chromatographically pure gangliosides from human and bovine brain contain another base which is homologous to the sphingosine *(1)*, but has a C_{20} chain instead of a C_{18} chain [11]. The sphingosines are saturated to an extent of about 10 %, *i.e.* about 10 % of the molecules do not contain C=C double bonds [12]. The C_{18}/C_{20} weight ratio varies with age: C_{18} predominates in the fetal brain, C_{20} greatly predominating in the brain of adults [13]. The C_{18}-sphingosine is the main component in the gangliosides isolated from the spleen [14].

There is also a variation in the fatty acids that are linked to the sphingosine. In each case, one of the fatty acids present is found in a particularly high concentration, the nature of this fatty acid depending on the source of the ganglioside; thus, it is stearic acid in the case of brain gangliosides, and lignoceric acid in the case of spleen gangliosides.

Glucose, galactose, *N*-acetylglucosamine, *N*-acetylgalactosamine, and fucose have so far been identified amongst the basic components of neutral oligosaccharides of the gangliosides. The neutral sugar linked to the ceramide moiety of the known gangliosides contains a maximum of four such sugar molecules forming a

[11a] *N. Z. Stanacev* and *E. Chargaff*, Biochim. biophysica Acta *59*, 733 (1962).

[11b] *N. Z. Stanacev* and *E. Chargaff*, Biochim. biophysica Acta *98*, 168 (1965); *K. Sambasivarao* and *R. H. McCluer*, Federat. Proc. *22*, 300 (1963).

[12] *K. A. Karlsson*, Acta chem. scand. *18*, 565 (1964).

[13] *L. Svennerholm*, Biochem. J. *98*, 20P (1966).

[14] *J. Menkes*, Biochem. biophysic. Res. Commun. *15*, 551 (1964).

tetrasaccharide *e.g.*, ganglio-*N*-tetraose in brain ganglioside and lacto-*N*-neotetraose in bovine erythrocytic or spleen ganglioside [15], but gangliosides with mono-, di-, and trisaccharides have also been isolated.

Gangliosides obtained from human erythrocytes and spleen contain mainly *N*-acetylneuraminic acid (NANA), while *N*-glycolylneuraminic acid (NGNA) is the predominating sialic acid (accompanied by NANA) in the gangliosides extracted from the erythrocytes and the spleen of other primates [16], as well as the horse and cattle.

Gangliosides may carry one or more molecules of sialic acid [17]. Sialic acid molecules are linked to the sugar in the ganglioside either singly or after they have been interconnected *via* 2 → 8 bonds [18]. When sialic acids are connected with another sialic acid molecule by a ketoside linkage in the 8-position, an inner ester is formed with particular ease. The resulting lactones are very unstable; they are easily cleaved by hydrolysis and can be detected by titration, reaction with hydroxamic acid, and paper electrophoresis.

The electrophoretic migration rate of gangliosides and their constituent sialic acid-containing oligosaccharides is greatly affected by the position in which the sialic acid is linked to the sugar residue. When two sialic acid molecules are interconnected, only one is strongly acidic in the paper electrophoresis at various pH values [19].

Of the α- and the β-ketosides of sialic acids, only the α-anomers are attacked by neuraminidase [20]. The linkage of the sialic acid must always be α-ketosidic here, since neuraminidase cleaves all the sialic acid molecules in the known gangliosides, though sometimes only after a certain hindrance has been eliminated [21]. This can be done *e.g.* in the case of $G_{GNT}1$ by removing the galactose and the *N*-acetylgalactosamine from the end of the sugar residue through partial acidic methanolysis or partial acetolysis, and then treating the resulting $G_{Lact}1$ with neuraminidase.

The gangliosides are generally detected by the colorimetric determination of the sialic acids with orcinol (*Bial*'s reagent [22]), *p*-dimethylaminobenzaldehyde (*Ehrlich*'s reagent [23]), thiobarbituric acid [24], diphenylamine [25], or 3,5-diaminobenzoic acid [26]. Sialic acids are relatively strong acids with p*K* 2–3, and therefore the gangliosides can be titrated acidimetrically.

The following techniques have been proposed for the identification and the quantitative determination of the sphingosine bases: Chromatographic identification of the base either in the free form or as the 2,4-dinitrophenyl derivative after the hydrolysis of the glycosphingolipid and isolation of the base (methanolic 1 N H_2SO_4 followed by ether extraction at pH > 7) [27]. The sphingosines can also be separated gas chromatographically after trimethylsilylation, and can be characterized with the aid of a mass spectrometer [28]. Furthermore, sphingosines may be characterized by the gas-chromatographic determination of the aldehydes or the fatty acids (as methyl esters) formed by the oxidative cleavage of the C=C double bond with ozone, $OsO_4/IO_4^{\ominus}$, or periodate/permanganate [11b, 29].

The fatty acids are analyzed by gas chromatographing the methyl esters after acidic methanolysis of the gangliosides.

3.1. Nomenclature of the Gangliosides [30]

Trivial or semitrivial names [30] are used to denote the oligosaccharides. The letter N attached to an oligosaccharide denotes a nitrogen-containing sugar. Trisaccharides and disaccharides that can be derived from one and the same tetrasaccharide are distinguished by I, II, *etc.*, I describing the sugar that originates from the non-reducing end of the tetrasaccharide (cf. Table 1).

Table 1. Abbreviations for oligosaccharides.

Oligosaccharide	Short designation	Abbreviation
Ganglio-*N*-tetraose	Gal(β1,3)GalNAc(β1,4)Gal(β1,4)Glc	GNT
Ganglio-*N*-triose I	Gal(β1,3)GalNAc(β1,4)Gal	GNTr I
Ganglio-*N*-triose II	GalNAc(β1,4)Gal(β1,4)Glc	GNTr II
Ganglio-*N*-biose I	Gal(β1,3)GalNAc	GNB I
Ganglio-*N*-biose II	GalNAc(β1,4)Gal	GNB II
Lacto-*N*-tetraose	Gal(β1,3)GlcNAc(β1,3)Gal(β1,4)Glc	LNT
Lacto-*N*-neotetraose	Gal(β1,4)GlcNAc(β1,3)Gal(β1,4)Glc	LNnT
Lacto-*N*-neotriose I	Gal(β1,4)GlcNAc(β1,3)Gal	LNnTr I
Lacto-*N*-triose II	GlcNAc(β1,3)Gal(β1,4)Glc	LNTr II
Lacto-*N*-neobiose I	Gal(β1,4)GlcNAc	LNnB I
Lacto-*N*-biose II	GlcNAc(β1,3)Gal	LNB II
Globo-*N*-tetraose	GalNAc(β1,3)Gal(β1,4)Gal(β1,4)Glc	GloNT

In abbreviations, G stands for ganglioside. The subscript, as in G_{GNT}, designates the sialic acid-free oligosaccharide. The Arabic numeral affixed to the abbreviation gives the number of sialic acid molecules. Different sialic-acid position isomers are distinguished by attaching a, b, *etc.* to the Arabic numeral (*e.g.* $G_{GNT}2a$ and $G_{GNT}2b$). If the sialic acid in a ganglioside is not NANA, but NGNA, this is specified by adding (NGNA) to the description.

4. Occurrence of Gangliosides

On the basis of quantitative determinations, gangliosides represent the following proportions of the total lipids [30, 31]:

one-day-old human brain	7.46 %
adult human brain	3.49 %
adult human *substantia grisea*	8.65 %
adult human *substantia alba*	4.16 %

[15] *R. Kuhn* and *H. Wiegandt*, Z. Naturforsch. *19b*, 80 (1964).

[16] *G. Uhlenbruck* and *J. Schmitt*, Naturwissenschaften *52*, 163 (1965).

[17] *R. Kuhn* and *H. Wiegandt*, in collaboration with *H. Egge*, Angew. Chem. *73*, 580 (1961).

[18] *R. Kuhn* and *H. Wiegandt*, Z. Naturforsch. *18b*, 541 (1963).

[19] *H. Wiegandt*, Habilitation thesis, Marburg University 1966.

[20] *P. Meindl* and *H. Tubby*, Mh. Chem. *96*, 802, 816 (1965); *R. Kuhn* and *H. Lutz*, Chem. Ber. *99*, 611 (1966); *H. Faillard*, *G. Kirchner*, and *M. Blohm*, Hoppe-Seylers Z. physiol. Chem. *347*, 87 (1966).

[21] *R. Ledeen* and *K. Salsman*, Biochemistry *4*, 48, 2225 (1965).

[22] *L. Svennerholm*, Ark. Kemi *10*, 577 (1957); *L. Svennerholm*, Biochim. biophysica Acta *24*, 604 (1957).

[23] *J. Werner* and *L. Odin*, Acta Soc. Med. Upsaliensis *57*, 230 (1952).

[24] *L. Warren*, J. biol. Chemistry *234*, 1971 (1959); *D. Aminoff*, Biochem. J. *81*, 384 (1961); *G. B. Paererls* and *J. Schut*, *ibid. 96*, 787 (1965).

[25] *A. Mukai Tohoko*, J. exp. Medicine *77*, 128, 233 (1962); *Z. Dische*, Mikrochemie *8*, 4 (1930); *A. Saifer* and *S. Gerstenfeld*, *Jr.*, J. Lab. clin. Med. *50*, 17 (1957).

[26] *H. H. Hess* and *E. Rolde*, J. biol. Chemistry *239*, 3215 (1964).

[27] *C. Michalec*, Biochim. biophysica Acta *116*, 400 (1966); *C. Michalec*, J. chromatogr. *24*, 228 (1966); *C. Michalec* and *Z. Kolman*, Clin. chim. Acta *13*, 529 (1966); *B. Weiss* and *R. L. Stiller*, J. Lipid Res. *6*, 159 (1965).

[28] *M. Popovic*, Biochim. biophysica Acta *125*, 178 (1966); *K. A. Karlsson* and *G. A. L. Holm*, Acta chem. scand. *19*, 2423, 2425 (1965).

After the separation of the *substantia alba* (white matter) into myelin and microsomes [32], the gangliosides are mainly present in the latter, in which the ganglioside content reaches 0.4 % of the dry weight. The concentration of the gangliosides in the *substantia grisea* (gray matter) of the frontal lobes of the brain and the *nucleus caudatus* (large ganglia of the brain stem) is about 1.2–1.6 % on dry weight (0.4 % lipid-NANA). This corresponds to a ganglioside-NANA content of about 10.4×10^{-12} g per ganglial cell [33].

Gangliosides occur in high concentrations also in the spleen (*e.g.* they form 3.3 % of the total lipids in human spleen [31]). The brain gangliosides are qualitatively the same in all the species investigated so far [man, cattle, rabbit, rat, hedgehog, chicken, crab (eye stalk) [10]], but the spleen gangliosides show strong interspecific variations, and so do the gangliosides of the visceral system in general.

Gangliosides are also found in the erythrocytes, leukocytes, serum, kidneys, adrenal glands, placenta, milk, blood-vessel walls, intestines, lungs, and in the lens of the human eye.

5. Chemical and Physical Properties

Gangliosides are colorless crystallizable substances melting with decomposition (*e.g.* the melting point of $G_{GNT}1$ is 189–190 °C, decomp.). They are insoluble in non-polar solvents, and their solubility in polar ones (water, alcohols, *etc.*) increases with the size of their sugar residue and their sialic acid content. In aqueous solutions, gangliosides form micelles having a molecular weight of about 200,000–250,000 [34]. In dimethylformamide or tetrahydrofuran, on the other hand, they form molecular solutions characterized by a molecular weight of 1000–3000 [35].

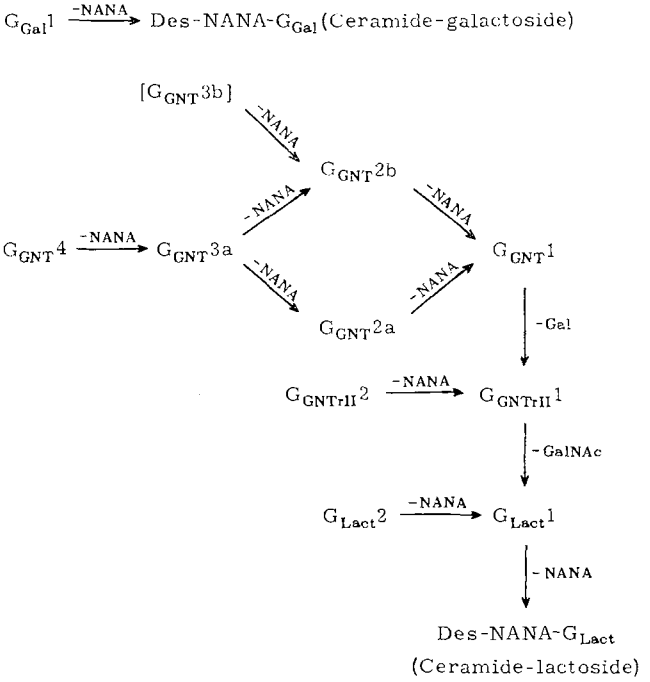
Gangliosides may form a lipid film on water. The minimum area required by a ganglioside molecule at the air/water interface of such a film at 30 dyne/cm [*] is 63 Å^2 for $G_{GNT}1$ and 95 Å^2 for a disialoganglioside [36]. Sphingomyelin, consisting of sphingosine and phosphorylcholine and containing mainly stearic acid as the fatty acid component, has an area requirement of 40 Å^2/molecule.

Urged by the concept that psychochemicals and local anesthetics can alter the physicochemical properties of biological membranes, *Van Deenen* [37] investigated a model system consisting of ganglioside films on water containing the substances mentioned above, and found that the latter penetrated through the films to various extents and modified the surface tension of the gangliosides.

Acidic lipids such as the gangliosides have a strong affinity for alkaline earth metal ions, but the fixation of $^{45}Ca^{2\oplus}$ on ganglioside films on water at pH 5.5 is considerably less pronounced than on phospholipid films [36]. Similarly to phospholipids (triphosphoinositide and phosphatidylserine), gangliosides have a higher affinity for $Ca^{2\oplus}$ than for $Mg^{2\oplus}$ ions in binary mixtures such as the chloroform/methanol/water system [38].

6. Brain Gangliosides

The main gangliosides in the brain are as follows: $G_{GNT}1$, $G_{GNT}2a$, $G_{GNT}2b$, and $G_{GNT}3a$. The first indication concerning their structural connection came from enzymatic degradation with neuraminidase [17]. By successive enzymatic cleavage of single sialic acid residues, it was possible to convert several gangliosides into $G_{GNT}1$, whose sialic acid could no longer be cleaved off by the enzyme (cf. the transformation of $G_{GNT}4$ to $G_{GNT}1$ in Scheme 2). The main



Scheme 2. Structural relationships between brain gangliosides.

brain gangliosides thus differ only in the number and/or the position of the sialic acid groups. In the case of the gangliosides $G_{GNT}1$ and $G_{GNTrII}1$, which are not cleaved by neuraminidase, the action of the enzyme is presumably obstructed by large substituents in the neighborhood [6]. The base carbohydrate carrying

[29] *H. P. Schwarz, J. Kostejk, A. Marmolejo,* and *C. Sarappa,* J. Neurochem. *14,* 91 (1967).

[30] *H. Wiegandt,* Ergn. Physiol. biol. Chem. exp. Pharmakol. *57,* 190 (1966).

[31] *A. N. Siakotos* and *G. Rouser,* J. Amer. Oil Chemists' Soc. *42,* 913 (1965).

[32] *E. F. Soto, L. Seminario de Bohner,* and *M. Delcarmen Calvino,* J. Neurochem. *13,* 989 (1966).

[33] *R. Landolt, H. Heuss,* and *C. Thalheimer,* J. Neurochem. *13,* 1331 (1966).

[34] *E. G. Trams* and *L. J. Lauter,* Biochim. biophysica Acta *60,* 350 (1962); *D. B. Gammack,* Biochem. J. *88,* 373 (1963).

[35] *E. Klenk* and *W. Gielen,* Hoppe-Seylers Z. Physiol. Chem. *319,* 283 (1960); *R. E. Howard* and *R. M. Burton,* Biochem. biophysica Acta *84,* 435 1964).

[*] At higher pressures, the ganglioside film is too unstable.

[36] *H. Halser* and *R. M. C. Dawson,* European J. Biochem. *1,* 61 (1967).

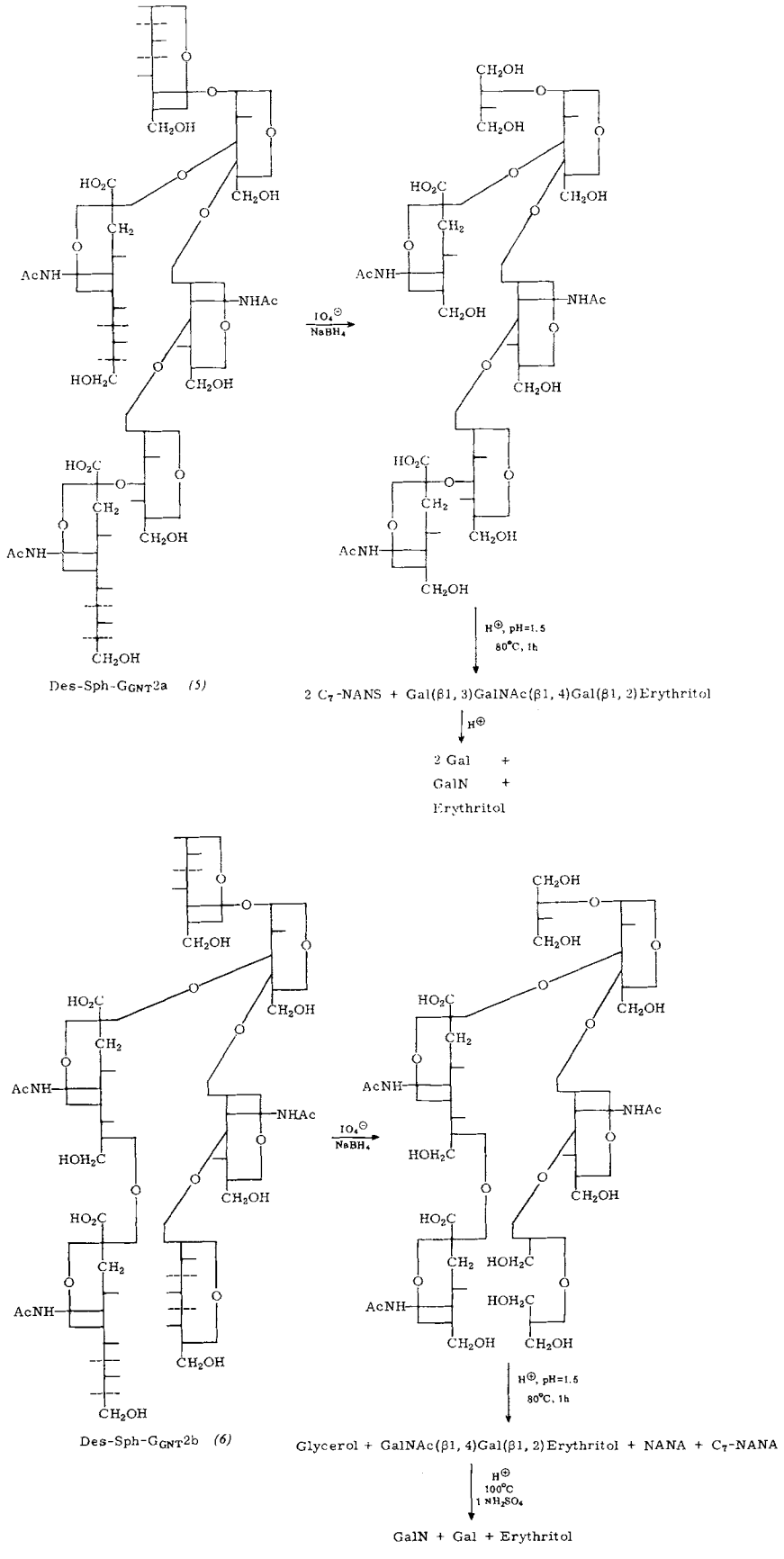
[37] *J. R. A. Demel* and *L. L. M. van Deenen,* Chem. Physics Lipids *1,* 68 (1967).

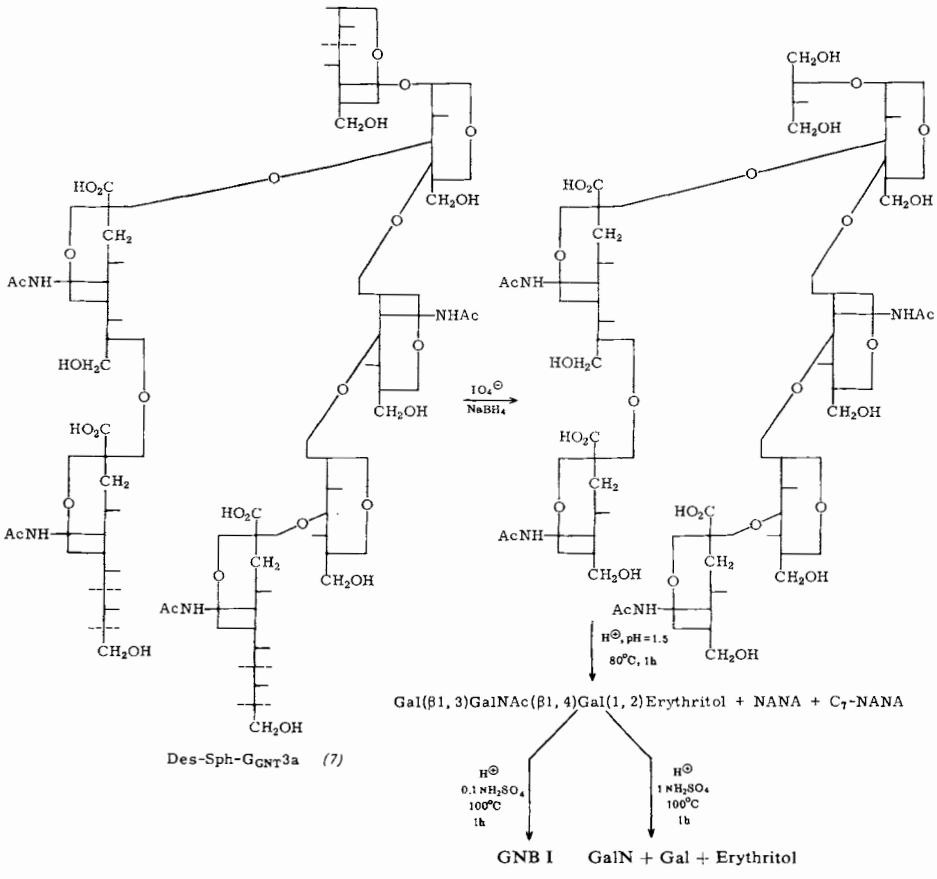
[38] *R. Quarles* and *J. Folch-Pi,* J. Neurochem. *12,* 543 (1965).

the sialic acid in these brain gangliosides is ganglio-*N*-tetraose *(4)*.

The determination of the points of attachment of NANA in the sialic acid-rich GNT gangliosides $G_{GNT}2a$, $G_{GNT}2b$, and $G_{GNT}3a$ was accomplished by the periodate oxidation[18] of Des-Sph-$G_{GNT}2a$ *(5)*, Des-Sph-$G_{GNT}2b$ *(6)*, and Des-Sph-$G_{GNT}3$ *(7)*, followed by acid hydrolysis.

In the ganglioside $G_{GNT}2a$, each of the two galactose molecules of the ganglio-*N*-tetraose at C_3 carries a NANA molecule. In the isomer $G_{GNT}2b$, on the other hand, the two sialic acid molecules are interconnected by a 2 → 8 keto-side linkage, and are attached to the 3-position of the front





galactose residue. The building units of $G_{GNT}2a$ and $G_{GNT}2b$ are combined in ganglioside $G_{GNT}3a$. These observations have recently been confirmed by *Klenk et al.*[39].

Besides these main components, several other gangliosides normally present in the brain in smaller quantities have been isolated, and their chemical structure has been determined[6, 40]. The ganglioside $G_{GNTrII}1$[6], earlier denoted by G_0, differs from $G_{GNT}1$ only in the absence of a terminal galactose residue. Therefore, it contains ganglio-*N*-triose II as the base carbohydrate. Owing to an enzyme defect in the biological synthesis or degradation, this ganglioside is accumulated in the infantile form of amaurotic idiocy of the Tay-Sachs type, and is therefore often referred to as Tay-Sachs ganglioside.

Other brain gangliosides contain ganglio-*N*-triose II with two NANA molecules ($G_{GNTrII}2$), or they contain lactose with one or two NANA molecules. The smallest ganglioside, $G_{Gal}1$, contains only one molecule of galactose, substituted by NANA at the 3-position. The structural relationships between the brain gangliosides are shown in Scheme 2, which also illustrates a path of the biological degradation.

7. Gangliosides in the Spleen and the Erythrocytes

Much less work has been done on the gangliosides of the visceral system than on those of the brain. In man, cattle, and the horse, the main ganglioside is $G_{Lact}1$. It has been possible to isolate several other higher gangliosides from the spleen and the erythrocytes of man and cattle, but the structure of these has not yet been elucidated. In these compounds, galactosamine is accompanied by glucosamine. A glucosamine-containing ganglioside $G_{LNnT}1$(NGNA) found in the red cells and the spleen of cattle contains lacto-*N*-neotetraose as the base carbohydrate, this compound having so far been known only as a component of human milk[15]. It cannot be excluded that parenchymatous organs contain also gangliosides that can be derived from glycosphingolipids carrying no sialic acid molecules, for such lipids are present in these organs (cf. Table 2). This is supported by the presence of $G_{Lact}1$ and the recent isolation of a hitherto unknown ganglioside from intestinal tissues and the lens of the human eye that comprises sphingosine, fatty acids, sialic acid, glucose, and galactose in a ratio of 1:1:1:1:2[41a].

The question arises whether the specific structure of certain lipid-bound or protein-bound oligosaccharides

Table 2. Glycosphingolipids containing no sialic acid molecules occurring in erythrocytes, spleen, kidneys, *etc.*

GalNAc(β1,3)Gal(β1,4)	Gal(β1,4)Glc-Ceramide	(Globoside)	[41b]
Gal —	Gal — Glc-Ceramide		
	Gal — Glc-Ceramide		
	Glc-Ceramide		

[39] *E. Klenk, L. Hof,* and *L. Gorgias,* Hoppe-Seylers Z. physiol. Chem. *348,* 149 (1967).

[40] *R. Kuhn* and *H. Wiegandt,* Z. Naturforsch. *19b,* 256 (1964).

[41a] *W. R. Vance, C. P. Shook,* and *J. M. McKibbin,* Biochemistry *5,* 435 (1966).

[41b] *T. Yamakawa, S. Yokoyama,* and *N. Kiso,* J. Biochemistry [Tokyo] *52,* 228 (1962); *M. M. Rapport, L. Graf,* and *H. Schneider,* Arch. Biochem. Biophysics *105,* 431 (1964).

are characteristic of certain cell structures such as cell surfaces for example. Available data suggest that compounds containing ganglio-*N*-tetraose are basically confined to the central nervous system, while compounds containing globo-*N*-tetraose are restricted to parenchymatous-stromatic elements of the body.

8. Accumulation Diseases

In sphingolipidoses, which are rare hereditary diseases transmitted *via* a recessive autosomal mechanism, sphingolipids are stored in the brain and often also in other organs such as the spleen, the kidneys, and the liver. This indicates that the enzymes involved in the metabolism of sphingolipids are not produced by the body, because the structural gene governing these enzymes suffers from a hereditary defect. In fact, a deficiency of such enzymes has already been observed in some of these diseases. Table 3 lists a number of such diseases, the main stored lipids, and – whenever known – the missing enzymes.

Table 3. Data for various forms of sphingolipidosis [a].

Name of disease	Main lipid stored	Missing enzyme
Amaurotic idiocy infantile form (Tay-Sachs type)	$G_{GNTrII}1$	specific hexosaminidase?
Late-infancy form (biochem. special form?)	$G_{GNT}1$	specific galactosidase?
Niemann-Pick disease	sphingomyelin	sphingomyelinase
Gaucher's disease	Cer-Glc	specific glucosidase
Metachromatic leukodystrophy	Cer-Gal-SO_3^-	sulfatase
Globoid cell leukodystrophy (type Krabbé)	Cer-Gal	specific cerebrosidesulfotransferase
Fabry's disease	Cer-Glc-Gal-Gal	specific galactosidase

[a] The gangliosides show a pathologic picture also in the juvenile and the adult forms of amaurotic idiocy, in gargoylism, and in Krabbe's disease (diffuse infantile familial sclerosis).

Changes in the gangliosides are by far the greatest in infantile amaurotic idiocy of the Tay-Sachs type. Lipid-bound sialic acid in this case exceeds the normal quantity by a factor of 2–3, and about 80 % of it is present in accumulated ganglioside $G_{GNTrII}1$, which under normal conditions features only in small amounts. All other mono-, di-, and trisialogangliosides constituting about 1 % of the dry weight exhibit a normal level [42].

In another form of lipidosis occurring in late infancy, the ganglioside picture is modified in such a way that about 80 % of all the ganglioside-NANA is contained in the ganglioside $G_{GNT}1$ [43], as compared to the normal value of about 18 %.

Whereas the ganglioside pattern is more or less normal in the juvenile and the late infantile forms of amaurotic idiocy, two monosialogangliosides (probably $G_{Gal}1$ and $G_{Lact}1$) show abnormally high levels in gargoylism, the Niemann-Pick disease, and Gaucher's disease [44].

An abnormally high level is also often found for the corresponding sialic acid-free ceramide oligosaccharides in all these diseases. The specific storage of gangliosides is thus accompanied by a more general disruption of the whole glycolipid metabolism in most cases of neurolipidoses.

9. Biosynthesis and Metabolism of Gangliosides

Sphingosine *(1)* is synthesized by the body from palmitaldehyde and serine:

$$CH_3\text{-}(CH_2)_{14}\text{-}CHO + HO_2C\text{-}\underset{\displaystyle NH_2}{\underset{|}{C}}H\text{-}CH_2OH \longrightarrow \longrightarrow$$

$$CH_3\text{-}(CH_2)_{12}\text{-}CH{=}CH\text{-}\underset{\displaystyle OH}{\underset{|}{C}}H\text{-}\underset{\displaystyle NH_2}{\underset{|}{C}}H\text{-}CH_2OH$$

(1)

Dihydrosphingosine, which is first formed, is subsequently dehydrogenated. According to recent investigations, each hexose molecule is attached in turn to the backbone molecule. For each monosaccharide, there is a separate class of transferases. They are used for the transfer of the same sugar-nucleotide, but they differ in their acceptor-specificity (cf. Table 4).

Table 4. Transferases.

Enzyme	Source	Acceptor	Product
NANA-transferases	*E. coli*	$(NANA)_n$	colominic acid
	Rat mammae	Lact	3′-NANA-Lact
	Goat colostrum	Lact	6′-NANA-Lact
	Submaxillary region of sheep	desialomucin	NANA(2→6)GalNAc-protein
	Chick embryo brain	ceramide lactoside (des-NANA-G_{Lact})	$G_{Lact}1$
	Chick embryo brain	$G_{GNT}1$	$G_{GNT}2a$
Galactose-transferases	Rat mammae	Glc	Lact
	Cow's colostrum and tissues	GlcNAc	*N*-acetyllactosamine
	Cow's colostrum and tissues	GlcNAc-protein	Gal-GlcNAc-protein
	Chick embryo brain	$G_{GNTrII}1$	$G_{GNT}1$

The stepwise synthesis of brain gangliosides $G_{GNT}2a$ and $G_{GNT}3a$ is shown in Scheme 3 [45].

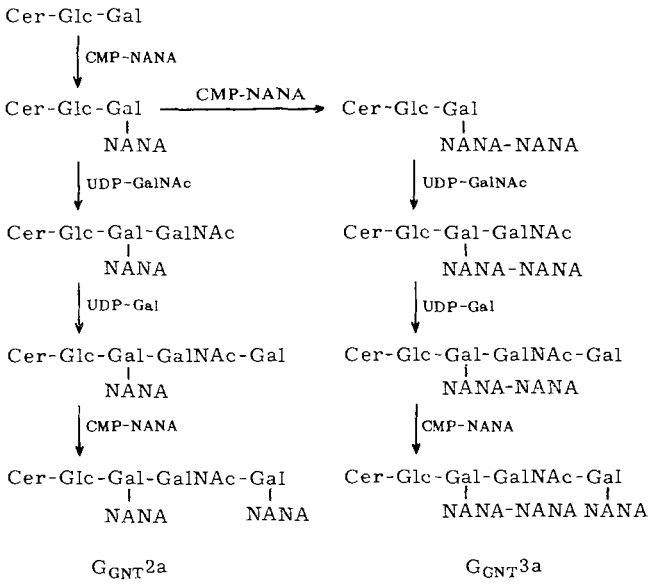
The steric hindrance observed in cleavage by neuraminidase appears to play a part also in the biosyn-

[42] *A. Wagner*, Klin. Wschr. *44*, 398 (1966).

[43] *H. Jatzkewitz* and *K. Sandhoff*, Biochem. biophysica Acta *70*, 354 (1963); *H. Jatzkewitz*, *H. Pilz*, and *K. Sandhoff*, J. Neurochem. *12*, 135 (1965); *K. Suzuki*, Life Sci. *3*, 1227 (1964); *N. K. Gonatas* and *J. Gonatas*, J. Neuropathol. exp. Neurol. *24*, 318 (1965).

[44] *H. Goodwin* and *J. N. Cummings*, J. Lipid Res. *7*, 337 (1966); *A. Taghavy*, *K. Salsman*, and *R. Ledeen*, Federat. Proc. *23*, 128 Nr. 163 (1964); *P. F. Borri*, *G. J. M. Hooghwinckel*, and *G. W. F. Edgar*, J. Neurochem. *13*, 1249 (1966).

[45] *A. Aree*, *H. F. Maccioni*, *R. Caputto*, Arch. Biochem. Biophysics *11*, 52 (1966); *J. C. Steigerwald*, *B. Kaufmann*, *S. Basu*, and *S. Roseman*, Federat. Proc. *25*, 587 No. 2247 (1966); *S. Banu*, *B. Kaufmann*, and *S. Roseman*, J. biol. Chemistry *240*, PC 4115 (1965); Federat. Proc. *25*, 587 No. 2248 (1966).



Scheme 3. Biosynthesis of the brain gangliosides $G_{GNT}2a$ and $G_{GNT}3a$.

thesis. When GalNac is already bound to the 4-position of the front galactose of GNTrII or GNT, sialic acid does not become attached to the same galactose at the 3-position. This also applies in the stepwise biochemical degradation of *e.g.* Cer-Glc-Gal-(NANA)-GalNAc-Gal-NANA ($G_{GNT}2a$). First the terminal NANA residue is split off, and then the next galactose residue. The GalNAc, which is now the end group, must become detached before the next group (NANA) can be eliminated, and so on.

10. Subcellular Localization and the Biological Properties of Gangliosides

To obtain more information concerning the function of gangliosides in the cell, the localization of these lipids inside the cell has been studied, and the results suggest that they occur in the neuronal membranes in the cell body, dendrites, axons, and synaptic junctions, *i.e.* in exactly those elements which are involved in the transmission of nerve impulses.

When *substantia grisea* is homogenized with great care, it is possible to retain some of the nerve endings (synaptosomes) which become detached from the nerves. These nerve endings can be purified by differential and density-gradient centrifugation [46] (cf. Fig. 1a). Basically, they consist of an outer membrane and inner small mitochondria and vesicles characteristic of synapses. The synaptic vesicles contain the chemical substances responsible for the transmission of impulses across nerves. They occur in greatly increased numbers on the direct synaptic contact sites, namely on presynaptic membranes. When lysis is conducted in a hypotonic medium [47], the synaptosomes burst and release their contents. The resulting fragments can be separated by centrifugation (Figs. 1b and 1c). Contrary to earlier assumption [48], the gangliosides are found not in the synaptic vesicles, but in the membrane components originally belonging to the outer membrane of the nerve endings, as shown by electron micrographs. No gangliosides have been found in the mitochondria [49].

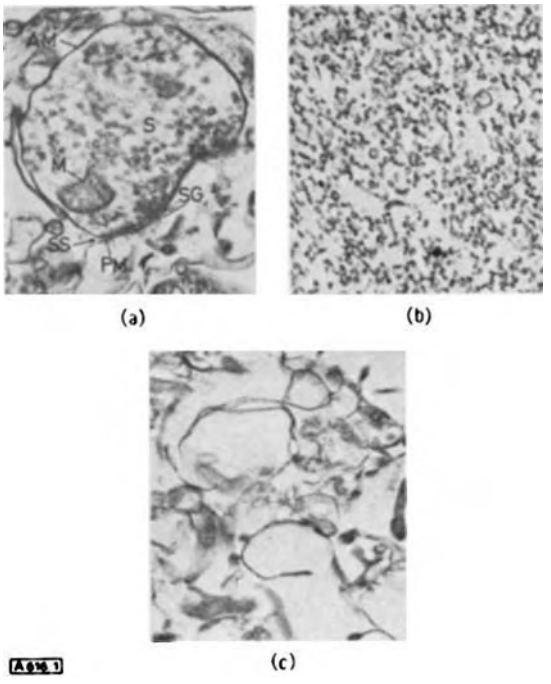


Fig. 1. a) Electron micrograph of a nerve ending isolated from bovine cerebral cortex (contrast coating with OsO_4 embedding in Vestopal W), × 45000. AM = outer membrane; S = synaptic vesicle; M = mitochondrion; SS = synaptic gap; PM = postsynaptic membrane; SG = subsynaptic web.

b) Electron micrograph of isolated synaptic vesicle material (× 40000).

c) Electron micrograph of ganglioside-containing membranes from nerve endings (× 40000).

Another possibility of concentrating ganglioside structures in subcellular fractions consists in treating the latter with the neutral detergent Triton X 100 (isooctylphenoxypolyethoxyethanol) [10], which dissolves gangliosides out of the membranes only to a small extent.

When the total microsome fraction from gray matter or the osmolyzed nerve ending fraction freed from mitochondria and synaptic vesicles is suspended in weakly alkaline Triton X 100, the various types of membranes are attacked with different intensities. Analysis of the membrane components that remain undissolved shows that they are the ones with a high ganglioside content.

Electron micrographs of nerve endings show structures rich in acidic carbohydrates on the outside of axonal membranes and in particular directly at the synaptic

[46] *E. De Robertis, A. Pellegrino de Iraldi, G. Rodriguez, de Lores Arnaiz,* and *L. Salganicoff,* J. Neurochem. *9,* 23 (1962); *V. P. Whittaker,* Biochem. J. *72,* 694 (1959); *E. G. Gray* and *V. P. Whittaker,* J. Anatomy *96,* 79 (1962).

[47] *E. De Robertis, G. Rodriguez de Lores Armaiz, L.Salganicoff, A. Pellegrino de Iraldi,* and *L. M. Zieher,* J. Neurochem. *10,* 225 (1963); *V. P. Whittaker, I. A. Michaelson,* and *R. J. A. Kirkland,* Biochem. J. *90,* 293 (1964).

[48] *R. M. Burton, R. E. Howrad, St. Baer,* and *J. M. Balfour,* Biochem. biophysica Acta *84,* 441 (1964).

[49] *H. Wiegandt,* J. Neurochem. *14,* 671 (1967).

gap [50]. Even the localization of gangliosides suggests that these typically membrane-forming amphiphile lipids, which indeed also carry electric charges, are involved in the impulse-conduction of neurons, and many observations on the physiological action of these lipids support this hypothesis.

Tetanus toxin is known to be fixed by gangliosides [51], at high toxin concentrations *e.g.* $G_{GNT}3$ fixing about 0.6 mole of the toxin (M.wt. $\approx$ 70,000). The action of tetanus toxin is thought to lie in blocking the inhibition synapses, *i.e.* impeding the liberation of neurotransmitter substances [52]. *Wolfe* has shown that the distribution of γ-aminobutyric acid – the presumed transmission substance at the inhibitory synapses – resembles that of the gangliosides [53].

The participation of gangliosides in the transmission of excitation is further supported by the following observation: After 5 h in a tris-buffered glucose Ringer solution at 0 °C, brain tissues no longer show extra respiration on electrical stimulation, but this cold treatment does not affect the normal respiration [55]. The addition of gangliosides to such a damaged system restores up to 80 % of the extra respiration. The author, *McIlwain*, attributed this to histones leaving the cell nuclei in the cold medium and reaching and blocking ganglioside sites.

When injected into the blood, gangliosides may provoke the formation of antibodies against themselves. The serologic specificity of gangliosides is localized in their carbohydrate moiety, the sialic acid also playing an essential part. The gangliosides in the $Rh_0(D)$ antigen-antibody system are found to be carriers of blood group properties [54]. In serologic tests, lacto-*N*-neotetraose from ganglioside $G_{LNnT}1$(NGNA) shows a specificity as regards the nature of the pneumococcus type XIV polysaccharide.

According to *McIlwain* [56], furthermore, the gangliosides lower the concentration of sodium and potassium in the non-inulin space by reducing the sodium space, increasing the potassium space, and depressing the concentration of potassium in the potassium space.

5-Hydroxytryptamine (serotonin) is thought to be a neurotransmitter in the central nervous system. According to *Wooley* and *Gommi* [57], the serotonin-receptor must contain sialic acid, and is probably a ganglioside. These authors demonstrated on a fundus preparation that the serotonin-sensitivity is disturbed by treatment with neuraminidase, but it can be restored by adding gangliosides, particularly $G_{Lact}2$, which fixes serotonin the most strongly. It seems probable that an equimolecular complex is formed in this process [58]. No complex is formed between a ganglioside and serotonin in the presence of $Ca^{2\oplus}$ ions, since gangliosides fix the latter even more strongly. Reserpine, too, liberates serotonin from the complex.

All these results suggest that gangliosides are involved in important functions of the central nervous system, and perhaps in the operations of membranes in general. The next task is to find a connection between the structure and the function of these compounds.

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Recent Results in the Field of Liquid Crystals

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Thermotropic mesomorphous phases such as occur in the melts of many organic substances are considered. Though mesomorphous melts were first observed by Reinitzer in 1888, fundamental structural problems regarding such melts have not, as yet, been completely solved. Part I of this article deals mainly with such structural problems and with the theories of crystalline organic liquids. Part II describes the use of nematic solvents for magnetic resonance studies on oriented molecules. Examples are given to illustrate the possibilities offered by this procedure, and some of the results obtained so far are reviewed.

Introduction

Liquid crystals, or crystalline liquids, are obtained when most organic substances are melted; they are formed at that stage of the melting when insufficient heat has been supplied to bring about the transition into the normal isotropic liquid. They are phases that are strongly anisotropic in some of their properties (a characteristic normally found only in solid crystals), though the phases themselves may be as mobile as water. These thermotropic crystalline phases are separated from the normal liquid and from the crystal by first-order transition points. A given substance may have several mesomorphous phases, and, so far as can be gathered from observations, these are then separated from one another by first-order transition points.

A second group of crystalline liquids occurs in solutions; these are more accurately described as lyotropic crystalline liquids. The best-known representatives of this group are aqueous soap solutions. The molecular structures of the soap-water systems have recently been studied in some detail. The reader is referred to the latest article[1] in a long series of reports[2] on this topic.

Several reviews[3–6] and a book[7] on crystalline liquids have appeared during the last ten years, and several recent articles deal with mesomorphous states in biological systems[8]. All the organic substances known through 1959 to possess mesomorphous properties have been listed by *Kast*[9], and the results of dielectric and refractometric measurements have been collected by *Maier*[10,11].

I. Structures, Theories, and Properties of Crystalline Liquids

1. Types of Crystalline Liquids

There are three principal types of crystalline liquids, which are described by the terms proposed by *Friedel*[12], *i.e.* nematic, cholesteric, and smectic. (A notable exception is formed by the mesomorphous melt of diisobutylsilanediol, which cannot be classified according to this scheme[13].) Molecules that form mesomorphous phases are more or less elongated. Figure 1 shows the schematic structures of the

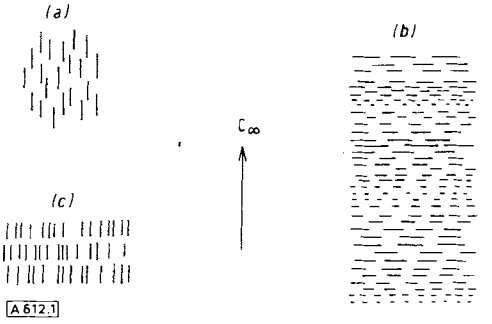

Fig. 1. Structures of mesomorphous phases and position of the principal axis of symmetry.
a) nematic, b) cholesteric, c) smectic.
The projections of the molecules in the plane of the drawing are shown by lines. The length of the lines in (b) illustrates the rotation of the preferred orientation along the C_∞ axis.

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mesomorphous phases. The order in all mesomorphous phases is characterized by the more or less complete orientation of the molecules with their long axes parallel. This orientation is apolar, *i.e.* a given molecular orientation and the orientation obtained from it by rotation through 180° are equally probable. Crystalline liquids are thus not ferroelectric. However, doubt is cast on this general conclusion by a number of recent investigations [14–16].

a) Nematic Liquids

Nematic liquids differ structurally from normal isotropic liquids only in the spontaneous orientation of the molecules with their long axes parallel (Fig. 1). In the absence of special measures, the preferred direction of the long axes is not constant over large areas, but varies (generally continuously) with position. Nematic liquids are characterized by the thread-like structures that can often be observed in thin films under the polarization microscope (Fig. 2). These are

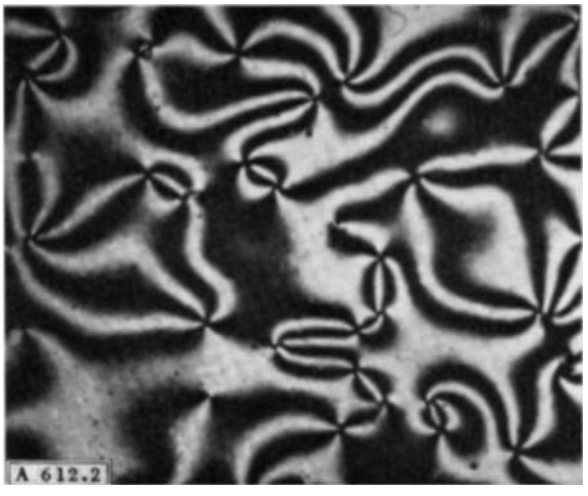

Fig. 2. Nematic fiber texture of 1,4-bis(*p*-ethoxybenzylidene)cyclohexanone. Crossed Nicols, magnification 100× (According to *Sackmann* and *Demus*).

striae resulting from a particularly strong dependence of the preferred direction on position in the vicinity of the axis of the thread. There may no longer be any definite preferred direction in the axis of the thread itself. Homogeneously aligned layers, *i.e.* layers having a constant preferred direction, behave optically in the same way as uniaxial crystals exhibiting positive birefringence, *i.e.* the ordinary ray has the lower refractive index. The optical axis coincides with the preferred direction of the long axis of the molecule.

The molecular orientation is not completely parallel, owing to the thermal motion pf the molecules. The parallelism is measured by the expression

$$S = (1/2) \langle 3 \cos^2 \Theta - 1 \rangle \qquad (1)$$

where θ is the angle between the long axis of a molecule and the preferred direction. The angular brackets indicate that the expected value, *i.e.* the average value of $\cos^2 \theta$, is to be used. For perfectly parallel orientation, *i.e.* for ideally nematic order, $S = 1$, while for the isotropic phase $S = 0$. In nematic liquids S is strongly temperature-dependent and increases with falling temperature. According to existing results, the value of S at the clear point, *i.e.* the transition point to the isotropic phase, is between 0.3 and 0.5. The highest S values observed in nematic liquids are about 0.8 (see Fig. 7, Section I.3).

Nematic liquids can readily be homogeneously oriented. Large samples are most easily oriented by magnetic fields of several thousand gauss [17]; the optical axis becomes parallel to the field axis. Thin films between glass plates can be oriented by boundary effects [18, 19]. By suitable surface treatment, it is possible to obtain two different homogeneous orientations *e.g.* with 4,4′-bis(methoxy)azoxybenzene. Rubbing of the surfaces of the glass in a given direction leads to "planar layers" in which the optical axis lies in the plane of the film and parallel to the rubbing direction; "erected layers", in which the optical axis is perpendicular to the plane of the film, are obtained by careful cleaning of the surfaces *e.g.* with sulfuric acid/bichromate.

b) Smectic Liquids

A given substance may give one or more smectic phases as well as a nematic phase. The smectic phases always occur – in agreement with the higher order – at lower temperatures. However, a smectic phase can also occur as the only mesomorphous phase. According to observations on homogeneously oriented erected smectic layers, smectic liquids, like nematic liquids, behave optically in the same way as uniaxial crystals having positive birefringence.

In thin, nonhomogeneously oriented films, smectic liquids can be recognized microscopically from their characteristic textures, which can be used for classification purposes [20]. Some examples are shown in Figures 3 and 4. The polygon texture in Figure 4 is a special case of the focal conic texture, which was studied and explained by *Friedel* [12].

The focal conic texture is characterized by ellipses, each with a corresponding hyperbolic branch, and which, like the nematic threads, can be seen because of the very strong dependence of the preferred direction on position in their vicinity. There is probably no longer a preferred direction on the ellipses and hyperbolic branches. An ellipse and the corresponding hyperbola lie in two mutually perpendicular planes, the major axis of the ellipse lying in the intersection of the two planes. The ellipse passes through the foci of the hyperbola, and the hyperbola (of which only one branch is visible) runs through the foci of the ellipse. In the region between the curves, the preferred directions lie along the

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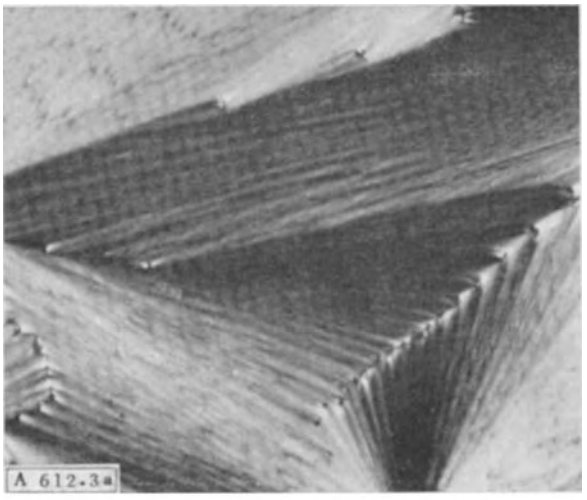

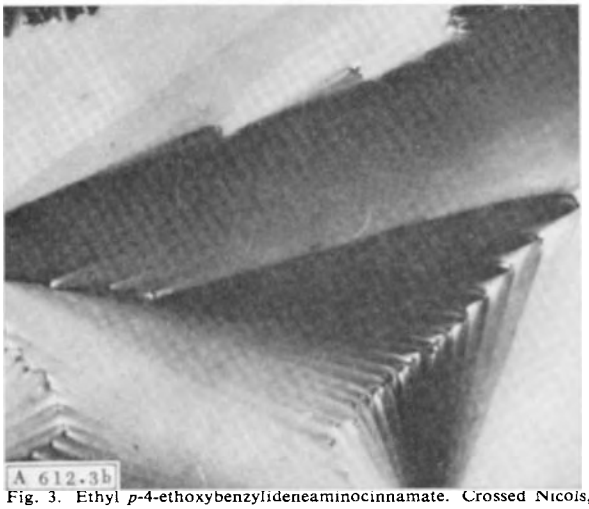

Fig. 3. Ethyl *p*-4-ethoxybenzylideneaminocinnamate. Crossed Nicols, magnification 100×. Fan texture: (a) 120°C, smectic phase A; (b) 110°C, smectic phase B, obtained by cooling of (a) (According to *Sackmann* and *Demus*.)

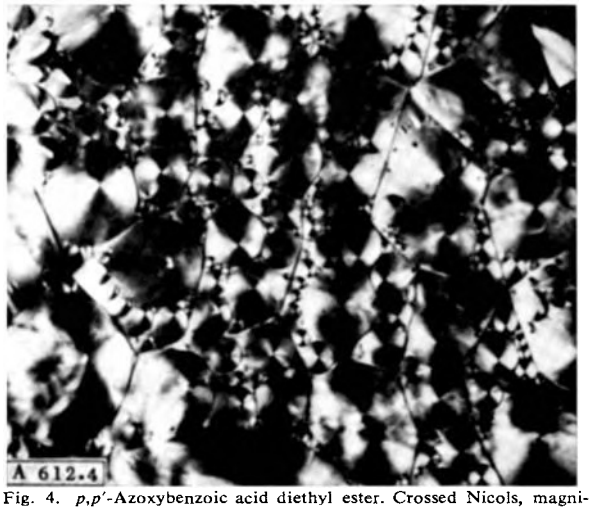

Fig. 4. *p,p'*-Azoxybenzoic acid diethyl ester. Crossed Nicols, magnification 100×, focusing on upper side of sample, 120°C. Smectic polygon structure. (According to *Sackmann* and *Demus*.)

straight lines running from the ellipse to the visible branch of the hyperbola. Equidistant parallel surfaces can be placed perpendicular to these lines (Dupin cyclides). In the polygon texture, the boundary faces show ellipses, which are gathered into groups within polygons (Fig. 4).

The classification of smectic phases has been studied in detail by *Sackmann*, *Arnold*, and *Demus* [20–25]. Their investigation of the miscibility of mesomorphous phases indicates the existence of at least three types of smectic phases, which are denoted by A, B, and C.

Most of the smectic phases observed belong to type A, which corresponds to the structure shown in Figure 1c [21]. Comparison with the nematic phases shows the existence of an additional optical principle in this case, *i.e.* the arrangement of the centers of gravity of the molecules in planes perpendicular to the preferred direction of the long axis of the molecule, and hence perpendicular to the optical axis. In type A, the distribution within the planes is irregular.

Smectic liquids of type B have been observed only in substances in which at least type A also occurs. Type B always occurs in the lowest temperature range. It probably differes from type A in that the arrangement of the centers of gravity of the molecules in the plane is hexagonal close-packed [26]; however, X-ray analyses have been carried out for only a few cases [27]. If type C and type A occur together, type C always exists at lower temperatures. This type C has a more highly ordered structure than type A, though it is not yet known in what respect.

Table 1 shows some recent results obtained by *Arnold* [26, 28, 29] for the heats of transition for transitions into and between mesomorphous phases. It can be concluded from the temperature-dependence and the magnitude of the birefringence [11] that the S values of smectic liquids vary only slightly with temperature and are higher than those of nematic liquids. IR measurements for the determination of S have been reported for 4,4'-bis(*n*-heptyloxy)azoxybenzene (type C); the value obtained was 0.9 [30].

c) Cholesteric Liquids

A cholesteric phase occurs only in optically active substances. It may be regarded as a special case of a nematic phase, since its molecular structure corresponds to a twisted nematic layer (cf. Fig. 1). In a homogeneously oriented layer, the preferred direction is no longer constant over the entire volume; there

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Table 1. Data for the transition of mesomorphous phases.

Where necessary, the type of transition is shown beside the temperature.

Compound	cryst. solid → cryst. liq.		smect. B or C →smect. A		smect. → nem.		cryst. liq. → isotrop. liq.	
	Temp. (°C)	Heat (kcal·mol^{-1})	Temp. (°C)	Heat (kcal·mol^{-1})	Temp. (°C)	Heat (kcal·mol^{-1})	Temp. (°C)	Heat (kcal·mol^{-1})
4,4′-Dimethoxy-azoxy-benzene	118 (→nem.)	7.06					135 (nem.→)	0.137
4,4′-Diethoxy-azoxy-benzene	137 (→nem.)	6.41					168 (nem.→)	0.326
4,4′-Dipropoxy-azoxy-benzene	115 (→nem.)	6.42					124 (nem.→)	0.161
4,4′-Dibutoxybenzene	102 (→nem.)	5.00					137 (nem.→)	0.247
4,4′-Dipentyloxybenzene	76 (→nem.)	3.48					123 (nem.→)	0.173
4,4′-Dihexyloxybenzene	81 (→nem.)	9.88					129 (nem.→)	0.250
4,4′-Diheptyloxybenzene	74 (→sm.C)	9.77			95 (sm.C→)	0.380	124 (nem.→)	0.243
4,4′-Dioctyloxy-azoxy-benzene	80 (→sm.C)	10.07			108 (sm.C→)	0.282	126 (nem.→)	0.343
4,4′-Dinonyloxy-azoxy-benzene	76 (→sm.C)	9.11			113 (sm.C→)	0.394	122 (nem.→)	0.421
4,4′-Didecyloxy-azoxy-benzene	78 (→sm.C)	9.21			121 (sm.C→)	0.553	123 (nem.→)	0.751
4,4′-Diundecyloxy-azoxy-benzene	81 (→sm.C)	9.81					121 (sm.C→)	2.40
4,4′-Didodecyloxy-azoxy-benzene	82 (→sm.C)	10.04					123 (sm.C→)	2.86
Ethyl 4-ethoxybenzylidene-4-amino-cinnamate	81 (→sm.C)	6.52	118 (B→A)	0.501	156 (sm.A→)	1.22	159 (nem.→)	0.12
Di-*n*-dodecyl 4,4′-azoxy-α-methylcinnamate	79 (→sm.C)	17.45	82 (C→A)	0.024			88 (sm.A→)	2.10

are instead parallel planes in which the preferred direction is constant. Thus though their order is no higher than that of true nematic liquids, these "cholesteric-nematic" liquids have a layer structure, which leads in many respects to behavior similar to that of smectic liquids. As one proceeds along a line perpendicular to the planes of constant preferred direction, the preferred direction rotates uniformly. The pitch of this rotation (rotation through 2π) varies widely, is usually temperature-dependent, and is generally between 0.2 and 20 μ. The temperature-dependence may be positive or negative.

The twisting cannot be detected directly by X-ray studies [31], which merely seem to confirm that the arrangement of the molecules over small regions containing only a few molecules is almost the same as that in the isotropic liquid. This is also true of nematic liquids [32, 33]. The twisting of the cholesteric liquids can be seen in the unusual optical behavior of homogeneously ordered layers:

1. On irradiation parallel to the axis of rotation, over a small wavelength range about $\lambda_R = pn$, where p is the pitch of the rotation and n is the average refractive index, only one circularly polarized beam is transmitted while the other is totally reflected; however, no reversal of the direction of rotation takes place in contrast to reflection from a metallic surface.

2. Outside this range, a strong optical rotatory power (up to 100 rotations per millimeter) can be observed on perpendicular irradiation [10]. The total reflection range separates wavelength ranges with opposite rotation directions.

If λ_R lies in the visible region, the total reflection gives rise to a bright color. Since p is strongly dependent on temperature for many substance, the color observed may also be strongly temperature-dependent. Thin homogeneously oriented layers of such substances can therefore be used to show directly the temperature distribution on a surface [34–37]. Another application is based on the dependence of p, and hence of the reflection color, on dissolved substances.

For example, the reflection color of a cholesteric mixture of 20 % of cholesteryl chloride and 80 % of cholesteryl nonanoate changes from the normal green to red on absorption of benzene and to blue on absorption of chloroform. The color changes are so sensitive that they can be used to detect even traces of vapors [34].

The twisting of the molecular structure of cholesteric liquids was deduced by *Friedel* [12] from observations made on their optical behavior. This conclusion is confirmed by more recent theoretical studies by *de Vries* [38] who investigated the optical properties of

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continuously twisted anisotropic layers for strong twisting with illumination only along the axis of rotation. He found that layers of this type have the same unusual properties as are observed in cholesteric liquids. Quantitative experimental checks were carried out by *Cano* and *Chatelain*[39], who studied the optical rotatory power of cholesteric mixtures as a function of the structural twisting.

Planar homogeneously oriented cholesteric layers, *i.e.* layers having a uniform axis of rotation, can be relatively easily produced between two plates of glass or mica. The axis of rotation is perpendicular to the plane of the layer. If, in wedge-shaped layers, the preferred direction at the interfaces is fixed by boundary effects, regular fringes (Grandjean fringes) are observed. The fringes follow the lines of constant thickness. The increase in thickness from one fringe to the next is equal to $p/2$; these fringes can be explained as resulting from the twisting[40].

Nonhomogeneously oriented cholesteric layers, like smectic liquids, can have the focal conic texture. In this case the parallel equidistant surfaces presumably coincide with the surfaces of uniform preferred direction and their normal directions with the straight axes of rotation[5,6]. They therefore differ from homogeneous layers in that the direction of the axis of rotation varies with position, but the twisting should otherwise be the same. However, no direct evidence of twisting is observed in the optical behavior of nonhomogeneous layers of this type. For example, they exhibit no unusual reflecting power, probably because of the nonuniform orientation of the axes of rotation.

Homogeneous, non-birefringent layers can also be obtained by cooling from the isotropic phase[7]; the focal conic texture develops in these layers only on further cooling. In this context, mention should also be made of another question that has not yet been answered. During viscosity measurements on cholesteryl stearate, *Porter* and *Johnson*[41] found no sudden change at the transition point from the cholesteric to the smectic phase. However, the authors could not establish whether a phase transition actually occurred in the sample examined.

No experimental details are known about the fluctuation of the molecular axes about the preferred direction in cholesteric liquids. The molecules are probably oriented to about the same extent as in true nematic liquids.

Optically active substances can form smectic phases as well as (or instead of) a cholesteric phase. The smectic phases then always exist at lower temperatures. These smectic phases show no peculiarities as compared with those of inactive substances. The criteria that the centers of gravity of the molecules should be arranged in equidistant planes and that the preferred directions should be perpendicular to these surfaces are not compatible with the twisting that characterizes the cholesteric liquids.

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2. Theories of Nematic Liquids

a) Swarm Theory

Thick layers of nematic liquids appear cloudy, and are reminiscent of emulsions. The turbidity is due to the fact that samples of this type are not homogeneously oriented unless special measures are taken. However, distinct turbidity, *i.e.* strong light scattering, is still found when the orientation is made homogeneous *e.g.* by means of a magnetic field. It may therefore be concluded that molecules in regions up to 0.1 μm in diameter exhibit random changes in orientation[42].

The strong light scattering is one of the main pieces of evidence in favor of the swarm theory, which was advocated in particular by *Ornstein* and *Kast*[43], and which is still favored for the interpretation of experimental results. This theory is essentially as follows. The molecules of nematic liquids group together to form swarms containing on average about 10^5 molecules. Within these swarms, the molecules lie parallel to one another. The directional component of the interaction between the swarms is small, so that the orientation of the axes of the swarms in relation to one another is random unless a uniform orientation is imposed by external agencies. The swarms have only a limited life, and are constantly being broken down and then reformed.

The assumption that only weak orienting forces exist between the swarms has not been confirmed. Observations on thin layers (<0.3 mm), some of which will be described in the next section, contradict this idea, as do *Maier*'s observations[17] on the behavior of thick layers. Complete orientation of the liquid in thick layers can be achieved even with relatively low magnetic field strengths (1000–2000 gauss). This is illustrated by Figure 5, which shows the dielectric anisotropy of 4,4'-bis(methoxy)azoxybenzene. The ascending part of the saturation curve is not shown, since the experimental reproducibility is poor. After the magnetic field has been switched off it may take

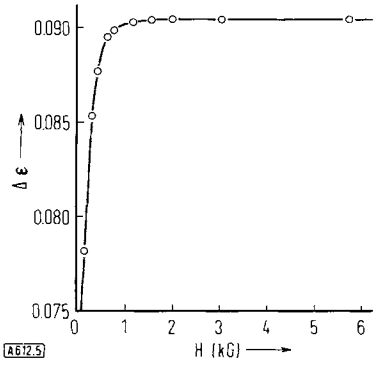

Fig. 5. Dielectric anisotropy of nematic liquid 4,4'-bis(methoxy)azoxybenzene according to *Zindel* [44]. Temperature 134.7 °C, measuring frequency 100 kHz, ε_1 dielectric constant parallel to the magnetic field, ε_2 perpendicular to the magnetic field, $\Delta\varepsilon = \varepsilon_2 - \varepsilon_1$.

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[43] *L. S. Ornstein* and *W. Kast*, Trans. Faraday Soc. *29*, 931 (1933).

[44] *D. Zindel*, unpublished.

several minutes before the system regains its initial state [17]. The deorientation of independent swarms should be much faster for nematic 4,4′-bis(methoxy)-azoxybenzene, owing to its low viscosity. The form of the saturation curve should also be different if the magnetic field has to orient independent swarms in opposition to the effects of thermal motion. This is shown by the fact that the dielectric anisotropy does not disappear completely even in the absence of external fields [17].

The alignment by a magnetic field can be equally easily explained without reference to any swarm structure. In the nematic liquid, which is aligned at the interfaces by boundary effects and in the body of the liquid by convection currents [17], the application of a magnetic field leads to uniform alignment of the molecules owing to the diamagnetic anisotropy of the volume elements and the free mobility of the molecules. The imposed alignment is such that the axis along which the diamagnetic susceptibility is lower lies parallel to the magnetic field. The saturation field strength will therefore obviously depend on the experimental conditions, *i.e.* on the strength and nature of the preorientation by boundary effects and convection currents, and is not a constant characteristic of the liquid. The alignment in the magnetic field is not associated with any appreciable change in entropy (see Fig. 5).

The small effect of a magnetic field on the thermal motion of the molecules was shown particularly impressively by *Chatelain* [45]. This author found that, in a layer more than 0.5 mm thick of 4,4′-bis(methoxy)-azoxybenzene that was homogeneously aligned by boundary effects, a 20000 gauss magnetic field parallel to the optical axis does not appreciably influence the birefringence, and so has less effect on the variation of the orientation of the molecules than a temperature change of 0.02 °C. The variation of the orientation is also substantially unaffected by boundary effects. The birefringence was found to be constant for layer thicknesses of 2 μm to 0.7 mm [45].

The structure of nematic liquids is more continuous than the original swarm theory assumed. Nevertheless, there is some justification for the imaginary breakdown of the liquid into swarms as a model for the description of collective random variations of orientation. One example of the use of this model is *Chatelain*'s treatment of light scattering [42].

b) Continuum Theory

When thin layers of nematic liquids are examined under the microscope, the liquid appears to be clear, and one gains the impression of one continuous structure. Observations of this nature form the main basis of the continuum theory, which is due to *Zocher* [46] and *Oseen* [47]. This theory is not confined to nematic liquids, but is also applicable to cholesteric and smectic liquids. It was recently revised and presented in a simple form by *Frank* [48].

The continuum theory is based on the assumption that at every point in an undisturbed crystalline liquid, there is a definite preferred direction for the orientation of the longitudinal axes. This preferred direction is assumed to vary continuously with position, except possibly at a few special surfaces or lines, where the preferred direction is naturally no longer definite.

As a consequence of these assumptions, crystalline liquids must be expected to have elastic flexible structures, since the preferred direction and its variation can be determined only if it affects the free energy and if the latter has a minimum for the prevailing boundary conditions. Following a small external disturbance, the molecules will return to the previous orientation.

The change in free energy as a result of a deformation, *i.e.* the deformation energy, can be calculated with the aid of elastic constants. In particular, a maximum of four constants [48] should be required to describe the deformation energy for small deviations from the homogeneous orientation in nematic liquids. Three of these constants belong to the fundamental deformations defined by *Zocher* [46] (Fig. 6). In the case of the twisting, the deformation energy is given by equation (2).

$$E_{\mathrm{def}} = \frac{1}{2} K_{\mathrm{d}} \varphi'^2 \qquad (2)$$

where K_{d} is the deformation constant and φ' is the derivative of the angle of rotation along the axis of rotation. Similar equations are valid for other fundamental deformations.

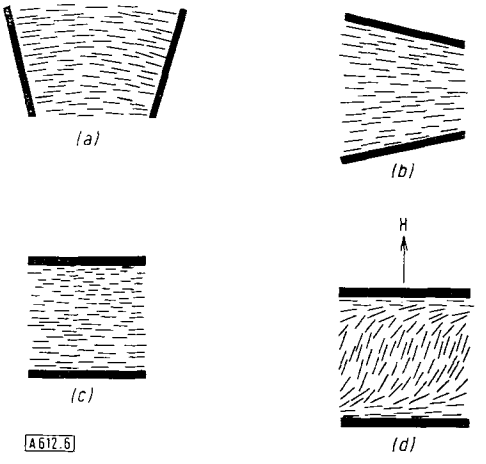

Fig. 6. Deformations of a nematic liquid. (a)–(c) Fundamental deformations: longitudinal bending, transverse bending, and twisting; (d) deformation of a planar layer in a magnetic field.

Experimental studies on bending behavior have so far been carried out only for nematic liquids, the properties observed being as expected. In these studies, a magnetic field was used to deform nematic layers that had been homogeneously oriented by boundary effects (Fig. 6), and the change in the optical properties

[45] *P. Chatelain*, Thesis, Paris 1937; Bull. Soc. Minéralog. franc. *50*, 280 (1937).

[46] *H. Zocher*, Z. Physik *28*, 790 (1927).

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[48] *F. C. Frank*, Discuss. Faraday Soc. *25*, 19 (1958).

was observed [49]. When the magnetic field is switched off, the molecules resume their original homogeneous orientation. The three constants of the fundamental deformations can be relatively easily determined by this procedure, but absolute determinations of the three constants have been reported only for 4,4′-bis(methoxy)azoxybenzene [50, 52]. The constants are strongly dependent on temperature, but their ratio remains constant [52]. The calculated deformation energies are low, even for considerable deformations.

Consider for example a nematic layer of 4,4′-bis(methoxy)azoxybenzene having imposed twisting. With $K_d = 3.7 \times 10^{-7}$ dyne at 125 °C [52] and for a pitch of 1 cm ($\varphi' = 2\pi$), the deformation energy is only 0.7×10^{-5} erg·cm^{-3}.

For a pitch of 1 μm, *i.e.* twisting of the same order of magnitude as the spontaneous twisting of many cholesteric liquids, the deformation energy increases to 730 erg·cm^{-3}, *i.e.* 0.004 cal·mole^{-1}.

It is interesting to compare this deformation with the energy liberated by spontaneous parallel orientation of the longitudinal axes. On the basis of the theory described in Section I.3, it can be estimated that for 4,4′-bis(methoxy)azoxybenzene at the same temperature this energy is about 300 cal·mole^{-1}, *i.e.* almost 10^5 times as great. The comparison suggests that in the statistical description of cholesteric liquids, the twisting may, to a good approximation, be disregarded in the treatment of the parallel orientation of the molecular axes, and that cholesteric liquids behave in the same way as normal nematic liquids in this respect.

A comparison of the energies also explains why a strongly twisted structure may be favored by optically active molecules and why normal nematic liquids also assume a cholesteric character when optically active substances are added, since even slight changes in the interaction between the molecules is sufficient to cause twisting.

3. Degree of Order and Statistical Treatment of the Nematic State

The degree of order $S = (1/2) \langle 3 \cos^2 \Theta - 1 \rangle$, which gives the average deviation of the orientation of the molecular axes, can be determined experimentally by various methods. It can be found from the principal refractive indices or from the principal diamagnetic susceptibilities [51, 53–55]. Other possibilities are the use of IR or UV dichroism [30, 54, 55], nuclear resonance spectra [56–58], or X-ray scattering [32]. Comparison and critical examination of the S values found by various methods for 4,4′-bis(methoxy)azoxybenzene [55] shows that the results agree to within the experimental error. Thus nematic liquids have a well-defined degree of order, which can be determined experimentally.

For a statistical treatment of the nematic state, it appears convenient to apply a long-range order theory similar to the Weiss theory of ferromagnetism as the simplest approximation; *Born* [59] attempted this as early as 1916. In this treatment we consider only the rotational degrees of freedom of the molecules and assume that the interactions between the molecules, in so far as they affect the orientation of an individual molecule, may be replaced by an internal field. Thus each molecule has assigned to it a potential energy $D = f(S, V, \Theta)$, which depends in the case in question on the angular position Θ of its longitudinal axis, the degree of order S, and the molar volume V. It is assumed in this treatment that the anisotropy of the molecules perpendicular to their longitudinal axes is negligible. Application of Boltzmann statistics then gives eq. (2a).

$$S = \frac{3}{2} \cdot \frac{\int_0^{\pi/2} \exp(-D/kT) \cdot \cos^2\Theta \cdot \sin\Theta \, d\Theta}{\int_0^{\pi/2} \exp(-D/kT) \sin\Theta \, d\Theta} - \frac{1}{2} \qquad (2a)$$

This gives S as a function of the temperature and of the molar volume if the expression for D is known explicitly.

If, in the determination of D, it is assumed that the nematic order is mainly due to dispersion forces, restriction to the pure dipole-dipole component [60] gives eq. (2b). The quantity A is as yet unknown.

$$D = -\frac{1}{2} \cdot \frac{A}{V^2} S (3 \cos^2 \Theta - 1) \qquad (2b)$$

It is not possible to list here the many assumptions involved in the statistical method and in the expression for D. Comparison of calculated and experimental data, and particularly a comparison of the S values, shows that these assumptions are justified, and that a qualitatively satisfactory description of the nematic state is obtained.

The quantity A, which is a characteristic of the substance, can be calculated from the transition temperature if the molar volumes of the nematic and of the isotropic liquid at the clear point are known. It must be assumed for this calculation that the molecular structure does not change during the phase transition. The available empirical data [60] indicates that, owing to the relatively small change in volume at the clear

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[53] *P. Chatelain*, Bull. Soc. franc. Minéralog. Cristallogr. *78*, 262 (1955).

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[58] *J. D. Rowell, W. D. Phillips, L. R. Melby*, and *M. Panar*, J. chem. Physics *43*, 3442 (1965).

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[60] *W. Maier* and *A. Saupe*, Z. Naturforsch. *13a*, 564 (1958); *14a*, 882 (1959); *15a*, 287 (1960).

point, eq. (2c) is approximately satisfied. In this equation, T_K is the clear point (°K) and $V_{n,K}$ is the molar volume of the nematic phase at the clear point.

$$A/kT_K V_{n,K}^2 = 4.55 \quad (2c)$$

It is convenient to introduce a reduced temperature τ, where V_n is the molar volume of the nematic phase at

$$\tau = T\, V_n^2/T_K V_{n,K}^2 \quad (2d)$$

the absolute temperature T. According to eq. (2c), a plot of S as a function of τ gives a curve which is generally valid.

Figure 7 shows the experimental values of S for various nematic liquids plotted against $T_{red} = 100\ T/T_K$ instead of against τ; this is permissible for a qualitative comparison. The curve shown is that calculated for 2,4-nonadienoic acid. The agreement is almost perfect for this substance and for 2,4-undecadienoic acid [54], which is not shown. On the other hand, the experimental S values are higher for 2,4-decadienoic acid (not shown) and for most other substances. One exception is 4,4′-bis(methoxy)azoxybenzene, which gives lower S values. It is interesting to note that 4,4′-bis(methoxy)azoxybenzene and 4,4′-bis(ethoxy)azoxybenzene, though differing only slightly in structure, differ considerably in their S values (Fig. 7). Two other higher homologs that have been studied by IR spectroscopy [30], *i.e.* 4,4′-bis(hexyloxy)azoxybenzene and 4,4′-bis(heptyloxy)azoxybenzene, have S values approximately equal to those of 4,4′-bis(ethoxy)azoxybenzene.

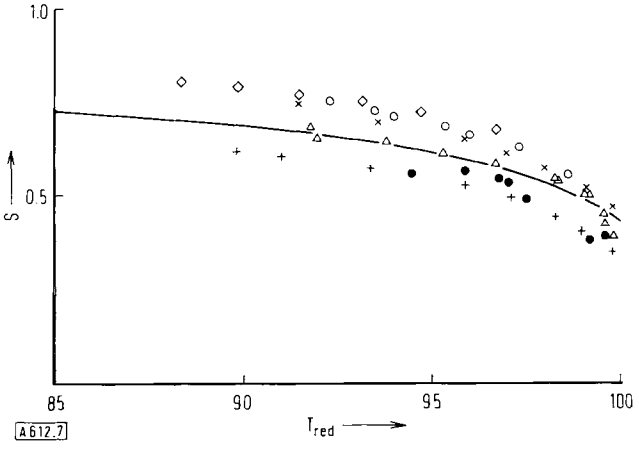

Fig. 7. S values of nematic liquids.
2,4-Nonadienoic acid (clear point 53 °C): Δ from IR data[54], continuous curve from theory [54, 60];
4,4′-bis(methoxy)azoxybenzene (clear point 136 °C): ● from NMR data, + from refractive indices [*];
4,4′-bis(ethoxy)azoxybenzene (clear point 168 °C):
○ from NMR data, × from refractive indices [*];
4-*n*-hexyloxybenzoic acid (clear point 154 °C):
◇ from NMR data [58].

[*] The S values were recalculated by the method described in [55] from experimental data reported by *Chatelain* and *Germain* [61]. The crystals were treated as optically uniaxial for the calculation of the internal field, *i.e.* the two somewhat different lower refractive indices were replaced by the average value $\bar{n}$:

$$\frac{\bar{n}^2-1}{\bar{n}^2+2} = \frac{1}{2}\left(\frac{n_p^2-1}{n_p^2+2} + \frac{n_m^2-1}{n_m^2+2}\right)$$

It was also assumed that the arrangement of the molecules in the crystal corresponds to ideal nematic order (*i.e.* $S = 1$ in the crystal).

In view of the rough manner in which the intermolecular interactions were taken into account and the very simple statistical approximation used, the agreement with the theory is good on the whole (In this context, the reader is referred to further applications [52, 61–64].) However, this theory does not permit a quantitatively correct description of the nematic state.

4. Dielectric Properties of Nematic Liquids

The behavior of crystalline liquids in electric fields has been the object of numerous experimental and theoretical investigations. It was hoped that these studies would lead to some elucidation of important structural problems [14–17, 65–71].

As has been mentioned, nematic liquids in thick layers (>0.1 mm) can be homogeneously oriented by magnetic fields. Homogeneously oriented layers of this type can be used for the measurement of the two principal dielectric constants, ε_1 parallel to the optical axis and ε_2 perpendicular to this axis; the first accurate measurements were carried out in 1954 by *Maier*, *Barth*, and *Wiehl* [65]. Further experimental studies have more recently been carried out on nematic and on some smectic liquids in the radio frequency [66] and microwave regions [67–69]. In the smectic phase, measurements could be carried out on partly oriented layers obtained by cooling isotropic or nematic layers in a magnetic field [66, 67].

A theoretical study by *Maier* and *Meier* [70] deals with the dependence of the static ε_1 and ε_2 values on the degree of order of the nematic liquid and on the molecular properties (*e.g.* on the magnitude and orientation of the permanent electric dipole moment in the molecule and on the polarizability anisotropy). Applications to nematic liquid 4,4′-bis(alkoxy)azoxybenzenes and 4,4′-bis(alkoxy)azobenzenes show that the dielectric anisotropy of the nematic phase and the values of ε_1 and ε_2 are understandable as a consequence of the average orientation described by the degree of order S [70]. At a measuring frequency of 100 kHz, the

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[63] *H. Arnold*, Z. Chem. *4*, 211 (1964).
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[70] *W. Maier* and *G. Meier*, Z. Naturforsch. *16a*, 262 (1961).
[71] *G. Meier* and *A. Saupe*, Molecular Crystals *1*, 515 (1966).

transition from the isotropic into the nematic phase is not accompanied by any appreciable change in the average contribution of the orientation polarization, from which it could be concluded that a specific and very pronounced dipole association occurs in the nematic phase. An obvious conclusion is that there is no ferroelectric or antiferroelectric short-range order in these liquids.

In all the substances that have been studied, ε_1 and ε_2 exhibit a normal Debye relaxation in a range of frequencies around 10^{10} Hz. A Debye relaxation of the isotropic liquid phases is also found in the same frequency range. However, the measurements on 4,4′-bis(*n*-alkoxy)azoxybenzene derivatives in the radio frequency range [66] led to the discovery of an additional relaxation region, which occurs only in the mesomorphous phases and affects ε_1, whereas ε_2 shows no dispersion between 100 kHz and 4 MHz.

The lower-frequency relaxation is assigned to the dipole moment of the azoxy group, or more precisely to the component of the dipole moment parallel to the longitudinal axis of the molecule. This component can be aligned with the optical axis simply by rotation of the molecule about a transverse axis. For this to happen, it is necessary to overcome a potential barrier associated with the parallel orientation in the mesomorphous phases. It is therefore understandable that the corresponding relaxation time becomes greater.

In contrast to the azoxy compounds, no low-frequency relaxation could be observed for the azo compounds [66]. This is in agreement with the above interpretation, since the azo group has no permanent dipole moment, and hence no dipole component that can be aligned simply by rotation about a transverse axis of the molecule.

Theoretical studies [71] based on an extended Debye expression show how the retardation of the relaxation is related to the angular distribution function of the molecules. Since the ε_1 relaxation times are found to increase by a factor of 10^2 to 10^3, it may be concluded that the probability of the perpendicular orientation of the molecules ($\Theta = 90\,^\circ$) is only about 1 % to 0.1 % of the value for a uniform distribution (isotropic phase). The height of the potential barrier can also be estimated. However, more detailed assumptions concerning the analytical form of the angular distribution function are then necessary.

From the expression $f(\Theta) = \sin\Theta \cdot \exp(C \cdot \cos^2\Theta / kT)$ for the angular distribution function, the factor g by which the dielectric relaxation time is increased by the nematic order is found to be given by equation (3) [71].

$$g = \frac{kT}{C}\,(e^{C/kT} - 1) \approx \frac{kT}{C}\,e^{C/kT} \qquad (3)$$

The height of the potential barrier found for 4,4′-bis-(methoxy)azoxybenzene [71], with the experimental value $g = 100$ at 121 °C, is $C = 5.1$ kcal/mole. (C = difference between the free energies in the perpendicular and parallel molecular orientations.) This potential can also be estimated from the degree of order found by experiment. By definition,

$$S = (3/2)\int_0^{\pi/2} \cos^2\Theta\, f(\Theta)\cdot d\Theta \Big/ \int_0^{\pi/2} f(\Theta)\cdot d\Theta - 1/2$$

With $S = 0.56$ at 121 °C for 4,4′-bis(methoxy)azoxybenzene, as follows from the diamagnetic susceptibilities [55], and with the above expression for the angular distribution function, $C = 3.2$ kcal/mole. (The statistical theory described in Section I.3 gives $C = 3.3$ kcal/mole.)

The main reason for the difference in the two experimental estimates is that the correlation of the rotational motions of adjacent molecules, which is of the utmost importance to the dielectric relaxation behavior, was not taken into account. Despite the differences, however, it is confirmed that the peculiarities of the dielectric relaxation behavior can be explained as resulting from the parallel orientation.

Whereas the dielectric properties of nematic liquids at frequencies above 100 kHz now seem to be essentially understandable, their behavior in static electric fields and in alternating fields having very low frequencies is still largely unexplained. The orienting action, at least in very low-frequency fields and in static fields, is not determined entirely by the dielectric anisotropy, as might have been expected.

More recent studies on this point have been carried out on macroscopic samples [58, 68] and on thin layers [14–16, 72–76].

Carr [68] has measured the dielectric losses in the microwave region in macroscopic samples, and so studied the orienting effect of low-frequency electric fields and of static electric and magnetic fields. Other studies on macroscopic samples were carried out by *Rowell*, *Phillips*, *Melby*, and *Panar* [58], who examined the nuclear magnetic resonance spectra of the samples. *Carr* [68] noted that the orientation behavior in very low-frequency or static electric fields is strongly dependent on impurities. He therefore assumed that this behavior is influenced by the conductivity, which is also strongly dependent on impurities.

In thin layers, the action of electric fields can be observed optically [14, 72–74] (Fig. 8) or can be studied by measurement of the IR dichroism [76]. The polarizability of thin nematic layers in very low-frequency electric fields can be extremely high and may exhibit hysteresis [15, 16, 75]. The behavior of the layers is thus similar to that of ferroelectric crystals.

Williams [14] discovered that thin nematic layers can form fairly regular patterns under the influence of a homogeneous electric field having a very low frequency and lying perpendicular to the plane of the layer. Photographs of some of these patterns are shown in Figure 8. *Williams* and *Heilmeier* believe that this behavior of thin layers points to ferroelectric properties [15]. These phenomena, which have not yet been explained, may be connected with currents set up in nematic liquids by static or low-frequency alternating electric fields. However, no satisfactory explanation has yet been proposed for these currents themselves.

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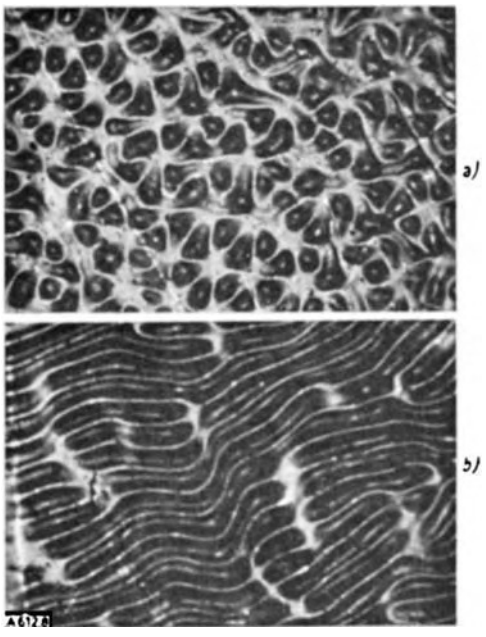

Fig. 8. Nematic liquid layers in an electric field. Layer thickness about 50 μm. Photographs taken with linearly polarized light at a magnification of 100—150× according to *Kassubeck* [74].

a) 4,4′-Bis(methoxy)azoxybenzene at 120 °C in a d.c. field. (1.6 kV/cm). The "flower pattern" can occasionally be observed shortly after the application of the field; a pattern of intertwined fringes is later formed.

b) 4,4′-Bis(methoxy)azoxybenzene at 120 °C in an alternating field (30 Hz, 1.6 kV/cm). Normal fringe pattern, typical of nematic liquid 4,4′-bis(alkoxy)azoxybenzene derivatives in low-frequency alternating fields.

II. Crystalline Liquids as Solvents for Magnetic Resonance Studies

1. Introduction

Crystalline liquids, and particularly those of the nematic type, can have solvent properties almost as good as those of isotropic liquids. However, the solubility depends in a different way on the properties of the solute. Differences in the molecular shape or in the polarizability anisotropy can have strong effects.

A greater dependence of the solubility on the molecular properties is of interest in chromatographic separations. Gas-chromatographic studies on disubstituted benzenes have in fact confirmed [77, 78] that crystalline liquids have a remarkable separating power. For example, *m*- and *p*-xylenes can be completely separated with a mesomorphous 4,4′-bis(alkoxy)azoxybenzene derivative as the separating liquid.

Solute molecules in mesomorphous solutions experience some orientation in the anisotropic environment. It therefore seems obvious to use nematic liquids that can readily be uniformly oriented by a magnetic field, or in thin layers by boundary effects, as solvents for experiments with oriented molecules, and particularly for spectroscopic investigations.

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IR and UV absorption measurements with polarized light [30, 54, 76, 79–81] and Raman measurements [82] have been carried out on pure nematic liquids, with the following results. The vibrational spectra of the molecules in the mesomorphous phases are practically the same as the spectra of the isotropic liquid phase. No marked frequency shifts or changes in intensity are found in the electronic transitions in the visible and near UV regions. Thus the spectra give no indication of specific associations of the molecules in the mesomorphous phase or of any change in the molecular structure. The degree of order of nematic and smectic phases was calculated from the pronounced dichroism in some frequency ranges [30, 54, 55, 76]. The polarization of the transitions can also be determined, and this facilitates the assignment of the transitions. Although crystalline liquids have not yet been used as solvents for IR or UV absorption measurements, their usefulness for this purpose will probably be limited by their own strong absorption.

Nematic crystalline liquids are fairly versatile solvents for nuclear magnetic resonance [80] and electron spin resonance studies [81]. The reader is referred to reviews [83, 84] and important theoretical articles [84–86] on this topic. The anisotropic components of the spin interactions are easy to observe in such solvents and generally cause very marked changes in the magnetic resonance spectra as compared with the normal solution spectra. In deuteron resonance the quadrupole interactions between the nucleus and the electron cloud become the dominant terms, and in fluorine and proton resonances the direct magnetic dipole-dipole interactions between the nuclei, whereas these interactions have no influence on the position and intensity of the resonance lines in isotropic solutions. In the ESR spectra of radicals, the differences between the spectra of isotropic and of nematic solutions are less pronounced. However, the splitting in the 9-line spectrum of the tetracyanoethylene anion changes at the transition point from 1.58 gauss in isotropic liquid 4,4′-bis-(methoxy)azoxybenzene to 0.94 gauss in nematic liquid 4,4′-bis(methoxy)azoxybenzene [87]. The number of resonance lines may be doubled in the case of biradicals [88].

2. Proton and Fluorine Resonance Spectra in Nematic Solutions

Magnetic resonance spectra of nuclei having spin 1/2, *e.g.* ^{1}H or ^{19}F, are determined by the interactions of the magnetic dipole moments of the nuclei with the external magnetic field and by the magnetic dipole-

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dipole interactions of the nuclei with one another. If the mobility of the molecules is high, the interactions are decreased in isotropic liquids and solutions. Thus the spin Hamiltonian operator, which determines the frequencies and intensities of the transitions, has the form given in equation (4).

$$\mathbf{H}_1 = -\frac{h H_o}{2\pi} \sum_p \gamma_p (1-\sigma_p) I_{zp} + h \sum_{\substack{p,q \\ p>q}} J_{pq} \mathbf{I}_p \mathbf{I}_q \qquad (4)$$

H_0 is the external magnetic field, which is assumed to be parallel to the z direction; $\mathbf{I}_p$ and $\mathbf{I}_q$ are the vectorial spin operators of the nuclei p and q; I_{zp} is the z component of the spin operator, and γ_p is the gyromagnetic ratio of p; the z component of the dipole moment is therefore given by $h\gamma_p/4\pi$.

The local magnetic field of the nuclei $H_0\ (1 - \sigma_p)$ differs from the external magnetic field, owing to screening by the electron sheath. For diamagnetic molecules, the screening constant σ_p is a small positive number ($\sigma_p \approx 3\times10^{-5}$ for protons), which depends on the orientation with respect to the magnetic field. The screening constant found in isotropic liquids is the average over all orientations, and is equal to one third of the trace of the screening tensor.

The magnetic resonance frequencies are given by eq. (5), provided that the second sum in (4), which contains the magnetic coupling of the nuclei with one another, is negligible.

$$\nu_p = \frac{H_o}{2\pi} (1-\sigma_p)\gamma_p \qquad (5)$$

σ_p depends on the nature of the chemical bond; the resonance frequencies are therefore subject to "Chemical shifts". However, the couplings generally lead to further splitting, so that the coupling constants J_{pq} involved in the splitting can be determined, as well as the chemical shifts, by analysis of the spectra. These are both important data for the determination of structures.

The magnetic interactions between the nuclei depend even more than the chemical shifts on the orientation of the molecule. The interactions may be direct or indirect (electron-coupled). The direct interactions may be visualized by consideration of the local magnetic fields. A nucleus p having spin 1/2 changes the field strength at q by the component of its magnetic dipole field in the H_0 direction:

$$\Delta H_{loc} = \pm \gamma_p \frac{h}{4\pi} \left(\frac{3\cos^2\Theta_{pq}-1}{r_{pq}^3} \right) \qquad (6)$$

where r_{pq} is the distance from p to q.

The positive sign in (6) applies to parallel orientation and the negative sign to antiparallel orientation of the spin p with respect to H_0; Θ_{pq} is the angle between r_{pq} and H_o. (H_o is assumed to be large in relation to the dipole fields of neighboring nuclei. The components perpendicular to H_o may therefore be disregarded.)

If we ignore the indirect interaction, the previously single resonance line of q should be split, according to the mean local field, into two lines at $\nu_q \mp B_{pq}^{dir}$, where B_{pq}^{dir}, is the average value defined in eq. (7)

$$B_{pq}^{dir} = -\frac{h\gamma_p\gamma_q}{4\pi^2} \cdot \frac{1}{2} \left\langle \frac{3\cos^2\Theta_{pq}-1}{r_{pq}^3} \right\rangle \qquad (7)$$

This calculation of the splitting frequency is based on the assumption that $\nu_p - \nu_q \gg B_{pq}^{dir}$. It is therefore generally useful only for qualitative studies.

B_{pq}^{dir}, and hence the direct interaction, disappears in isotropic liquids, since the degree of order of the internuclear axis, $S_{pq} = \langle 3\cos^2\Theta_{pq} - 1\rangle/2$, is zero. The "scalar" coupling constants J_{pq} are the average values of the indirect interactions, which are propagated mainly along the chemical bonds and are passed on by the magnetic couplings between the nucleus and the electrons. "Scalar" coupling constants generally occur only between nuclei that are separated by only a few bonds. They are smaller than 30 Hz for $^1H^1H$, $^1H^{19}F$, and $^{19}F^{19}F$ couplings in organic molecules.

For oriented molecules, owing to the additional couplings, the spin Hamiltonian operator becomes $\mathbf{H} = \mathbf{H}_1 + \mathbf{H}_2$. The first term has the form given in eq. (4); only the screening constants have changed. $\mathbf{H}_2$ is given by eq. (8)

$$\mathbf{H}_2 = h \sum_{\substack{p,q \\ p>q}} B_{pq}(3_z I_{zp} I_q - I_p I_q) \qquad (8)$$

The "anisotropic" coupling constant B_{pq} is the sum of an indirect component B_{pq}^{indir} and the direct component B_{pq}^{dir} given by eq. (7).

The mean direct interaction between adjacent molecules in solid crystals cannot be disregarded. The nuclei throughout the crystal are therefore magnetically coupled with one another. The resulting nuclear magnetic resonance spectrum consists of an absorption signal several kiloherz wide, often with no structure, so that no coupling constants can be found from the spectrum.

There is no fixed spatial order in nematic liquids. The molecules can diffuse as rapidly as in the normal isotropic liquids. For intermolecular interactions, therefore, B_{pq} becomes disappearingly small, owing to its dependence on distance and on angle. For intramolecular interactions, on the other hand, B_{pq} does not have a disappearingly small average value, owing to the partial orientation of the molecules. This averaging is based on the facts that the molecules still have a high rotational mobility despite the partial orientation, and that the nematic solution is uniformly oriented by the magnetic field. Thus the use of the average values in the Hamiltonian operator is justifiable only if these values are reached by averaging, even over a short time, irrespective of the starting position of the molecule in question. The corresponding correlation times in the present case must therefore be shorter than 10^{-6} sec [89].

[89] *A. Abragam*: The Principles of Nuclear Magnetism. Oxford University Press, Oxford 1961.

The proton resonance spectra in Figure 9 show the effect of the orientation obtainable in nematic solutions on the spectra, the example chosen in this case being benzene. The spectra shown were recorded with non-spinning samples.

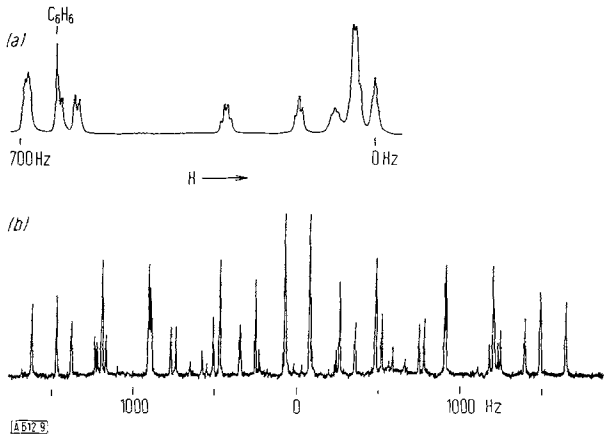


Fig. 9. Proton resonance spectra of benzene in a solvent mixture of 60 % of heptyloxy-4'-ethoxyazobenzene and 40 % of 4-hexyloxy-4'-ethoxyazobenzene at 100 MHz. (a) isotropic solution, 120 °C, (b) nematic solution, 50 °C.

The spectrum of the isotropic liquid solution above the clear point is a normal solution spectrum, in which only one sharp resonance line is observed for benzene. The total splitting of about 700 Hz is mainly due to the difference between the chemical shifts of aliphatic and aromatic protons. In the solvent molecules the couplings give rise to numerous closely spaced signals, so that no really sharp individual lines can be observed.

The spectrum of the nematic solution contains only benzene lines; of the 76 transitions allowed by symmetry [90], more than 50 can be recognized. The total splitting is more than 3000 Hz. It is due to the direct couplings. For the spectrum shown, $B_{12} = 435.7$ Hz, $B_{13} = 82.3$ Hz, $B_{14} = 54.5$ Hz, and the degree of order S of the principal axis of symmetry is $S = -0.11$.

The nuclear magnetic resonance in nematic liquids may be observed by the same measuring technique as is used for isotropic solutions. The homogeneous orientation of the sample is produced by the constant magnetic field H_0, the only other function of which is to provide the Zeeman splitting of the spin levels. However, the sample cannot rotate about an axis perpendicular to H_0 to compensate for field inhomogeneities, since this would disturb the alignment of the molecules. The unavoidable field inhomogeneities therefore have a much stronger effect on the line widths of proton and fluorine resonances in nematic solutions than in isotropic solutions. The half-value widths in proton and fluorine resonance spectra in nematic solutions are a few Hz, so that resolution is still good, but the signal/noise ratio deteriorates because of the greater line width.

[90] *A. Saupe*, Proc. XIII Colloque Ampère 320 (1964); Z. Naturforsch. *20a*, 572 (1965).

At high resolution, the resonance frequencies in the nematic solution are strongly dependent on the temperature and on the concentration of the solution. The temperature and concentration in the measuring volume must therefore be constant if the line width is to be uniformly small over the entire spectrum. These two conditions are not easy to satisfy. The solvent used for the spectra in Figure 9 was a eutectic mixture with a particularly low melting point. Mixtures having even lower melting points have recently been found [91, 92]. A mixture of 4'-ethoxy-4-hexyl-oxyazo(or azoxy)-benzene (20 mole-%) and butyl 4-ethoxyphenyl terephthalate may be used as a nematic solvent for measurements at room temperature [91].

The proton resonance spectrum of the nematic carrier substance should also consist of sharp lines. Recent studies on pure nematic liquids [58, 85] led in a few cases (particularly that of 4,4'-bis(methoxy)azoxybenzene) to spectra with differentiated fine structures. In general, however, a broad signal with no appreciable structure is obtained owing to the large numbers of protons. The proton resonance spectra of oriented molecules are still simple enough for resolution into individual lines only in systems having a small number of interacting nuclei (up to about eight per molecule). Solvent molecules containing large numbers of protons are therefore advantageous for ^{1}H–NMR studies in nematic solutions, since the spectra of simpler solute molecules can then be observed without appreciable disturbance against the broad background signal of the solvent (see *e.g.* Figs. 9 and 10).

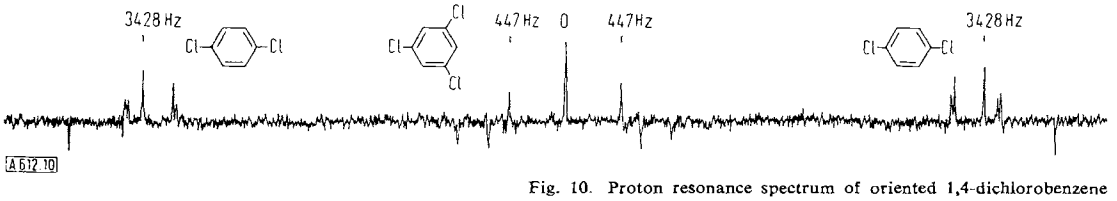


Fig. 10. Proton resonance spectrum of oriented 1,4-dichlorobenzene and 1,3,5-trichlorobenzene in nematic liquid 4,4'-bis(*n*-hexyloxy)azoxybenzene (60 MHz, 70 °C). The lines pointing downward are side bands at a distance of 4036 Hz from the main signals.

The structure of the spectra of oriented molecules is strongly dependent on the molecular geometry. Figure 10 shows the spectra of 1,3,5-trichlorobenzene and of 1,4-dichlorobenzene recorded in the same solution. In isotropic solutions the proton resonance spectra of both substances consist of single resonance lines, which are only slightly displaced in relation to the benzene line.

The symmetrical three-line spectrum having the intensity ratio 1:2:1 (middle part of Fig. 10) is characteristic of an oriented three-proton system in which all the coupling constants are the same, *i.e.* of a three-proton system with a threefold axis of symmetry. The distance between the lines is equal to 3 B_{pq}. In the spectrum shown, $B_{pq} = 149$ Hz.

The three anisotropic coupling constants of 1,4-dichlorobenzene ($B_{23} = B_{56} = 2240$ Hz, $B_{25} = B_{36} = -131.3$ Hz, $B_{26} = B_{35} = +8.3$ Hz) show that C–C four protons in the molecule are situated at the corners of a

[91] *H. Spiesecke* and *J. Bellion-Jourdan*, Angew. Chem. *79*, 475 (1967); Angew. Chem. internat. Edit. *6*, 450 (1967).

[92] *D. Demus*, Z. Naturforsch. *22a*, 285 (1967).

rectangle whose sides are in the ratio 1:1.72 [93]. The ratio found experimentally differs only slightly from $1:\sqrt{3}$, which is the value calculated on the assumption that all the bond angles are 120° and that all C–C distances are equal. The coupling constants found for benzene show that the protons are arranged at the corners of a regular hexagon.

The deduction of the geometric data is based on the assumption that B_{pq}^{indir} is negligible in comparison with B_{pq}^{dir}. Thus B_{pq} is equated to B_{pq}^{dir}. On this assumption, eq. (9) is valid for "rigid" molecules.

$$B_{pq} = -\frac{h}{4\pi^2}\,\gamma_p\gamma_q\,\frac{S_{pq}}{r_{pq}^3} \tag{9}$$

r_{pq} is really an average distance, which differs somewhat from the equilibrium distance mainly because of zero-point vibrations.

If r_{pq} is known, the degree of order S_{pq} can be calculated from eq. (9). No other method is known at present for the reliable determination of S_{pq}; consequently, (9) cannot be used directly for the determination of internuclear distances. However, it is possible to determine bond angles and ratios of internuclear distances, since the various S_{pq} values are interdependent (see eq. (11a)).

The mean orientation of a rigid molecule can generally be described by a matrix having a maximum of five elements, which are independent of one another within certain limits [85].

To define the order matrix, we denote the axes of a molecularly fixed system of coordinates by ξ, η, and ζ, while Θ_ξ, Θ_η, and Θ_ζ are the angles of these axes with respect to the optical axis of the nematic liquid (Fig. 11). The matrix elements are given by the average values defined in eq. (10).

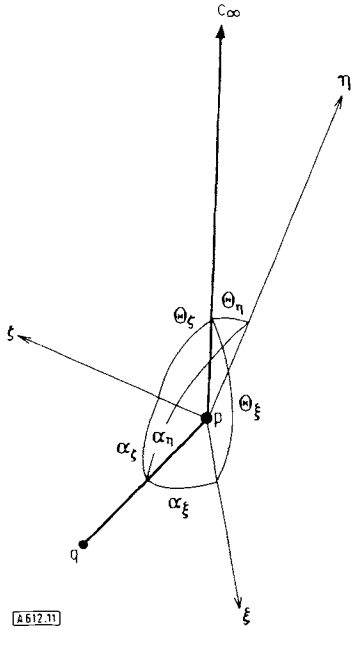


Fig. 11. ξ, η, ζ: Molecularly fixed system of cartesian coordinates. $\Theta\xi$, $\Theta\eta$, $\Theta\zeta$: Angles with respect to the spatially fixed optical axis. α_ξ, α_ζ, α_ζ: Angles with respect to the molecularly fixed p,q axis.

[93] *A. Saupe*, Molecular Crystals *1*, 527 (1966).

$$S_{ij} = (1/2)\,\langle\, 3\cos\Theta_i\cos\Theta_j - \delta_{ij}\,\rangle\;;\; i,j = \xi,\eta,\zeta$$
$$\delta_{ij} = 0 \text{ for } i \neq j;\ \delta_{ii} = 1 \tag{10}$$

The matrix is symmetrical by definition, and $S_{\xi\xi} + S_{\eta\eta} + S_{\zeta\zeta} = 0$. Thus there remain only five independent elements.

If α_ξ, α_η, and α_ζ are the angles between the pq axis and the ξ, η, and ζ axes of the coordinate system (Fig. 11), the degree of order of the pq axis is given by eq. (11a).

$$S_{pq} = \sum_{i,j} \cos\alpha_i \cos\alpha_j\; S_{ij} \tag{11a}$$

The relationship between the S_{pq} values is implicit in this equation. To determine the structure, the S_{pq} values for an assumed molecular structure are determined from the coupling constants B_{pq} by means of equation (9), and the S matrix is calculated with some (at most five) of these values. The remaining S_{pq} values can then be calculated once more from eq. (11a). The results are used to check the assumed molecular structure by comparison with the values found from B_{pq}.

The procedure is very easy to use in the case of symmetrical molecules, since the S matrix can be brought into the diagonal form by principal axis transformation. In 1,4-dichlorobenzene, for example, the principal axes are determined by symmetry (2,3 axis, 2,6 axis, normal to the plane of the molecule). In this case, according to eq. (11a),

$$S_{25} = (r_{23}^2/r_{25}^2)\,S_{23} + (r_{26}^2/r_{25}^2)S_{26}$$

Since $r_{25}^2 = r_{23}^2 + r_{26}^2$, we find, from eq. (9), a relationship between the ratio of the internuclear distances r_{23}/r_{26} and the coupling constants:

$$B_{25}\,(1 + \rho^2)^{5/2} = B_{23} + \rho^5 B_{26}\;(\rho = r_{23}/r_{26}).$$

Molecules having an at least threefold axis of symmetry are easiest to deal with. If the axis of symmetry is chosen as the ζ axis, the S matrix is in the diagonal form, and $S_{\xi\xi} = S_{\eta\eta} = -S_{\zeta\zeta}/2$. Eq. (11a) simplifies to (11b).

$$S_{pq} = \frac{1}{2}\,(3\cos^2\alpha_\zeta - 1)\,S_\zeta \tag{11b}$$

Thus all the axes in the molecular plane of benzene and of 1,3,5-trichlorobenzene have the same degree of order. It follows that in benzene, for the assumed planar structure, $B_{12}:B_{13}:B_{14} = 1:0.1925:0.1250$. On the other hand, the coupling constants given above for Figure 9 lead to 1:0·1912:0·1251. The differences are within the limits of accuracy of the measurements. Though real differences are undoubtedly present owing to the vibrational motions of the protons, they have not yet been reported.

According to the results for benzene, the assumption that $B_{pq} = B_{pq}^{dir}$ is permissible for $^1H,^1H$ couplings. On the other hand, B_{pq}^{indir} cannot be completely neglected in $^{19}F,^{19}F$ couplings. Measurements on hexafluorobenzene in nematic solutions show that B_{pq}^{indir}

contributes several percent to B_{pq} [94, 95]. Consequently, accurate structural data cannot be obtained from anisotropic fluorine couplings.

In $^{13}C,^{1}H$ couplings, B_{pq}^{indir} again seems to be so small that no appreciable error is introduced by the use of $B_{pq} = B_{pq}^{dir}$ in structural determinations. Thus the molecular structure of pure hydrocarbons can be determined to within the unit of measurement if the $^{13}C,^{1}H$ coupling constants are known as well as the $^{1}H,^{1}H$ coupling constants. The natural abundance of ^{13}C is too low to give isotope lines in the spectra obtained by a single pass, as in Figures 9 and 11. It is necessary to use compounds enriched in ^{13}C. If a data store is used, the natural abundance of ^{13}C is sufficient [96]. This gives a practicable procedure for the determination of structures in a liquid phase.

Table 2 shows a comparison of the H–C–H bond angles of CH_3 groups, as calculated from ^{1}H–NMR measurements in nematic solutions on the assumption that B_{pq}^{indir} was negligible, with the values found from microwave data. The agreement is good in view of the facts that (i) the bond angles are averages, (ii) the two methods correspond to different averages, and (iii) the microwave data refer to gases and the ^{1}H–NMR data to nematic solutions

Table 2. Bond angles of CH_3 groups determined in nematic solutions from proton resonance spectra [97, 98] and in dilute gases from microwave spectra [99–101].

Compound	Solvent	From ^{1}H–NMR-data ∢HCH	From microwave data ∢HCH	∢DCD
Acetonitrile	[a]	108° 56′ ± 2′	109° 16′	109° 21′
	[b]	109° 2′ ± 2′		
Methanol	[a]	110° 3′ ± 8′	109° 2′ ± 45′	
Methyl iodide	[b]	111° 42′ ± 2′	111° 25′	111° 37′

[a] *p-n*-Octyloxy-benzoic acid; [b] 4,4′-Bis(*n*-hexyloxy)azoxybenzene.

The results obtained by *Snyder* and *Meiboom* [96] for tetramethylsilane and neopentane in nematic solutions are interesting in this connection. These molecules, which are assumed to have tetrahedral symmetry, should not exhibit any orientation effects and should give only single sharp lines; however, splittings of up to 15 Hz have been observed. The molecules must therefore be deformed in the solution; the bond angles change by up to about one tenth of a degree [96].

The signs of the coupling constants J_{pq}, which are important for theoretical studies, can also be determined by measurements in nematic solutions. Analysis of the nuclear resonance spectra, as in isotropic solutions, gives only the relative signs of the coupling constants, since the spectra remain unchanged when the signs of all the coupling constants are changed. Thus even the signs of the S values are unknown at first. In many cases, however, preferred orientations can be established with sufficient certainty from the molecular structure. For example, very elongated molecules, which do not form associates, preferentially have their long axes parallel to the optical axis, so that the S value of the longitudinal axes is positive. In planar molecules, the parallel orientation of the planes is preferred for similar reasons; the S value of the normal to the plane of the molecule is therefore negative. The signs of nearly all the S values given in this article have been determined by considerations of this nature.

A qualitative knowledge of the preferred orientation of the molecules leads directly to a knowledge of the signs of at least some coupling constants B_{pq}. It is then also possible to determine the absolute sign of scalar coupling constants J_{pq}, provided that the relative signs are known from the analysis of the spectrum.

Another property that can be determined experimentally only with difficulty or not at all, and which is of interest in connection with bond properties and magnetic screening, is the anisotropy of the chemical shift.

In nematic solutions, the screening constant differs from its value in isotropic solutions by the amount given by eq. (12a).

$$\sigma_p(\text{nem}) - \sigma_p(\text{iso}) = \frac{2}{3} \sum_{i,j} S_{ij}\, \sigma_{ij} \qquad (12a)$$

σ_{ij} denotes the components of the screening tensor in the molecularly fixed coordinate system. For molecules having a three- or more-fold axis of symmetry, eq. (12a) simplifies to eq. (12b) if the axis of symmetry is again chosen as the ζ axis.

$$\sigma_p(\text{nem}) - \sigma_p(\text{iso}) = \frac{2}{3} S_{\zeta\zeta}(\sigma_{\zeta\zeta} - (\sigma_{\xi\xi} + \sigma_{\eta\eta})/2) \qquad (12b)$$

Table 3 shows experimental results for the anisotropy of the chemical shifts of protons and of fluorine. The chemical shifts were measured above the clear point in isotropic solution and at lower temperatures in nematic solution. $\Delta\sigma = \sigma_{\xi\xi} - (\sigma_{\xi\xi} + \sigma_{\eta\eta})/2$ can be calculated, using eq. (12b), from the differences of the

Table 3.

Compound	S_ζ	Δσ(Proton) (×10⁻⁶)	Δσ (Fluorine) (×10⁻⁶)	Ref.
Benzene	−0.10	−2.9	—	[90, 102–104]
1,3,5-Trichlorobenzene	−0.17	−4.9	—	[93, 103]
1,3,5-Trifluorobenzene	−0.15	−2.6	+101	[95]
Hexafluorobenzene	−0.26	—	+159	[94]
N≡C–CH_3	+0.12	—	—	[97]
HC≡CH	−0.014	+ 8.1 [a]	—	[97]
H–C≡C–CH_3	+0.08	+11.0 [a]	—	[97]
H–C≡C–C≡C–CH_3	+0.18	+13.1 [a]	—	[97]
H_3C–C≡C–C≡C–CH_3	+0.28	—	—	[97]

[a] Values for the acetylene proton.

[94] *L. C. Snyder* and *E. W. Anderson*, J. chem. Physics *47*, 3336 (1965).

[95] *J. Nehring* and *A. Saupe*, unpublished.

[96] *L. C. Snyder* and *S. Meiboom*, J. chem. Physics *44*, 4057 (1966).

[97] *G. Englert* and *A. Saupe*, Molecular Crystals *1*, 503 (1966); *G. Englert*, *A. Saupe*, and *J.-P. Weber*, Z. Naturforsch., in press.

[98] *A. Saupe*, *G. Englert*, and *A. Povh*, Advances chem. Ser. *63*, 51 (1967).

[99] *L. F. Thomas*, *E. I. S. Sherrerd*, and *J. Sheridan*, Trans. Faraday Soc. *51*, 619 (1955).

[100] *P. Venkatesvarlu* and *W. Gordy*, J. chem. Physics *23*, 1200 (1955).

[101] *S. L. Miller*, *L. C. Aamodt*, *G. Dousmanis*, *C. H. Townes*, and *S. Kraitschman*, J. chem. Physics *20*, 1112 (1952).

[102] *A. Saupe* and *G. Englert*, Physic. Rev. Letters *11*, 462 (1963).

[103] *G. Englert* and *A. Saupe*, Z. Naturforsch. *19a*, 172 (1964).

[104] *L. C. Snyder* and *E. W. Anderson*, J. Amer. chem. Soc. *86*, 5023 (1964).

chemical shifts and the values of the degree of order S of the nematic solution. Tetramethylsilane was used in both solutions as the internal standard. It may be assumed that the weak orientation effects observed for tetramethylsilane in nematic solutions[96] have no appreciable influence on the screening of the protons.

The S values in Table 3 present an idea of the degree of order reached with these molecules. The orientation is strongly dependent on the temperature and concentration. The lowest orientation that can be reached in the neighborhood of the clear point can be up to 30 % lower than the values indicated, and the highest orientation at low concentrations and low temperatures up to 30 % higher. No marked dependence of the orientation on nematic solvents is to be expected for these molecules.

Systematic studies on the orientation behavior of chlorinated benzene derivatives[93] show that their mean orientations are substantially independent of the nature of the nematic solvent. The electric dipole-dipole interactions between chlorobenzenes and solvents are relatively unimportant to the orientation. On the other hand, the directional components of the dispersion interactions appear to be decisive.

3. Deuteron Resonances

Whereas proton and fluorine resonances (which involve nuclei having spin 1/2, and hence having no quadrupole moment) in nematic solutions can be used for the study only of relatively small molecules, owing to the strong magnetic coupling of these nuclei with one another, this limitation practically disappears in the case of deuteron magnetic resonance. Deuterons have spin 1 and possess a quadrupole moment; no coupling with other nuclei is observed in most cases. The resonance spectra are then easy to analyze, since they consist of a superposition of doublets corresponding to deuterons with different effective quadrupole interactions.

The spin Hamiltonian operator, including the quadrupole interactions, can be expressed as the sum of three terms: $\mathbf{H} = \mathbf{H}_1 + \mathbf{H}_2 + \mathbf{H}_3$, where $\mathbf{H}_1$ and $\mathbf{H}_2$ are defined in equations (4) and (8) and $\mathbf{H}_3$ in eq. (13)

$$H_3 = h \sum_p B_{pp} I_{zp}^2 \tag{13}$$

$\mathbf{H}_3$ contains the interactions between the electric quadrupole moments of the nuclei with the electron cloud and the adjacent nuclei. A strong magnetic field is assumed, *i.e.* all terms that are not interchangeable with $\Sigma_p I_{zp}$ are neglected.

If the magnetic interactions with other nuclei are negligible, the spectrum of a nucleus having spin 1 consists of a doublet with a distance $2B_{pp}$ between the lines. For nuclear spin 1, B_{pp} is given by (14a)

$$B_{pp} = \frac{1}{2h} eQ_p \sum_{i,j} V_{ij}^p S_{ij} \tag{14a}$$

In this equation, eQ_p is the electric quadrupole moment and V_{ij}^p represents the second derivative of the electrostatic potential V_p that acts on the nucleus p $\left(V_{\xi\xi}^p = \frac{\partial^2 V_p}{\partial \zeta^2},\ V_{\zeta\eta}^p = \frac{\partial^2 V_p}{\partial \xi \partial \eta}, \ldots\right)$.

In the evaluation of the measurements described below, it was assumed that the tensor V_{ij} is rotationally symmetrical about the axis of the corresponding CD bond. If the ζ axis is taken parallel to the bond, the situation for the corresponding ^2H is given by eq. (14b).

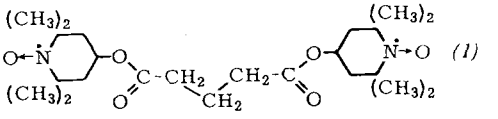
$$B_{pp} = -\frac{3}{4\pi} eQ_p V_{\zeta\zeta}^p S_{\zeta\zeta} \tag{14b}$$

^2H–NMR spectra of partly deuterated nematic liquid 4,4′-bis(alkoxy)azoxybenzenes and alkoxybenzoic acids have been studied, as have the ^2H–NMR spectra of deuterated benzene, toluene, naphthalene, stilbene, and benzoic acid[58,105]. S values can be calculated from the observed splittings; the quadrupole coupling constants for ideal orientation were measured in crystalline powders at low temperatures.

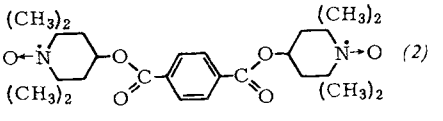
The D–C–D angle of the CD_3 group in deuterated toluene was determined on the assumption that the quadrupole couplings for the aromatic deuteron in the p position and for the deuterons of the CD_3 group are the same and that the quadrupole tensors are rotationally symmetrical with respect to the axes of the C–D bonds. The value found for the C–D–C angle was 111.9 °[58].

4. Electron Spin Resonances

ESR measurements in nematic solutions are easier to carry out than nuclear magnetic resonance studies, partly because the ESR transitions are much more intense, and partly because the homogeneity of the magnetic field is not very important, owing to the greater natural line widths. However, the method is limited by the fact that it can be used only for the study of radicals that are sufficiently stable in mesomorphous solvents. Measurements on diphenylpicrylhydrazyl, the tetracyanoethylene anion[87], Coppinger's radical[106], perinaphthenyl[107,108], and two biradicals[88], *i.e.* bis(2,2,6,6-tetramethylpiperidyl oxide-4-yl) glutarate *(1)* and terephthalate *(2)*, have been reported so far.



(1)



(2)

[105] *W. D. Phyllips, J. D. Rowell,* and *L. R. Melly,* J. chem. Physics *41,* 2551 (1964).

[106] *G. R. Luckhurst,* Molecular Physics *11,* 205 (1966).

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The anisotropic coupling constants between unpaired electron spin and the nuclei can be determined from the ESR spectra of the nematic solutions. The spin Hamiltonian operator is of the same form for monoradicals in the two liquid solutions, but the values of the coupling constants change. The effective anisotropic coupling components are obtained from the coupling constants observed in nematic solutions by subtraction of the scalar coupling constants. The magnitudes of the scalar coupling constants can be reliably determined in the isotropic solution above the clear point.

To calculate a degree of order from an experimentally determined anisotropic coupling component, the corresponding coupling tensor must be known, *e.g.* from theoretical studies or from independent measurements. As in the case of nuclear magnetic resonances, the sign of a scalar coupling can be determined if the preferred orientation is known. The results obtained for the tetracyanoethylene anion, for example, confirm the positive sign of the scalar coupling to the nitrogen [87].

In the case of biradicals, the magnetic dipole-dipole interaction between the impaired electrons is no longer completely balanced out in nematic solutions. An additional coupling therefore occurs and this leads to the splitting of the resonance lines [82].

Glarum and *Marshall* [107] carried out particularly comprehensive studies on the perinaphthenyl radical. A comparison of the observed scalar and anisotropic coupling constants with calculated values showed good agreement. The g tensor was determined: $g_\xi = g_\eta = 2.00278$ and $g_\zeta = 2.00226$ (ζ axis perpendicular to the plane of the molecule). g_ζ is roughly equal to the g value of the free electron, $g_e = 2.00232$. The planar radical is highly oriented in nematic liquid 4,4′-bis(methoxy)azoxybenzene. On average, the parallelism of the plane to the magnetic field is as good as that of the longitudinal axes of the solvent molecules.

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Direct Synthesis of Organohalogenosilanes

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The direct synthesis of organohalogenosilanes, particularly methyl- and phenylchlorosilanes, is the main process for the production of the monomers required for silicone polymers. This complex heterogeneous catalytic reaction involves the interaction of a gaseous component (the organic halide) with two solid components (silicon and copper), the relative quantities of which change as the reaction proceeds. The mechanism of the direct synthesis has not yet been conclusively established. The free-radical mechanism originally proposed supposes the formation of organic free radicals. On the other hand, the chemisorption mechanism suggested later postulates the dissociative adsorption of the organic halide on the silicon-copper double center (the silicon and the copper being joined by a chemical bond). The results obtained so far indicate that the chemisorption mechanism is of decisive importance, but it is not impossible that both mechanisms operate simultaneously.

1. Introduction

The keystone of modern processes for the production of organosilicon compounds is the direct synthesis of monomeric organohalogenosilanes, the starting materials for the polymerization. This direct synthesis was discovered by *Rochow* [1,2] in 1940, and independently by *Müller* [3] and *James* [4] somewhat later. The rapidly growing demand for silicones led to fast development of this method, which is technologically and economically much better than the older processes based on the Grignard synthesis. However, because of

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the difficulties encountered in scaling up the reactor for the direct synthesis and the extremely poor reproducibility of the preparation of the active contact mass, further improvements are still necessary. The interest being attracted by the development of the direct synthesis of organohalogenosilanes is shown by the large number of publications and patents on this topic, which have been discussed in reviews [5–7a].

2. Reaction with Hydrogen Chloride

The reaction of hydrogen chloride with silicon, which was already known in the last century [8–10], may be regarded as the forerunner of the direct synthesis of organohalogenosilanes. It is interesting to note that, even at that time, copper was used as a catalyst in a number of cases, though this reaction, unlike the direct synthesis of organochlorosilanes, will also proceed without a catalyst. *Fischer* and *Wolf* [11] derived equations from which the equilibrium composition of the reaction mixture can be calculated as a function of the temperature and pressure. Three papers deal with the kinetics of this reaction [12–14].

3. Reaction with Methyl Chloride

The reaction of methyl chloride with silicon in the presence of copper at about 300 °C yields methylchlorosilanes. On stoichiometric grounds, the only product should be dimethyldichlorosilane:

$$2\ CH_3Cl + Si \xrightarrow[300°C]{Cu} (CH_3)_2SiCl_2 - 40\ kcal \qquad (1)$$

However, partial pyrolysis of the methyl groups at the temperature of the reaction leads to a mixture of products, in which, as a whole, more chlorine atoms than methyl groups are attached to silicon. Apart from dimethyldichlorosilane, methyltrichlorosilane is also obtained as a main product, and trimethylchlorosilane, methyldichlorosilane, tetramethylsilane, trichlorosilane, and tetrachlorosilane are formed in smaller quantities (cf. Table 1).

Table 1. Main products of the direct synthesis of methylchlorosilanes [18].

Compound	B.p. (°C)
$(CH_3)_4Si$	26.6
$HSiCl_3$	31.8
$(CH_3)_2HSiCl$	36.0
$(CH_3)HSiCl_2$	41.0
$(CH_3)_3SiCl$	57.7
$SiCl_4$	57.6
CH_3SiCl_3	65.7
$(CH_3)_2SiCl_2$	70.0

The methylchlorosilanes are difficult to separate, partly because of the small differences in their boiling points, and partly because of the formation of the azeotropic trimethylchlorosilane/tetrachlorosilane mixture (1:1; b.p. 54.5 °C) [15]. Apart from the azeotropic mixture, the methylchlorosilanes can be separated by distillation in a column having 60–100 theoretical plates [16, 17].

In addition to these substances, the reaction mixture contains a large variety of by-products with and without Si; according to *Rochow* [19], 41 compounds are formed alongside dimethyldichlorosilane. The crude product contains 5–10 wt.-% of compounds whose boiling points exceed that of $(CH_3)_2SiCl_2$. This fraction consists mainly of compounds of the type $\equiv SiOSi\equiv$, $\equiv SiSi\equiv$, and $\equiv SiCH_2Si\equiv$ (some have been identified and are listed in Table 2). Silicon-free products include hydrogen, methane, ethane, and ethylene [22],

Table 2. Some by-products containing Si and boiling above 70 °C that are obtained in the direct synthesis of methylchlorosilanes [21].

Compound	B.p. (°C/torr)
$(CH_3)(C_2H_5)SiCl_2$	101/749
$C_2H_5SiCl_3$	97.9/760
$(C_2H_5)_2HSiCl$	100.5/760
$(CH_3)(C_3H_7)SiCl_2$	119/737
$C_3H_7SiCl_3$	122/740
$(CH_3)_2ClSi-O-SiCl(CH_3)_2$	139/739
$(CH_3)Cl_2Si-O-SiCl_2(CH_3)$	138/760
$(CH_3)_2ClSi-O-SiCl_2(CH_3)$	142/739
$(CH_3)_2ClSi-O-SiCl_3$	147/735
$(CH_3)Cl_2Si-SiCl_2(CH_3)$	158–760
$(CH_3)_3Si-SiCl_2(CH_3)$	–
$(CH_3)_2ClSi-SiCl_2(C_2H_5)$	181/744
$(C_2H_5)_2ClSi-SiCl_2(C_2H_5)$	187/731
$(CH_3)Cl_2Si-CH_2-SiCl_2(CH_3)$	187/734
$(CH_3)_2ClSi-CH_2-SiCl_2(CH_3)$	189–192/760
$(CH_3)Cl_2Si-CH_2CH_2-SiCl_2(CH_3)$	209/746

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as well as 2- and 3-methylpentanes, 2- and 3-methylhexanes [23], and other aliphatic and aromatic hydrocarbons [24].

It was formerly thought that the nonvolatile reaction products deposited on the contact mass consist mainly of carbon formed by the decomposition of the methyl radicals

$$\bullet CH_3 \rightarrow C + 3/2\ H_2 \quad (2)$$

However, it was recently shown [25] that these products consist predominantly of polymethylenes, which are formed by the interaction of methyl radicals adsorbed on the surface of the catalyst:

$$CH_3Cl_{(g)} \rightarrow \bullet CH_{3(ads)} + \bullet Cl_{(ads)} \quad (3)$$

$$2\ \bullet CH_{3(ads)} \rightarrow \overset{\bullet}{\underset{\bullet}{}}CH_{2(ads)} + CH_{4(g)} \quad (4)$$

$$n\ \overset{\bullet}{\underset{\bullet}{}}CH_{2(ads)} \rightarrow [CH_2]_{n(s)} \quad (5)$$

In spite of its complex course, the direct synthesis of methylchlorosilanes can be made very selective by a suitable choice of the reaction conditions, and it is possible to obtain in the liquid condensate 70–90 % of dimethyldichlorosilane [26, 27]. The optimum temperature depends on the activity of the contact mass, and lies between 250 and 380 °C. The decomposition of the methyl groups generally becomes more pronounced with rising temperature [22], and the overall chlorine content of the products increases. This is economically unfavorable since methyltrichlorosilane is less desirable than dimethyldichlorosilane. This effect of higher temperatures can be countered to some extent by the use of higher flow rates of methyl chloride. Since the reaction rate is proportional to the partial pressure of methyl chloride, it is advantageous to increase the pressure; the optimum pressure [28] is between 5 and 7 atm. The reaction of methyl chloride with silicon is strongly exothermic [29], and effective removal of heat is therefore essential.

Methyl chloride may contain various, generally undesirable, impurities (water, methanol, dimethyl ether, dichloromethane, vinyl chloride, *etc.*), depending on how it is prepared [30, 31]. The catalytic activity of the copper used depends on the quality of its surface. Stamped copper or copper powdered in a ball mill, the crystal lattice of which is highly disordered, has proved most suitable. Chemically precipitated copper may also be used, whereas electrolytic copper has proved to be less suitable. While methyl chloride and copper having reproducible properties can be prepared without difficulty, the properties of silicon depend, not only on its chemical composition, but also on its phase structure, which strongly influences the rate of the reaction and the composition of the product. In the heterogeneous system, silicon reacts rather slowly with methyl chloride, because of oxidic passivity of the surface [7].

The contact mass generally used in the direct synthesis of methylchlorosilanes consists of 90 wt.-% of Si and 10 wt.-% of Cu. This catalyst mass may be prepared *e.g.* by pelletizing powdered silicon and copper, the pellets being sintered in an atmosphere of hydrogen at temperatures below the melting point of copper [32]. In another process, water glass [33] or hydrolyzed ethyl silicate [34] is used as a binder for silicon and copper. These pelletized catalysts have the disadvantage of poor heat removal, and a simple mechanical mixture of silicon and copper or a finely powdered Si–Cu alloy is therefore used in industrial manufacture.

The addition of metals or salts to the contact mass, both to improve the reproducibility of the course of the synthesis and to increase the yield of one of the products, has been the subject of innumerable publications.

Addition of Al, Zn, or Mg [35] increases the content of trimethylchlorosilane in the reaction product from 3 to 10 %. On the other hand, small quantities of Zn (<0.5 %) or zinc halides increase the content of dimethyldichlorosilane [36]. *Golubtsov et al.* [37, 38] found that Sb is an activator up to a certain low concentration, but poisons the catalyst when present in higher concentrations. As, $ZnCl_2$, and P in the presence of Sb also function as activators, while P, Pb, S, Be, Bi, and Ti act as inhibitors. *Dvořák*, *Šnobl*, and *Čermák* [39] emphasize the favorable effect of Mg (< 1 %) on the reaction arte and on the dimethyldichlorosilane yield. *Rossmy* [40] studied the effect of metals incorporated into semiconductor silicon as electron donors or acceptors; he claims that the elements of Group VA of the periodic system favor the formation of methyltrichlorosilane, whereas In and Zn favor that of dimethyldichlorosilane.

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The addition of various gases (nitrogen[41], hydrogen[42], chlorine[43], and hydrogen chloride[44,45]) has also been studied as a means of influencing the composition of the reaction product. Hydrogen increases the yield of methyldichlorosilane[42]; an equimolar mixture of hydrogen and methyl chloride at 390 °C gives a product having a methyldichlorosilane content of 15–17 % instead of the usual content of 1–2 %. Addition of hydrogen chloride increases the contents of methyltrichlorosilane[41,42] and of methyldichlorosilane[45–47] in the reaction product.

The kinetics of the direct synthesis of methylchlorosilane has received relatively little attention[39,48–51]. According to *Joklík*, *Kraus*, and *Bažant*[48], who studied the reaction of methyl chloride with silicon as a heterogeneously catalyzed reaction in a closed system at pressures up to 1000 torr, the kinetics of this reaction can be expressed by the general relationship

$$r = \frac{k K_A p_A}{[1 + \sqrt{K_A p_A} + K_R p_R]^2} \quad (6)$$

deduced by *Hougen* and *Watson*[52]. In this equation, r is the reaction rate (*i.e.* the number of molecules of methyl chloride that react per hour per kg of contact mass), k is the rate constant, K_A is the equilibrium adsorption coefficient of methyl chloride, K_R is the equilibrium adsorption coefficient of dimethyldichlorosilane, p_A is the partial pressure of methyl chloride, and p_R is the partial pressure of dimethyldichlorosilane. It can be seen, therefore, that the adsorption of the methyl chloride is accompanied by dissociation and that the surface reaction is the rate-determining step. A relationship of the same form has also been derived for the reaction of methyl bromide with Si[53]. Equation (6), which was calculated for pressures up to 1.3 atm, has been applied successfully to reactions in a flow system, in one case for pressures up to 9 atm[49], and in another case[51] even up to 41 atm. *Dvořák* and *Čermák* recently determined the rate of reaction of methyl chloride with an Si–Cu alloy in a flow reactor[39] and obtained substantially the same results.

4. Reaction with Ethyl Chloride and Higher Alkyl Halides

Ethyl chloride[1,2,54–59] reacts more readily than methyl chloride with silicon in the presence of copper, but the selectivity of the reaction for the formation of the bifunctional dialkyldichlorosilane is lower. In addition to diethyldichlorosilane and ethyltrichlorosilane, an appreciable percentage of ethyldichlorosilane is formed; the main products of the direct synthesis of ethylchlorosilanes are shown in Table 3.

Table 3. Main products of the direct synthesis of ethylchlorosilanes [18].

Compound	B.p. (°C)
$HSiCl_3$	31.8
$SiCl_4$	57.6
$(C_2H_5)HSiCl_2$	74.8
$C_2H_5SiCl_3$	97.9
$(C_2H_5)_2HSiCl$	99.7
$(C_2H_5)_2SiCl_2$	129.0
$(C_2H_5)_3SiCl$	143.5
$(C_2H_5)_4Si$	154.0

Table 4. Some by-products containing Si and boiling above 154 °C that are obtained in the direct synthesis of ethylchlorosilane.

Compound	B.p. (°C/torr)
$(C_3H_7)_2SiCl_2$	172/730
$(C_2H_5)Cl_2Si-O-SiCl_2(C_2H_5)$	186/726
$(H)Cl_2Si-CH_2CH_2-SiCl_3$	189/742
$Cl_3Si-CH_2CH_2-SiCl_3$	201/745
$[Cl_2Si-CH_2CH_2]_2$	219/740
$(C_2H_5)Cl_2Si-CH_2CH_2-SiCl_3$	226–227/730
$(C_2H_5)Cl_2Si-CH_2CH_2-SiCl_2(C_2H_5)$	248–249/730

Substances that boil above the boiling point of tetraethylsilane are also formed (see Table 4)[60,61]. According to *Krylov et al.*[54], the formation of ethylchlorosilane is a first order reaction (activation energy 22 kcal/mole). The kinetics of this reaction have also been studied by *Bažant* and *Kraus*[57] with the purpose of elucidating its mechanism.

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The reactions of higher alkyl chlorides have received less attention. The dialkyldichlorosilane content in the reaction product decreases rapidly with the increasing chain length of the organic residue, while the content of alkyldichlorosilane, alkyltrichlorosilane, tetrachlorosilane, and trichlorosilane increases. The reactions studied were those of propyl and isopropyl chlorides [62] and of butyl and isobutyl chlorides [63].

Among the reactions of the unsaturated aliphatic halides, that of vinyl chloride with silicon is important. This reaction proceeds only very slowly in the presence of Cu [64], and other catalysts were therefore sought. Those studied included Mg, Sn [65], and Ni [66,67], of which Ni proved to be the best. Unlike vinyl chloride, allyl chloride reacts readily with silicon [64].

5. Reaction with Polyhalogenoparaffins

The reactions of silicon with organic halides whose molecules contain more than one halogen atom [68–82] are very complex. A large number of interesting compounds are formed that are otherwise difficult to obtain [6,83].

Petrov et al. concluded from the reaction behavior of several chloroalkyltrichlorosilanes [84–89] that chloroalkyltrichlorosilanes do not occur as intermediates in the reaction of dihalogenoalkanes with silicon, because both halogens react almost simultaneously. The only case in which the second halogen could be retained was the reaction of 1,3-dichloro-2-butene [85] with silicon at low temperatures, which yielded 3-chloro-2-butenyltrichlorosilane and 3-chloro-2-butenyldichlorosilane; the chlorine atom attached to the double-bonded carbon atom also reacted at higher temperatures.

6. Reaction with Aryl Halides

Next to methylchlorosilanes, phenylchlorosilanes [2] are the most important components of polymeric silicone products produced on an industrial scale.

In the reaction with aryl halides, the catalyst (Ag, Cu, Fe, Ni, Pt, or Sb) is used either as a mechanical mixture or as an alloy with silicon. Ag [90] gives a more selective reaction course than other catalysts (as in the synthesis of methylchlorosilanes, "selectivity" refers here to the highest possible yield of diaryldichlorosilane). Cu increases the reaction rate, and consequently also the reactor capacity, because the rate of feed of chlorobenzene can be very substantially increased without excessively decreasing the conversion. It can thus be appreciated that despite its lower selectivity, Cu is probably the only catalyst suitable for use in direct synthesis on an industrial scale.

If no other reaction activators are added, side reactions become so important in this case that at most only about half of the chlorobenzene reacts to form phenylchlorosilanes. An Si–Cu alloy has been found to be unsuitable, since chlorobenzene, unlike methyl chloride, probably does not cause the intermetallic compound Cu_3Si to decompose. For this reason it is preferable to use a mechanical mixture of silicon and copper in a weight ratio of between 7:3 and 8:2.

The reaction is carried out on an industrial scale with technical silicon, whose principal impurities are Al and Fe. The presence of Al in the contact mass leads to more pronounced decomposition [91], the main products being benzene,

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biphenyl, and hydrocarbon-like products, which are deposited on the catalyst. Al promotes the formation of diphenyldichlorosilane, particularly in the early stage of the reaction, and shortens the induction period; however, its effect on the course of the direct synthesis of phenylchlorosilanes has not been fully explained. The aluminum chloride formed in the reaction causes the decomposition of phenylchlorosilanes during the distillation of the reaction product. Attempts have therefore been made to complex the aluminum chloride, *e.g.* in the form of the nonvolatile adduct $NaAlCl_4$, which has a smaller tendency to cleave the Si-phenyl bond [92]. In contrast to Al, Fe has practically no effect on the course of the reaction. Ni, Pt, and Sb (10 %) have not proved to be effective as catalysts. Like the metal chlorides, the contact surface itself can act as a Lewis acid by adsorption of chlorine atoms [93], and it can then attack the Si-phenyl bond.

Since the copper-catalyzed direct synthesis of phenylchlorosilanes from silicon and chlorobenzene has not led to satisfactory yields, attempts have been made to improve the course of the reaction by the addition of solid components to the contact mass or by the addition of volatile substances to chlorobenzene.

It was found that Zn and Sn inhibit the side reactions and favor the formation of diphenyldichlorosilane, whereas Pb or lead chloride, Sb, and Mg have no appreciable effect. Addition of $SnCl_4$ and of $TiCl_4$ does not increase the quantity of phenylchlorosilanes formed, but rather inhibits the favorable action of Sn and Zn; $SiCl_4$ and $SiHCl_3$ suppress the side reactions and promote in particular the formation of phenyltrichlorosilane. Hydrogen chloride [90,95] shortens the induction period of the reaction and increases the yield of phenylchlorosilanes; the addition of 30 to 50 mole-% of hydrogen chloride to chlorobenzene suppresses the side reactions that lead to the formation of carbon [*], and so prevents the loss of reactivity of the contact mass [94]. Hydrogen also inhibits the side reactions leading to biphenyl and chlorinated biphenyls. However, the content of benzene in the products simultaneously increases as a result of the reaction of hydrogen with the phenyl groups. Raising the reaction temperature favors side reactions and decreases the selectivity of the reaction [97,98], as in the direct synthesis of methylchlorosilanes. This undesirable effect can be countered to some extent by an increase in the flow rate of chlorobenzene.

Pyridyl chloride [99] and naphthyl chloride [100] have also been used instead of chlorobenzene for the reaction with silicon.

The reactions of aromatic bromides were studied mainly for theoretical reasons, because these compounds react better and more selectively; the compounds used were bromobenzene [101], *o*-, *m*-, and *p*-bromotoluene [102], and *p*-fluoro-, *p*-chloro-, *p*-isopropyl-, and *p*-*tert*-butylbromobenzene [103].

The reaction of bromobenzene with Si/Cu to give diphenyldibromosilane is heterogeneously catalyzed [52], and the rate-determining step is the surface reaction, which involves two dissociatively adsorbed bromobenzene molecules [101]. A comparison of the reactivities of bromobenzene and the isomeric bromotoluenes [102] shows that methylation in the benzene ring leads to a decrease in the reactivity of the aryl bromide; the least reactive of these compounds is *o*-bromotoluene, probably because of the steric effect of the methyl group.

The initial reaction rates of *p*-substituted bromobenzenes have been correlated with the aid of the Hammett constants [103]. A similar correlation was obtained for the relative specific adsorption capacities of bromobenzene, *m*- and *p*-bromotoluene, *p*-ethylbromobenzene, and *p*-fluorobromobenzene (adsorption of the aryl bromides on the contact mass was measured gas-chromatographically by the pulse technique [104]). It may be concluded from the high values of the correlation coefficient ($\approx$ 0.98) that the substituent exerts an inductive effect.

7. Mechanism of the Direct Syntheses

Joklík and *Bažant* [13] deduced the probable mechanism of the reaction of hydrogen chloride with silicon from kinetic studies. While the main product in the reaction of methyl chloride with silicon is the bifunctional dimethyldichlorosilane, the corresponding reaction of hydrogen chloride leads to the trifunctional trichlorosilane

$$Si + 3\,HCl \rightarrow SiHCl_3 + H_2 \qquad (7)$$

The formation of trichlorosilane can be explained by dissociative adsorption of hydrogen chloride on the contact mass followed by recombination of the hydrogen atoms to form hydrogen molecules, which are desorbed from the contact surface. The chlorine atoms react to form ($SiCl_2$), which reacts in turn with further hydrogen chloride to form trichlorosilane:

$$Si + 2\,HCl \rightarrow 2\,H + (SiCl_2) \qquad (8)$$

$$2\,H \rightarrow H_2 \qquad (9)$$

$$(SiCl_2) + HCl \rightarrow SiHCl_3 \qquad (10)$$

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[*] It was shown in further investigations that this is not carbon, but compounds of the polyphenylene type $(C_6H_{3-4})_x$, the rings being linked mainly in the *para* position; crosslinking of the linear phenyl chains also takes place at higher reaction temperatures [96].

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Hurd and *Rochow* [105] proposed the following reaction scheme for the direct synthesis of methylchlorosilanes:

$$2\,Cu + CH_3Cl \rightarrow CuCl + CuCH_3 \quad (11)$$

$$CuCH_3 \rightarrow {}^{\bullet}CH_3 + Cu \quad (12)$$

$$Si + CuCl \rightarrow (SiCl) + Cu \quad (13)$$

$$(SiCl) + {}^{\bullet}CH_3 \rightarrow (CH_3SiCl) \quad (14)$$

$$(SiCl) + CuCl \rightarrow (SiCl_2) + Cu \quad (15)$$

The reaction continues up to the formation of the volatile methylchlorosilanes, which are then desorbed leaving an unoccupied surface. This scheme accounts for the dissociation of methyl chloride on copper, the activation of silicon by the chlorine atom of copper(I) chloride, and the transfer of the free methyl radical with the aid of methylcopper. *Krahé* and *Rochow* [106] recently used gold as the catalyst instead of copper, and observed the formation of volatile, unstable organogold compounds. *Müller* and *Gümbel* [107] confirmed the validity of the free-radical mechanism, but also stressed the need for the presence of aluminum chloride or ferric chloride, which accelerate the reaction

$$CH_3Cl + Cu \xrightarrow{AlCl_3} CuCl + CH_3^{\bullet} \quad (16)$$

However, they were unable to detect the existence of methylcopper.

Czernotzky [108] studied the interaction of free methyl radicals with dimethyl ether added to the ingoing stream of methyl chloride in the direct synthesis, and on the basis of his results he supports the free-radical mechanism. *Setínek*, *Bažant*, and *Šorm* [109] investigated the inhibition of the direct synthesis of methylchlorosilane by nitrous oxide. These authors interpret the results by assuming the presence of two types of methyl radical in the reaction zone: a small number is present in the gas phase, and their reaction leads to the formation of silicon-free by-products; however, most of the methyl radicals are bound to the surface of the contact mass, and their further reactions yield methylchlorosilanes.

Several objections have been raised against the free-radical mechanism. One of the most important arguments is the fact that the direct synthesis can be carried out very selectively (yield: 80 to 90 % of dimethyldichlorosilane); such high selectivities have not so far been observed in free-radical reactions. Another objection [110] to the reaction course proposed by *Hurd* and *Rochow* is that the direct synthesis of some alkyl- and alkenylchlorosilanes can be carried out at temperatures below 260 °C, whereas it is only at this temperature that the chlorination of silicon by copper(I) chloride begins.

As an alternative to the free-radical mechanism, *Klebanskiĭ* and *Fichtengolz* [110] and *Trambouze* [111] suggested a chemisorption mechanism. According to these authors, the intermetallic compound Cu_3Si ("η phase") must first be formed in the contact mass, (i) by melting Cu and Si, (ii) by sintering the compressed powdered mixture in a current of hydrogen, or (iii) by the reaction of copper(I) chloride with silicon; methylchlorosilanes are formed only by the reaction of Cu_3Si with methyl chloride. Owing to its dipole moment, methyl chloride is adsorbed on the surface of the intermetallic compound with the methyl group situated on silicon and the chlorine atom on copper. However, this does not result in the formation of copper(I) chloride, since the copper carrying the halogen remains in the crystal lattice. Chlorine bound in this way is more reactive than that in copper(I) chloride, and this is why some direct syntheses proceed at temperatures below 260 °C.

This view is supported by *Voorhoeve* and *Vlugter* [27, 112, 113], who studied the composition of the reaction product at the beginning of the reaction as a function of the contact mass, which in one case (a) contained only silicon and the intermetallic compound, and in the second case (b) copper also. In case (a), the condensate contained 90 % of dimethyldichlorosilane from the very beginning of the reaction, while in case (b) the dimethyldichlorosilane content gradually increased from 60 to 90 %; thus (b) required an induction period for the formation of the intermetallic compound from the free copper and silicon. The authors therefore concluded that the presence of Cu_3Si in the contact mass is essential to the formation of dimethyldichlorosilane, and that free copper is responsible for the pyrolysis of the methyl groups. To verify this assumption, they added hydrogen sulfide to the methyl chloride. Hydrogen sulfide should bind free copper as the sulfide, but should not react with the intermetallic compound. The dimethyldichlorosilane content in the reaction product increased slightly; however, the reaction of hydrogen sulfide with methylchlorosilanes evidently was not taken into account in the evaluation of this experiment. The question of whether methyl chloride is adsorbed with the methyl group on silicon and with chlorine on copper was also investigated with the aid of a series of silicides with decreasing positive charge on the metal (Ca, Cu, Cr, Fe). The ratio of methyl groups to chlorine atoms in the reaction mixture, as expected, decreased with the decreasing positive charge on the metal atom of the respective silicide.

Krylov and co-workers [54, 114] found that both active and inactive copper alloys contain Cu_3Si. The intermetallic compound decomposes rapidly in the active alloys during the reaction, but only slowly or not at all in the less active alloys. The authors conclude that the true catalyst is copper in the active form, which is formed only on decomposition of the intermetallic compound.

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According to *Golubtsov, Andrianov, et al.* [115–117], the reaction of copper(I) chloride with silicon yields volatile dichlorosilene, which then reacts with methyl chloride adsorbed on copper to form methylchlorosilanes.

$$2\,CuCl + Si \rightarrow SiCl_2 + 2\,Cu \quad (17)$$

$$(SiCl_2) + CH_3Cl{\cdot}Cu \rightarrow (CH_3SiCl_2) + CuCl \quad (18)$$

$$(CH_3SiCl_2) + CH_3Cl{\cdot}Cu \rightarrow (CH_3)_2SiCl_2 + CuCl \quad (19)$$

Zuckerman [6] mentioned the possibility of a relationship between the semiconductor properties of silicon and the reactivity of silicon in the direct synthesis of methylchlorosilane. *Dragojević* [118] presented theoretical arguments for this possibility while *Rossmy* [40] adopted an opposite view.

Some n type (foreign element P, O) and some p type (foreign element B, Al) semiconductor silicons have been examined in this connection by *Joklík* and *Bažant* [119]. Silicon doped with aluminum reacted best, the material containing phosphorus was poorer and reacted only at higher temperatures, and the samples with boron and with oxygen were practically nonreactive. It follows that there is no relationship between the semiconductor properties of silicon and its reactivity in the direct synthesis of methylchlorosilanes. The reason for the observed reactivity of the samples in question is the ability of methyl chloride to react with those impurity elements that can replace silicon in the crystal lattice or can be deposited at higher concentrations at the lattice dislocations. These experiments do suggest that the reaction of methyl chloride with silicon proceeds *via* the dislocations in the silicon crystal.

Experiments with ethyl chloride and silicon in a flow reactor (with provision for the removal of gas samples at various points along the reactor) [57] showed that ethylchlorosilanes are formed by parallel reactions. Addition of hydrogen chloride to the ethyl chloride does not lead to an increased yield of ethyldichlorosilane. Thus contrary to the view that has prevailed in the past, ethyldichlorosilane is not formed by the reaction steps

$$C_2H_5Cl \rightarrow HCl + CH_2{=}CH_2 \quad (20)$$

$$C_2H_5Cl + HCl + Si \rightarrow C_2H_5SiHCl_2 \quad (21)$$

and ethyl chloride is not decomposed into ethylene and hydrogen chloride on copper under the conditions in question. The experimental results can be interpreted as follows. Ethyl chloride is first dissociatively adsorbed on the surface of the contact mass. The next step is the adsorption of the second carbon atom of the ethyl group on the adjacent center, with elimination and adsorption of hydrogen. The ethylene biradical is then either desorbed as ethylene or else forms a compound having the skeleton $\equiv SiCH_2CH_2Si\equiv$. The hydrogen atom may be desorbed as molecular hydrogen or it may react with the ethyl radical to form ethane, or form an Si–H bond. An excess of chlorine atoms on the contact surface leads to the formation of ethyltrichlorosilane, ethyldichlorosilane, tetrachlorosilane, and trichlorosilane.

Hurd and *Rochow* [105] believe that the mechanism of the direct synthesis of phenylchlorosilanes is similar to that of the direct synthesis of methylchlorosilanes, and assume that free radicals are involved. However, this mechanism does not explain the formation of appreciable quantities of benzene and biphenyl. The first reaction step

$$C_6H_5Cl + 2\,Cu \rightarrow C_6H_5Cu + CuCl \quad (22)$$

should be followed by the decomposition of phenylcopper into free phenyl radicals, which would be a fast step; these radicals should then react in the gas phase with the excess of chlorobenzene to give chlorinated hydrocarbons. This assumption was verified by a model experiment with phenyl radicals produced by the pyrolysis of benzil. From an analysis of the reaction products of the direct synthesis it was found, however, that chlorobiphenyl and higher aromatic chlorides are formed in much smaller quantities than benzene and biphenyl. *Vavruška* [120] used this observation to explain the formation of benzene, biphenyl, and the higher hydrocarbons by surface reactions between the phenyl groups adsorbed on the copper.

$$^{\bullet}C_6H_5 + {}^{\bullet}C_6H_5 \rightarrow (^{\bullet}_{\bullet}C_6H_4) + C_6H_{6(ads)} \quad (23)$$

$$^{\bullet}C_6H_5 + {}^{\bullet}C_6H_5 \rightarrow C_{12}H_{10(ads)} \rightarrow C_{12}H_{10(g)} \quad (24)$$

$$2\,{}^{\bullet}C_6H_5 + (^{\bullet}_{\bullet}C_6H_4) \rightarrow C_{18}H_{14(ads)} \rightarrow C_{18}H_{14(g)} \quad (25)$$

$$^{\bullet}C_6H_5 + (^{\bullet}_{\bullet}C_6H_4) \rightarrow (^{\bullet}_{\bullet}C_6H_3) + C_6H_{6(ads)} \quad (26)$$

$$C_6H_{6(ads)} \rightarrow C_6H_{6(g)} \quad (27)$$

The course of the direct synthesis of phenylchlorosilanes has been quantitatively followed as a function of time for various chlorobenzene feed rates and at various temperatures [97]. The composition of the product becomes constant after the induction period. However, the increase in the reactivity of the contact mass is related, not only to the increase in the surface of the contact mass, but mainly to the increase in the number of active sites. During the induction period, the surface gradually becomes occupied by phenyl radicals and chlorine atoms formed by dissociative adsorption of chlorobenzene. The chlorine atoms react with silicon; the adsorbed phenyl radicals can form bonds with silicon (which is activated by partial chlorination), thus yielding diphenyldichlorosilane

[115] *S. A. Golubtsov, K. A. Andrianov, R. A. Turetskaya, Z. V. Belyakova, I. V. Trofimova,* and *N. G. Morozov,* Doklady Akad. Nauk SSSR *151*, 1329 (1963); Chem. Abstr. *59*, 14016 (1963).

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[119] *J. Joklík* and *V. Bažant,* Collect. czechoslov. chem. Commun. *32*, 3803 (1967).

[120] *M. Vavruška,* Collect. czechoslov. chem. Commun. *22*, 1814 (1957).

and phenyltrichlorosilane, or they can also react with one another on the contact surface to form benzene, biphenyl, and polyphenylenes.

All these reactions proceed simultaneously. The extent to which they compete with one another depends primarily on the temperature.

It is extremely difficult at the present stage to prove conclusively the validity of any one mechanism. The chemisorption mechanism appears more likely, though a series of observations and many of the compounds formed suggest that the two mechanisms can operate simultaneously, *i.e.* the chemisorption mechanism may be accompanied to a small extent (depending on the reaction conditions) by the free-radical mechanism.

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The Mechanism of the Wolff-Kishner Reduction, Elimination, and Isomerization Reactions[**]

BY H. H. SZMANT[*]

The mechanism of the Wolff-Kishner reaction is discussed in the light of accumulated information about the kinetics, thermodynamics, and solvent effects of the process. Wolff-Kishner reduction under normal conditions is thought to involve the trans hydrazone anion, which, in the rate-determining step, exhibits a more or less concerted proton capture at the carbanion terminal and undergoes a solvent-induced proton loss at the nitrogen terminal. The stereochemistry of the Wolff-Kishner reduction is believed to be affected by the presence of "ortho" substituents and by a change to a nonpolar, aprotic reaction medium. The mechanism elaborated for the Wolff-Kishner reduction is extended to the Wolff-Kishner elimination and isomerization reactions. Conformational analysis of the intermediates permits correlation of the competitive reduction and elimination processes with the structures of acyclic systems.

1. Introduction

The information available concerning the Wolff-Kishner reduction in protic solvents[1], in a polar aprotic solvent such as dimethyl sulfoxide[2] (DMSO), and in a nonpolar solvent such as toluene[2d], permits the elaboration of a self-consistent mechanistic pattern for the three Wolff-Kishner processes (reduction, elimination, and isomerization). As in previous publications[1,2b] on this subject, the discussion is limited to base-catalyzed, homogeneous Wolff-Kishner reactions; pyrolytic reactions catalyzed by platinum[3] are not included. In the first part of this paper, the mechanism of the Wolff-Kishner reduction is discussed, first for protic conditions, and then when other types of solvents are employed. In the later sections the mechanism of the Wolff-Kishner reduction is extended to include the competitive side reactions such as elimination and isomerization,

2. The Mechanism of Wolff-Kishner Reduction

In the Wolff-Kishner reaction, a ketone (or an aldehyde) is first converted into the hydrazone which decomposes to yield the corresponding hydrocarbon and nitrogen when heated at about 200 °C with sodium alkoxide in anhydrous alcohol.

Seibert[4] was the first to suggest that the formation of the hydrazone anion *(2)* is the initial step of the Wolff-Kishner reaction, but the first-order dependence of the rate on the concentration of base catalyst was only demonstrated in a subsequent kinetic study[1a]. This base-dependence is maintained in all solvents investigated so far, although the reported[3c] success of some Wolff-Kishner reductions carried out with an excess of hydrazine, indicates that hydrazine is a sufficiently strong base to function as a catalyst.

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[1] a) *H. H. Szmant, H. F. Harnsberger, T. J. Butler,* and *W. P. Barie,* J. Amer. chem. Soc. *74*, 2724 (1952); b) *H. H. Szmant* and *C. H. Harmuth, ibid. 86*, 2909 (1964).

[2] a) *D. J. Cram, M. R. V. Sahyun,* and *G. R. Knox, ibid. 84*, 1734 (1962); b) *H. H. Szmant* and *M. N. Roman, ibid. 88*, 4034 (1966); c) *H. H. Szmant* and *A. Birke,* unpublished work; d) *M. F. Grundon, H. B. Henbest,* and *M. D. Scott,* J. chem. Soc. (London)*1963*, 1855.

[3] a) *A. A. Balandin* and *D. N. Vaskevich,* Ž. obšč. Chim. *6*, 1878 (1936); b) *D. Todd,* J. Amer. chem. Soc. *71*, 1356 (1949); c) *D. Todd*: Organic Reactions. John Wiley, New York 1948, Vol. IV, pp. 378–422.

[4] *W. Seibert,* Chem. Ber. *80*, 494 (1947); *81*, 266 (1948).

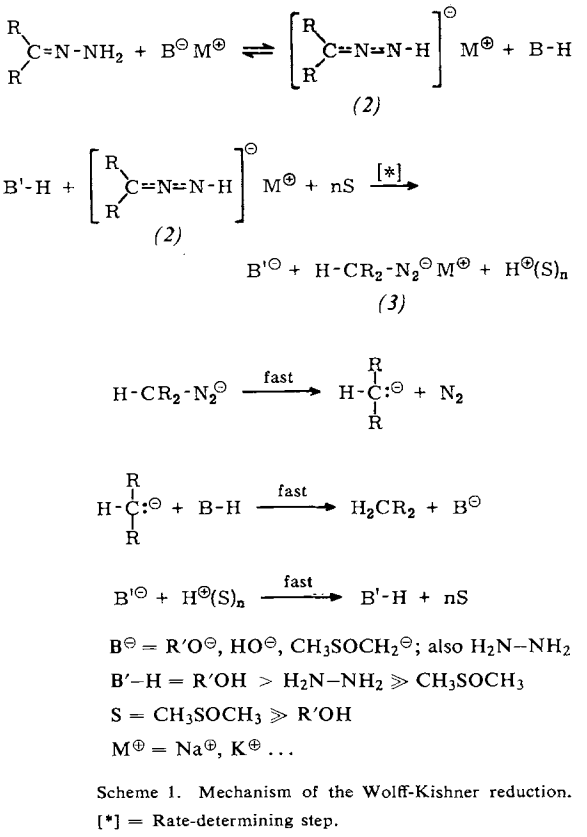
While the formation of the hydrazone anion is undoubtedly the first step of the Wolff-Kishner reaction, it cannot be the rate-determining step, since benzophenone hydrazone can be converted into its anion in anhydrous DMSO by means of the anion derived from DMSO without any appreciable evolution of nitrogen [2c]. The results of our investigations [2b], namely that the rate of the reaction depends also on the concentration of a hydroxylic solvent, and that the association of the hydroxylic solvent with the hydrazone anion is temperature dependent, support the idea that the formation of a new C–H bond at the carbon terminal in the delocalized hydrazone anion is an essential part of the rate-determining step of the Wolff-Kishner reaction.

If the latter conclusion is correct, then one should expect the reaction to fail when the carbon terminal of the hydrazone anion resists the acquisition of the negative charge. This may be precisely the reason why the hydrazone of 2-phenylbenzo-3-tropone *(1)* fails to produce a Wolff-Kishner reaction in

(1)

spite of prolonged heating at 200 °C in the presence of base catalyst. The distribution of electrons expected in such a system may also be responsible for a considerable decrease in the acidity of the N–H bonds and the consequent reluctance to form the hydrazone anion [5a]. For other non-Wolff-Kishner behavior of substituted tropolones see the work of *Mukai et al.* [5b].

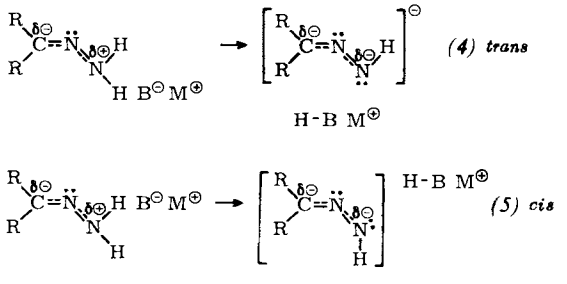
However, the following evidence suggests that the capture of a proton by the carbanion terminal in the hydrazone anion is only a part of the rate-determining step: (i) the nonlinear Hammett relationship established [1b] for the Wolff-Kishner reduction of a large series of hydrazones; (ii) the gradual lowering of the enthalpy of activation [2b] by DMSO in a concentration range (6.75 – 9 M) in which its effect can no longer be attributed merely to a change in the dielectric constant of the hydroxylic reaction medium; and (iii) the pronounced influence of "*ortho*" substituents on the rate of the Wolff-Kishner reaction [1,4]. On the basis of this evidence it is concluded that, as a general rule, in the rate-determining step of the Wolff-Kishner reduction of ordinary hydrazones the proton capture at the carbon terminal in the hydrazone anion is coupled, in a more or less concerted fashion, with a solvent-induced proton abstraction at the nitrogen terminal to form *(3)*. Recent work by *Kosower* and *Huang* [6] not only provides evidence for the existence of the elusive diimide structure *(3)*, but also demonstrates its ease of ionization. The latter observation supports the view that a nucleophilic solvent participates in the formation of the diimide ion in the rate-determining step of the Wolff-Kishner reduction by promoting the ionization of the N–H bond. Scheme 1 depicts the mechanism of the Wolff-Kisher reaction.



Scheme 1. Mechanism of the Wolff-Kishner reduction. [*] = Rate-determining step.

It is noteworthy that the observed [2b] favorable response of the rate to an increase in the dielectric constant of the reaction medium agrees with the postulated rate-determining step since the charge of the hydrazone anion becomes localized as the diimide ion is formed, and additional ionic species are generated as well.

The stereochemistry in the formation of the hydrazone anion is of interest even when one is dealing with a symmetrical hydrazone, $R_2C{=}N{-}NH_2$, in view of the nonequivalence of the two N–H bonds. *A priori*, it can be assumed that the base attacks preferentially at the hydrogen farthest removed from the lone pair on the central nitrogen atom. Thus the *trans* anion *(4)* is believed to be formed rather than the *cis* anion *(5)*.



(4) trans

(5) cis

This preferential formation of the *trans* anion should be greatest in the presence of protic solvents which can be expected to form a hydrogen bond to the carbon terminal of the hydrazone anion to a greater extent than in the case of simple carbanions [7] because of the cooperative effect of the nonbonding electrons

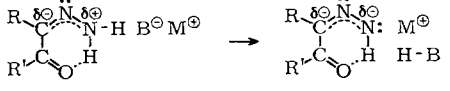
[5] a) *W. Davey* and *H. Gottfried*, J. org. Chemistry *26*, 3699 (1961); b) *T. Mukai*, *H. Tsuruta*, and *T. Nozoe*, Tetrahedron Letters *1966*, 1063.

[6] *E. M. Kosower* and *Pih-kuei C. Huang*, J. Amer. chem. Soc. *87*, 4645 (1965); *89*, 3910, 3911 (1967).

[7] *D. J. Cram*, Pure Appl. Chem. *7*, 155 (1963).

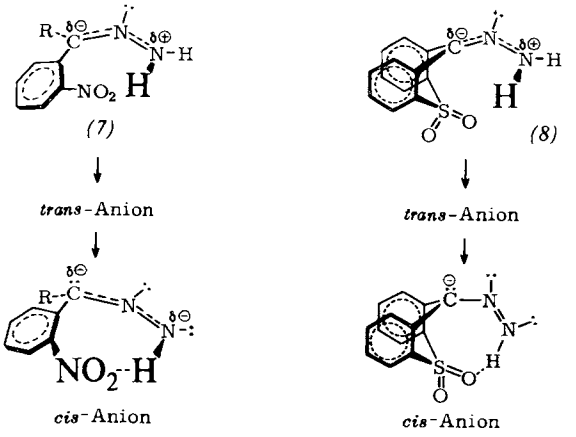
on the nearby nitrogen atom. There is no reason to suppose that the difference between the geometrical isomers of the hydrazone anion is less real than the isomerism of the allylic carbanions [8]. The geometry of the latter is determined by the structure of the starting material, their stability depends on the degree of delocalization (coplanarity), and each geometrical isomer gives a different olefinic product. On the other hand in the case of the isomers of hydrazone anions, the predominance of one of the geometrical isomers is subject to kinetic control, their stability depends not only on delocalization but also on the mutual repulsion of the neighboring nitrogen atoms, and, while both isomers lead to the same product, their geometry may modify somewhat the mechanism of the reaction.

A substituent capable of promoting a strong intramolecular hydrogen bridge with the terminal nitrogen of the hydrazone should also induce the formation of the *cis* hydrazone anion. A suitable substituent for this purpose is an α-carbonyl group [9]; another substituent, the α-hydroxyimino group, is discussed in the last section of this paper. In the case of the α-carbonyl hydrazones, the coplanarity and appropriate ring size of the system combine to create an ideal situation for the generation of a *cis* anion *(6)*. A similar situation may also exist in the hydrazones of 2-pyridyl carbonyl compounds [1b].



(6)

Since the hydrazone anion is, generally speaking, a relatively long-lived species [2c], one can also visualize the possibility of a *trans-cis* isomerization, with the subsequent participation of the *cis* isomer in the rate-determining step. Such an isomerization should take place when a substituent is present which can form an intramolecular hydrogen bond with the *cis* anion but not with the hydrazone proper. This type of situation exists, for example, in hydrazones of aromatic carbonyl compounds containing an *o*-nitro or *o*-carbonyl group, and in structures in which a transannular hydrogen bond is formed. The difference between the hydrazone and its anion resides in the lower coplanarity of the anion in which the carbon terminal of the hydrazone moiety acquires considerable carbanion character and thus approaches sp^3 hybridization. The localization of the negative charge at the carbon terminal is favored by the strong electron-withdrawing nature of the majority of the substituents which form intramolecular hydrogen bonds. The isomerization under discussion may be illustrated by the hydrazone of an *o*-nitroarayl carbonyl compound *(7)* and the hydrazone of thioxanthone dioxide *(8)*.



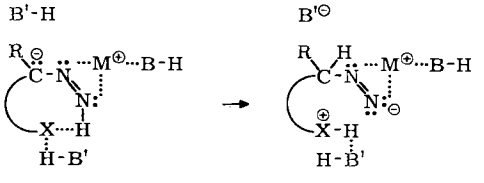
(7) *(8)*

trans-Anion *trans*-Anion

cis-Anion *cis*-Anion

Both of these systems [1b,4,10] as well as the monohydrazones of α-dicarbonyl compounds [4], are reduced at exceptionally low temperatures in protic solvents by the Wolff-Kishner method. This property is attributed to a combination of two circumstances: (i) the relatively strong carbanion character of the carbon terminal in the hydrazone anion, and (ii) the "internal solvation" of the N–H terminal by the functional groups enumerated above.

Regardless of the details of the isomerization of the hydrazone anion, the fact that *ortho* substituents capable of hydrogen bonding with the N–H terminal cause a significant lowering of the enthalpy of activation of Wolff-Kishner reduction is considered as strong evidence in favor of the conclusion that the breaking of the N–H bond is part of the rate-determining step. The rate-determining step with the participation of an *ortho* substituent (X) is represented in Scheme 2.



Scheme 2. Rate-determining step of the Wolff-Kishner reduction of the hydrazone of an "*ortho*" substituted compound. X = α-Carbonyl, α-hydroxy, *o*-carbonylaryl, *o*-nitroaryl, 2-pyridyl, transannular SO_2, *etc.* See Scheme 1 for the meanings of abbreviations.

The role of the different types of solvents in the Wolff-Kishner reduction can now be examined, starting with the most common reaction medium, namely hydroxylic solvents [11].

In an exclusively hydroxylic solvent, the mechanism of the Wolff-Kishner reduction, leading to and including the rate-determining step, can be formulated as shown in Scheme 3.

When a hydroxylic solvent and DMSO are present together in such concentrations that both solvent molecules participate in the rate-determining step, then each solvent performs the function for which it is best suited.

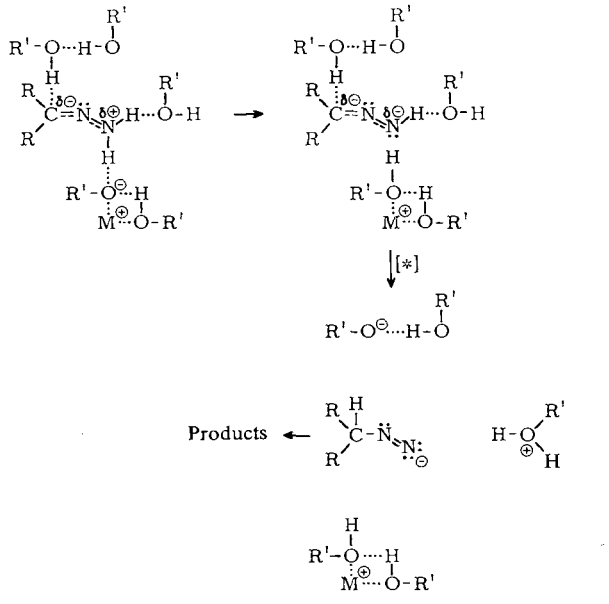
The most important difference between the rate-determining steps when ROH and R'OH + DMSO are

[8] *D. H. Hunter* and *D. J. Cram*, J. Amer. chem. Soc. *86*, 5478 (1964).

[9] Compare the situation in ethoxycarbonylhydrazones discussed by *M. Rosenblum*, *V. Nayak*, *S. K. DasGupta*, and *A. Longroy*, J. Amer. chem. Soc. *85*, 3874 (1963).

[10] *H. Kloosterziel* and *H. J. Backer*, Recueil Trav. chim. Pays-Bas *71*, 361 (1952).

[11] The reaction condition described by *Huang-Minlon*, J. Amer. chem. Soc. *68*, 2487 (1946), is included in the present considerations.

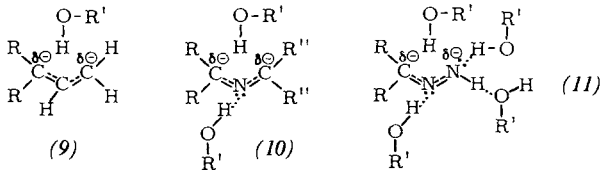


Scheme 3. Wolff-Kishner reduction in a hydroxylic solvent [12].
[*] = Rate-determining step.

used as solvents is the participation of DMSO in the breaking of the N–H bond and in the solvation of the metal cation. The former effect is believed to predominate in the concentration range 6.75–9.00 M and to account for the gradual lowering [2b] of the enthalpy of activation. The simultaneous increase [2b] in the negative entropy of activation must be the result of an increase in the organization of the DMSO molecules caused by the ionic products of the rate-determining step.

It is noteworthy that the intermolecular proton transfer suggested in Scheme 3 is analogous to the mechanism of the base-catalyzed isomerization of imines [13], and differs from the intramolecular proton transfer demonstrated by *Cram* and *Uyeda* [14] for the base-catalyzed isomerization of allylic hydrocarbons. However, the comparison of the respective anions *(9)–(11)* of Scheme 4 reveals that the increasing number of nonbonding electrons available for solvation with protic solvent molecules must necessarily promote the intermolecular proton transfers.

When the hydrazone anion is generated in an aprotic polar solvent such as DMSO by means of an alkoxide, then the newly formed alcohol must serve as the



Scheme 4. Solvation in allylic, imine, and hydrazone anions.

[12] Only the minimum number of solvent molecules is shown in this diagram. The R'OH molecules should be visualized either above or below the plane of the hydrazone.

[13] Work of *Wilson*, *Ossorio*, and *Ingold* summarized by *C. K. Ingold*: Structure and Mechanism in Organic Chemistry. Cornell University Press, Ithaca, New York 1953, p. 574. See also: *D. J. Cram* and *R. D. Guthrie*, J. Amer. chem. Soc. *87*, 397 (1965).

[14] *D. J. Cram* and *R. T. Uyeda*, J. Amer. chem. Soc. *86*, 5466 (1964).

proton source at the carbanion terminal. Judging by the absence of a kinetic isotope effect in the alkoxide-catalyzed exchange reaction of hydrocarbons when DMSO is employed [15] as the solvent, the diffusion of alcohol molecules must be a slow process, and thus the Wolff-Kishner reaction has to depend on a proton transfer by the newly formed alcohol.

The intramolecular proton transfer under these circumstances resembles the proton transfer in the allylic hydrocarbons [14], and explains the observation [2c] that the generation of an alcohol molecule within the solvent cage that encloses the hydrazone anion is more effective than the addition of relatively large amounts of alcohol to a solution of the hydrazone anion in DMSO. Also, the slow migration of the alcohol toward the carbanion terminal, and the known capacity of DMSO molecules to capture the alcohol through hydrogen bonding, explains the relatively high degree of azine formation when the Wolff-Kishner reduction is carried out in DMSO [2a, 2d].

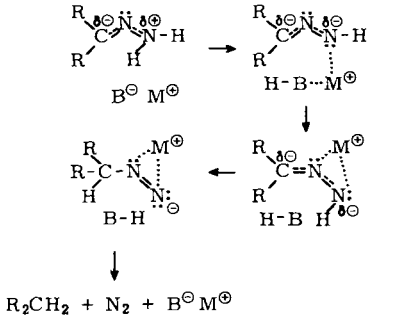
Next to be considered is the Wolff-Kishner reaction in anhydrous DMSO [2c] in which the hydrazone anion is generated by means of the anion derived from DMSO. It is now known [2c] that the addition of benzophenone hydrazone to a solution of dimsylsodium in DMSO causes a rapid (k_2 at 25 °C *ca.* 10^{-3} lmole^{-1} sec^{-1}) formation of the benzophenone hydrazone anion which gives a characteristic absorption maximum at 3930 Å ($\varepsilon = 2\times10^4$). In the absence of oxygen the solution of the hydrazone anion is stable over a period of several days. Thus it is apparent that the Wolff-Kishner reaction fails to occur in DMSO free of hydroxylic components and this behavior must be attributed to the low acidity of DMSO (pK_a 31.3) [16] as compared with the acidity of either the carbon or nitrogen acids derived from the benzophenone hydrazone anion. The weaker of the two acids, namely the carbon acid in benzhydryldiimide, should have a pK_a value lower than that reported for diphenylmethane in DMSO (28.6) [16] because of the electron-withdrawing effect of the diimide group, and thus the proton donating ability of DMSO turns out to be too small for the formation of the new C–H bond in the rate determining step of the Wolff-Kishner reaction. The failure to observe a Wolff-Kishner reaction of the hydrazone anion in a truly aprotic medium also excludes the possibility of an intramolecular proton transfer from the nitrogen to the carbon terminal.

Finally, the mechanism of the Wolff-Kishner reduction in an essentially aprotic, nonpolar solvent such as toluene [2d] may be considered. In view of the limited solvating capacity of such a medium, the ionic species will tend to exist as intimate ion pairs, and, following the formation of equimolar quantities of hydrazone anion and alcohol, the metal cation can be expected to coordinate both species in a tightly held complex. This situation should favor a rapid proton

[15] *J. E. Hofmann*, *A. Schriesheim*, and *R. E. Nickols*, Tetrahedron Letters *1965*, 1745.

[16] *E. C. Steiner* and *J. M. Gilbert*, J. Amer. chem. Soc. *87*, 382 (1965).

capture by the carbanion terminal, and this expectation is indeed realized in view of the greater velocity [2d] of the Wolff-Kishner reaction in toluene than in DMSO. However, one must still account for the breaking of the N–H bond in the hydrazone anion when the solvent is unable to participate in the rate-determining step. The choice is between the alkoxide ion shuttling back to the N–H bond following proton capture at the carbanion terminal or the more plausible alternative of a *trans-cis* isomerization of the hydrazone anion aided by the chelating capacity of the metal cation and the subsequent intramolecular proton transfer depicted in Scheme 5.

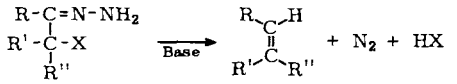


Scheme 5. Wolff-Kishner reduction in nonpolar, aprotic solvents.

Regardless of the solvent conditions, the final step of the Wolff-Kishner reduction is the collapse of the diimide anion in the presence of a proton source into the hydrocarbon and a nitrogen molecule. This step is identical with that studied by *Cram et al.* [17] in connection with the stereochemistry of carbanions. These authors found that the retention of the configuration in the transition state increases when the "leaving group" is a nitrogen molecule (as compared with carbon, oxygen, or hydrogen "leaving groups"), and also that the degree of retention depends on the proton-donating capacity of the medium and its dielectric constant. Applying these results to the collapse of the diimide anion in the Wolff-Kishner reduction, we conclude that this step is a rapid one, either because of a rear attack by the protic solvent, or because the formation of the nitrogen molecule creates a "low pressure region" in the liquid structure which assists in "pulling in" the carbanion and proton donor from opposite directions. The conclusion with regard to the fast base-catalyzed collapse of diimide is born out by recent work of *Kosower* [6] on phenyl- and *tert*-butyldiimides.

3. The Mechanism of the Wolff-Kishner Elimination

The elimination which occurs in the course of a Wolff-Kishner reduction has been known since the days of *Kishner* [18], who observed the formation of 2,5-dimethyl-2-octene during the attempted reduction of 2,6-dimethyl-2-hydroxy-3-octanone. However the conditions propitious for the Wolff-Kishner elimination to form *(12)* have never been properly defined, and



(12)

the occurrence of the elimination remained somewhat erratic.

Thus, while the Wolff-Kishner elimination was shown [19] to be strongly dependent on the ring size of cyclic ketones (subjected to the Huang-Minlon procedure [11]) and on the conformational equilibria in acyclic ketones, it was reported to occur with great reluctance [20] with either type of ketone in spite of the presence of excellent leaving groups [11]. Several groups of investigators [21] found that the elimination takes place in the course of the Wolff-Kishner reduction of steroidal ketones, and *Turner et al.* [22] suggested some of the stereochemical requirements for the elimination process without dwelling on the details of the competition between the elimination and reduction paths.

The strict stereochemical requirements for the Wolff-Kishner elimination suggests that the critical step of this reaction occurs after the original trigonal carbon (of the ketone or hydrazone) has assumed the tetrahedral configuration. This implies that the reaction follows the general pattern of a *trans* elimination, and that the proton capture at the carbanion terminal of the hydrazone anion determines the orientation of the nitrogen moiety. The data on the Wolff-Kishner elimination in steroids offer substantial support for this conclusion. In most of the examples in which the elimination predominates, the hydroxyl next to the carbonyl group has an axial orientation. Thus, solvation of this hydroxyl group by protic solvents is expected to promote an equatorial proton capture at the carbanion terminal of the hydrazone anion, and, in the final analysis, the hydroxyl and the nitrogen moiety are *a,a-trans* with respect to each other in an ideal orientation for the *trans*-elimination [23]. This process is illustrated in Scheme 6 for the 5-hydroxy-6-oxo steroid system which is common to several investigations [21d, 21e]. A similar situation exists in the 9-hydroxy (or epoxy)-11-oxo steroids [21e], and in both systems the Wolff-Kishner reaction follows the elimination path almost exclusively. In the 11-hydroxy-12-oxo steroids such as *(13)* [21e], on the other hand,

[17] a) *D. J. Cram, J. S. Bradshaw, W. Lwowski,* and *G. R. Knox,* J. Amer. chem. Soc. *84,* 2832 (1962); b) *D. J. Cram* and *J. S. Bradshaw, ibid. 85,* 1108 (1963).

[18] *N. Kishner,* J. Russ. Phys. Chem. Soc. *45,* 973 (1913).

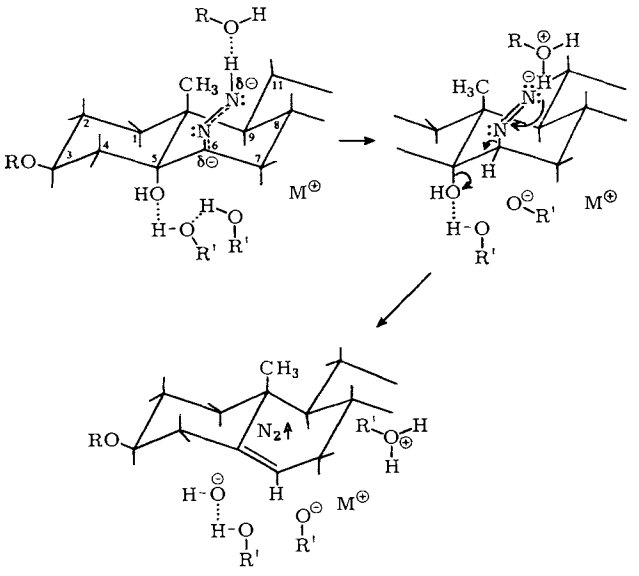
[19] a) *N. J. Leonard* and *R. C. Sentz,* J. Amer. chem. Soc. *74,* 1704 (1952); b) *N. J. Leonard* and *J. Gelfand, ibid. 77,* 3269, 3272 (1952).

[20] *P. S. Wharton, S. Dunny,* and *L. Soto Krebs,* J. org. Chemistry *29,* 958 (1964).

[21] a) *L. Ruzicka* and *H. F. Meldahl,* Helv. chim. Acta *23,* 513 (1940); b) *C. W. Shoppe* and *D. A. Prins, ibid. 26,* 185 (1943); *27,* 8 (1944); c) *T. F. Gallagher et al.,* J. biol. Chemistry *162,* 521, 523 (1946); d) *D. H. Barton et al.,* J. chem. Soc. (London) *1949,* 2456; *1951,* 2752; *1954,* 3045; e) *L. F. Fieser* and *H. Heymann,* J. Amer. chem. Soc. *73,* 5252 (1951).

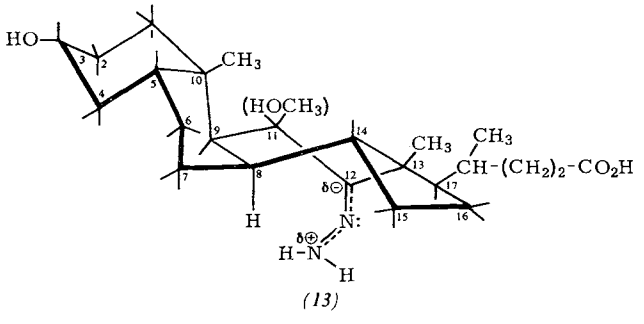
[22] *R. B. Turner, R. Anliker, R. Helbling, J. Meier,* and *H. Heusser,* Helv. chim. Acta *38,* 411 (1958).

[23] *E. L. Eliel, N. L. Allinger, S. J. Angyal,* and *G. A. Morrison*: Conformational Analysis. Interscience Publishers, New York 1965, p. 293.



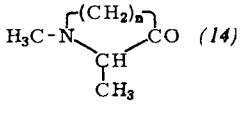
Scheme 6. Wolff-Kishner elimination in 5-hydroxy-6-oxo-steroids.

the elimination and reduction processes occur in nearly equal proportions regardless of whether the hydroxyl group is oriented alpha or beta. This can be understood by examining the stereochemistry of the steroidal C ring. Because of the *cis*-junction of the C ring with the 5-membered D ring, and because of the repulsive interactions between the axial substituents at C-13 and C-17, the C ring will tend to assume a twisted conformation. As a result, the hydroxyl group at C-11 is oriented either semi-axially or semi-equatorially, and in this ambiguous situation some of the stereospecificity in the proton capture step is lost.



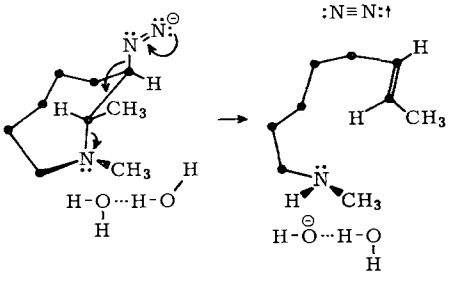
(13)

On the basis of these results, the relative reluctance of the 2-halogen substituted cholestanones [20] to undergo a Wolff-Kishner elimination can be attributed to the equatorial orientation of the potential "leaving groups". Also the interesting differences in the behavior of the cyclic oxoamines [19] can be explained on the basis of the relative ease with which a *trans* orientation of the critical moieties can be achieved. Thus, in the



(14)

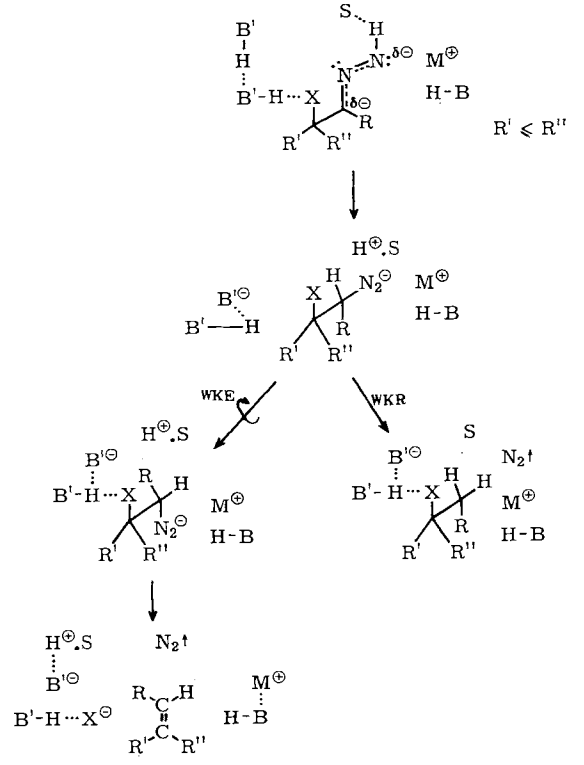
system *(14)* no elimination could be detected when $n = 3$, while the yield of the elimination product increased from 44 % to 99 % as the value of n changed from 4 to 5. These results agree with the release of tension in the conformation as the size of the ring increases (see Scheme 7).



Scheme 7. Wolff-Kishner elimination in cyclic systems.

The results obtained for acyclic α-substituted ketones are more difficult to rationalize because these systems possess a large degree of rotational freedom. Following the guidelines established for the relatively rigid cyclic systems, one must search for a correlation between conformational preferences and the *trans* orientation of the diimide ion moiety and the potential "leaving group", which is assumed to be a structural requirement for the elimination process.

Let us consider first the conformation of the hydrazone in which the potential "leaving group" X and the hydrazone moiety are oriented *cis* with respect to each other. This conformation follows the pattern established for unsaturated molecules [24] and permits a high degree of solvation at both polar groups. The solvation by protic solvents determines the stereo-



Scheme 8. Wolff-Kishner reduction (WKR) and Wolff-Kishner elimination (WKE) in acyclic systems (S = solvent molecule).

[24] *E. L. Eliel, N. L. Allinger, S. J. Angyal,* and *G. A. Morrison*: Conformational Analysis. Interscience Publishers, New York 1965, p. 19.

Table 1. Yields of Wolff-Kishner elimination (E) and reduction (R) products in acyclic systems (see Scheme 8) [a].

X	R′	R″	R	% E	% R
Piperidino	H	H	$C_6H_5CH_2$	14	75
Piperidino	H	C_6H_5	CH_3	19	74
Piperidino	H	CH_3	C_6H_5	37	40
Piperidino	H	C_6H_5	C_6H_5	40	5
C_6H_5—NH	H	C_6H_5	CH_3	6	70
$C_6H_5CH(CH_3)NH$	H	p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$	34	0
HO [b]	CH_3	CH_3	C_6H_{13}		
C_2H_5O	H	C_6H_5	C_6H_5	44	0
$C_5H_{11}O$	H	H	$C_6H_5CH_2$	70	18
RNH [c]	H	H	t-Bu	41	37
R_2N [c]	H	H	t-Bu	36—54	21—48
Piperidino	H	H	t-Bu	29	64
Cyclic N [c]	H	H	t-Bu	15—41	42—65
C_6H_5O	H	H	t-Bu	80	0
RCO—O [c]	H	H	t-Bu	52—58	0
RS [c]	H	H	t-Bu	76—95	0

[a] All data from ref. [19] except that marked [b].

[b] Ref. [18].

[c] For meaning consult Ref. [19].

chemistry of proton capture at the carbanion terminal in the hydrazone anion, as shown in Scheme 8, in accord with the relative size of the substituents R′ and R″ at the carbon atom containing the potential "leaving group". The diimide ion which results from this process has an unfavorable eclipsed conformation, and its destiny will depend on the relative stability of the two conformations in which either the group R or the nitrogen moiety are oriented *trans* with respect to the potential "leaving group" X. An examination of a number of individual cases (see Table 1) reveals that, barring the effect of factors which are enumerated below, the Wolff-Kishner reduction path is suppressed to the extent to which the repulsion between the *gauche* oriented groups R, R′ and R′, R″ increases. This is apparent from the first six entries in Table 1, in which the "leaving groups" (X) are similar, and on relating the nature of the groups R″ and R to the decrease in the yield of the reduction product.

It is apparent that the reduction path is suppressed the most when both R′ and R″ are aromatic groups, and in the combination of one alkyl and one aryl group the repulsion seems to be greater when the aryl group is located near the diimide anion. In the last seven entries in Table 1, the structural variation resides only in the nature of the X group. The first four of these entries illustrate [18] the partial dependence of the yield of the elimination product on the strain at the nitrogen atom of the "leaving group" while the last three entries, together with the other cases where X = OH or OR, illustrate the suppression of the reduction path when X is a superior "leaving group".

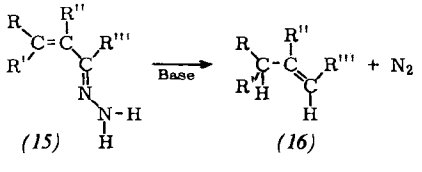
Grundon et al. [2d] have recently demonstrated the nearly complete absence of the Wolff-Kishner elimination when a toluene solution of the hydrazone of 3,3-dimethyl-1,2′-methylpiperidinobutan-2-one is treated with potassium *tert*-butoxide. The same hydrazone gave a 38 % yield [19a] of the elimination product under protic reaction conditions.

The observation of *Grundon et al.* fits the mechanisms evolved here for the Wolff-Kishner reaction in aprotic, nonpolar solvents and for the Wolff-Kishner elimination. It is clear that the 1:1 complex of the highly polar hydrazone anion and of the alcohol will tend to be coordinated by the metal cation into a tight complex when these species are surrounded by solvent molecules of low polarity such as those of toluene, and this situation is not conducive to the migration of the alcohol toward the potential "leaving group" for the purpose of hydrogen bonding to the latter. Thus, the nitrogen is expelled from the diimide ion, and the resulting carbanion and nearby alcohol molecule collapse to the final hydrocarbon product, in preference to an elimination process.

Apart from the conformational factors mentioned above, the reluctance of the Wolff-Kishner reaction investigated by *Wharton et al.* [20] to give elimination products can also be attributed to the relatively nonprotic reaction medium employed (1,2-dimethoxyethane plus 2 to 3 equivalents of 95 % hydrazine in the absence of any other base catalyst). Assuming that the hydrazone anion is formed satisfactorily under these conditions, the limited quantity of protic components of the reaction mixture will tend to form hydrogen bonds with the ether linkages of the solvent rather than participate in the elimination process.

4. The Mechanism of the Wolff-Kishner Isomerization

The Wolff-Kishner isomerization consists in the migration of a double bond during Wolff-Kishner reduction [*e.g. (15)* → *(16)*].

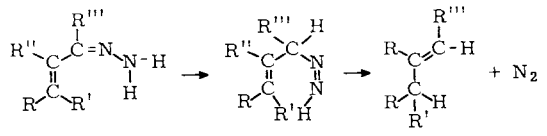


(15) *(16)*

The reaction was first observed by *Lardelli* and *Jeger* [25] who also suggested a cyclic mechanism for this transformation (see Scheme 9).

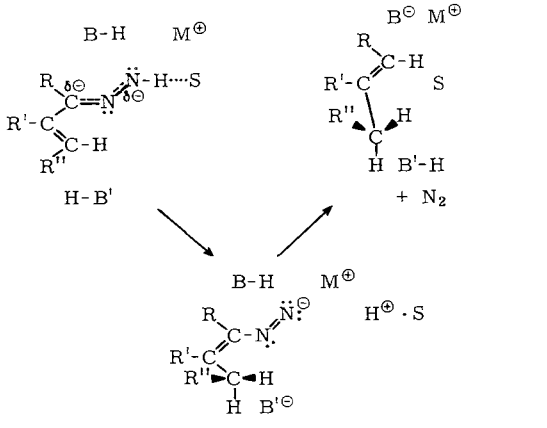
This mechanism does not seem satisfactory because it does not clarify the conversion of the hydrazone to

[25] a) *G. Lardelli* and *O. Jeger*, Helv. chim. Acta *32*, 1817 (1949); b) *R. Fischer, G. Lardelli*, and *O. Jeger, ibid. 33*, 1335 (1950); *34*, 1577 (1951).



Scheme 9. Wolff-Kishner isomerization according to *Lardelli* and *Jeger* [25].

the diimide, and because it attributes to the double bond the capacity to induce the *cis* structure in the diimide. Even though hydrogen bonding to olefinic π electrons is not unknown [26], it is doubtful that this phenomenon can be responsible for the stereospecificity suggested above, and it is therefore preferable to attempt to interpret the isomerization within the framework of the general mechanism of the Wolff-Kishner reactions. The improbability of the mechanism in Scheme 9 is further supported by the complete suppression of isomerization when the Wolff-Kishner reaction is carried out in toluene [2d]. In the absence of competitive hydrogen bonding between the hydrazone or its anion and the solvent molecules, the intramolecular association assumed in the "cyclic mechanism" should be favored and hence also the isomerization process. The contradicting results point to an active participation of the protic solvent in the isomerization, and a mechanism for the latter is suggested in Scheme 10.



Scheme 10. Newer conceptions about the Wolff-Kishner elimination.

Steric interference between the substituents at the olefinic bond and the solvated N–H terminal casts serious doubts on the possibility of extending the delocalization of the hydrazone moiety to include the olefinic system while the nitrogen and olefinic systems are pointing toward each other; for this reason the *anti* hydrazone structure is assumed.

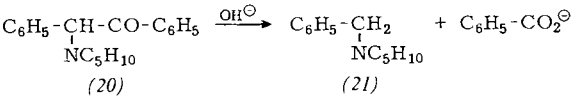
A novel isomerization has been observed [34] in the course of the Wolff-Kishner reaction of the tetracyclic ketone *(17)*. In addition to the expected reduction product *(18)* there was also 15 % of an isomeric product *(19)* isolated. The formation of the latter can be considered to result from a competitive protonation of the intermediate carbanion (during the collapse of the hydrazone anion in the final phase of the Wolff-Kishner mechanism) at one of carbon atoms neighboring the original carbonyl group: These carbon atoms exhibit an olefin-like character associated with the presence of the cyclopropane ring system. One is tempted to predict that the isomeric product *(19)* would be suppressed if the Wolff-Kishner reaction were to be carried out in an essentially aprotic medium.

(17) *(18)* *(19)*

A not dissimilar ring opening occurs [35] during the Wolff-Kishner reduction of α,β-epoxy ketone. As may well be expected, the intermediate carbanion suffers a unidirectional opening of the neighboring epoxide with the resulting formation of an allylic alcohol.

5. Side Reactions During the Wolff-Kishner Reaction

In the course of attempted or partially successful Wolff-Kishner reactions side reactions are encountered that have no bearing on the mechanism of the process as such [27]. One of these is the base-catalyzed cleavage of certain α-substituted ketones illustrated by the cleavage [19] of α-phenyl-α-piperidinoacetophenone *(20)* to *N*-benzylpiperidine *(21)* in 25 % yield,



(20) *(21)*

The same type of reaction accounts for the isolation of benzoates from the attempted [28] Wolff-Kishner reduction of α-hydroxyiminopropiophenone hydrazone, and the formation [29] of 8-benzhydryl-1-naphthoic acid in the attempted Wolff-Kishner reduction of 2,2-diphenyl-1-acenaphthenone.

Another such side reaction occurring in conjunction with the Wolff-Kishner elimination reaction consists of the reduction of the expected olefin to the saturated hydrocarbon. The Huang-Minlon procedure [11] favors this side reaction because an excess of hydrazine is used; probably the atmospheric oxidation of hydrazine to diimide [30] leads to the hydrogenation of the olefin. An example of the occurrence of this side reaction is the isolation [19] of *p,p'*-dimethoxybibenzyl instead of the corresponding stilbene from the Wolff-Kishner elimination of 4-methoxy-α-4'-methoxyphenyl-α-(α'-phenylethylamino)acetophenone hydrazone and another is the isolation [31] of cholestane instead of 2-cholestene during

[26] a) *A. W. Baker* and *A. J. Shulgin*, J. Amer. chem. Soc. *80*, 5358 (1958); b) *R. West*, *ibid. 81*, 1614 (1959); c) See review by *Eiji Osawa*, Ph. D. Thesis, Kyoto University, 1965.

[27] Not included in this discussion are the cyclizations of hydrazones by classical internal condensations such as the reactions described by *R. A. Braun* and *W. A. Mosher*, J. Amer. chem. Soc. *80*, 4919 (1958); *E. D. Bergmann* and *R. Ikhan*, *ibid. 78*, 2831 (1956); *C. Fisher*, *H. Beyer*, and *K. Zaicker*, Liebigs Ann. Chem. *486*, 55 (1931).

[28] *H. Rapoport* and *W. Nilsson*, J. Amer. chem. Soc. *83*, 4262 (1961).

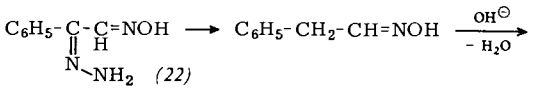
[29] *R. L. Letsinger* and *P. T. Lansbury*, J. Amer. chem. Soc. *81*, 935 (1959).

[30] a) *S. Hünig*, *H. R. Müller*, and *W. Thier*, Angew. Chem. *77*, 368 (1965); Angew. Chem. internat. Edit. *4*, 271 (1965); b) *A. Furst*, *R. C. Berlo*, and *S. Hooton*, Chem. Reviews *65*, 64 (1965); c) *E. E. van Tamelen*, *R. S. Dewey*, and *R. J. Timmons*, J. Amer. chem. Soc. *83*, 3725 (1961).

[31] *L. Ruzicka*, *P. A. Plattner*, and *M. Furrer*, Helv. chim. Acta *27*, 727 (1944).

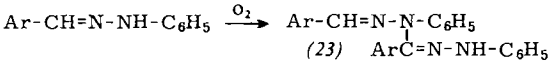
the Wolff-Kishner elimination reaction of 2-acetoxy-3-cholestanone.

Finally, the possibility exists of the decomposition of an aldehyde derivative in which the attack of the base upon the aldehydic hydrogen can be accompanied by the departure of a suitable "leaving group". This situation is illustrated by the isolation[28] of phenylacetic acid in 78% yield from the Wolff-Kishner reduction of α-hydroxyiminoacetophenone hydrazone *(22)*.



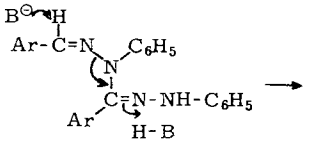
(22)

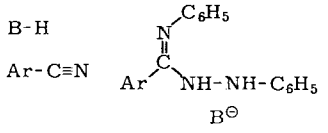
A similar reaction is the base-catalyzed decomposition of some phenylhydrazones of aromatic aldehydes[32]. The base-catalyzed decomposition is preceded by an oxidative coupling of the phenylhydrazone to a hydrazidine *(23)*; the final



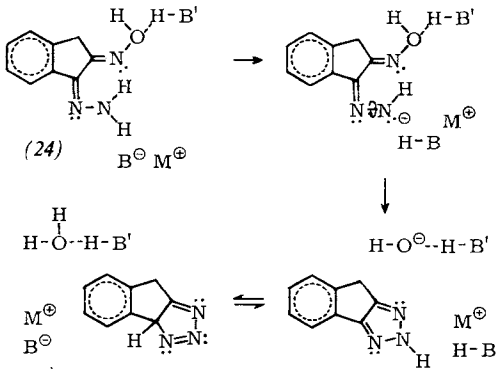
(23)

elimination reaction occurs with the latter species in which an excellent "leaving group" is now available:





A side reaction which does have a direct bearing on the Wolff-Kishner reaction is the formation[28] of *vic*-triazoles observed during the reaction of some α-hydroxyiminoketones. The acyclic representatives undergo a normal Wolff-Kishner reduction to the corresponding oximes (unless one of the side reactions described above happens to interfere), but the α-hydroxyiminoketone hydrazones *e.g. (24)* in which both functional groups are forced into coplanarity produce a *vic*-triazole. This result seems to confirm the hypothesis that the hydrazone anion is a relatively long-lived species even in the presence of protic molecules, since an intramolecular displacement reaction (see Scheme 11) can occur in



(24)

Scheme 11. Triazole formation on the Wolff-Kishner reduction of α-hydroxyimino hydrazones.

competition with a proton capture typical of the Wolff-Kishner reduction. Since *(24)* contains an "*ortho*" substituent capable of strong intramolecular hydrogen bonding, it is assumed that the *cis*-hydrazone anion is formed in preference to the *trans* isomer, and the fact[28] that the yield of *vic*-triazoles decreases to 1 and 0% when a methyl or phenyl substituent is introduced at the terminal nitrogen atom is strong evidence that the formation of the *cis*-hydrazone anion is indeed the initial step of the reaction[32]. Once the *cis*-anion is formed, the repulsion of the nonbonding electron pairs on the vicinal nitrogen atoms aids *cis-trans* isomerization, and then a nucleophilic attack of the hydrazone anion terminal on the nitrogen of the oxime produces ring closure. The nucleophilic character of the hydrazone anion is not unexpected if one considers that a hydrazone proper is able to cause a nucleophilic displacement of a nitro group in certain *o*-nitroarylketone hydrazones[33], and that nucleophilic attack on the nitrogen of a variety of derivatives of oximes occurs during the acid-catalyzed cyclizations of α-hydroxyiminoketohydrazones to *vic*-triazoles[27].

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German version: Angew. Chem. *80*, 141 (1968)

[32] *M. F. Grundon* and *M. D. Scott*, J. chem. Soc. (London) *1964*, 5674.

[33] *H. H. Szmant* and *C. M. Harmuth*, J. Amer. chem. Soc. *81*, 962 (1959).

[34] *N. A. LeBel* and *R. N. Liesemer*, J. Amer. chem. Soc. *87*, 4301 (1965).

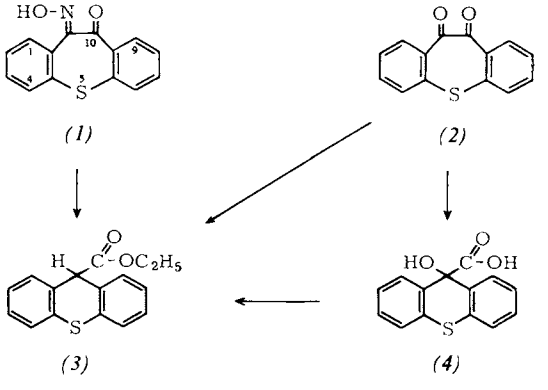
[35] *Huang-Minlon* and *Chung Tungehun*, Scientia Sinica *15*, 487 (1966).

COMMUNICATIONS

Acid-catalyzed Ring Contraction of Dibenzothiepin-10,11-dione

By *A. Lüttringhaus* and *G. Creutzburg*[*]

On acid hydrolysis of dibenzothiepin-10,11-dione monoxime *(1)* in aqueous ethanol we obtained, instead of the expected diketone *(2)*, ethyl 9 *H*-thioxanthene-9-carboxylate *(3)*, which was formed in more than 70% yield by ring contraction and reduction. The diketone *(2)* prepared by a different route[1] is converted into *(3)* under similar conditions. 9-Hydroxythioxanthene-9-carboxylic acid *(4)*, accessible from *(2)* by a normal base-catalyzed benzilic acid rearrangement, is converted into *(3)* even faster than are *(1)* and *(2)* under the same conditions.



(1) *(2)* *(3)* *(4)*

The ester *(3)* formed in each case is identical with a sample obtained by esterification of the authentic 9 *H*-thioxanthene-9-carboxylic acid[2] as regards mixed melting point and IR and NMR spectra (8 aromatic protons give a multiplet at $\tau = 2.6$; a benzylic proton gives a singlet at $\tau = 4.9$; CH_2 quadruplet at $\tau = 5.8$, $J = 7.5$ Hz; CH_3 triplet at $\tau = 8.9$, $J = 7.5$ Hz; TMS as internal standard, in $DCCl_3$).

Under the same conditions no reaction occurs with dibenzothiepin-10,11-dione *S,S*-dioxide, with benzil, with phenanthraquinone, or with 5 *H*-dibenzo[*a,d*]cyclohepta-1,4-diene-10,11-dione. We consider this to be evidence that the sulfur atom, with its free electron pairs, is concerned in the reaction mechanism (cf.[3]).

Preparation of (3):

1.45 g of dibenzothiepin-10,11-dione monoxime *(1)* is dissolved in a warm mixture of 100 ml of ethanol and 30 ml of concentrated hydrochloric acid (or 50% sulfuric acid) (red coloration) and then boiled for 3 h. On addition of 100 ml of water and cooling, colorless crystals of *(3)* separate, m.p. 100 °C (ethanol/water); mixed m.p. with authentic *(3)*, 100 °C; yield 1.1 g (71.4%). Conversion of *(2)* and *(4)* into *(3)* is carried out analogously. If during the reaction a current of nitrogen is passed through the solution into an ice-cooled receiver containing a little water, the acetaldehyde formed can be trapped as 2,4-dinitrophenylhydrazone, m.p. 147 °C.

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[1] *J. Rigaudy* and *L. Nedeleć*, C. R. hebd. Séances Acad. Sci. *236*, 1287 (1953); *K. Mirwald*, Dissertation, Universität Saarbrücken, 1961; *G. Creutzburg*, Dissertation, Universität Freiburg, 1966.

[2] *E. D. Bergmann* and *M. Rabinovitz*, J. org. Chemistry *25*, 828 (1960).

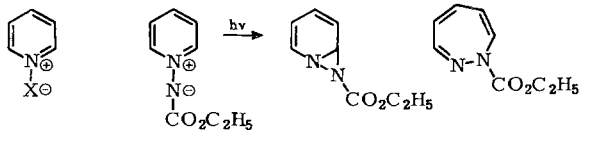
[3] *A. Lüttringhaus*, *M. Mohr*, and *N. Engelhard*, Liebigs Ann. Chem. *661*, 84 (1963); *N. Engelhard* and *A. Kolb*, *ibid. 673*, 136 (1964).

Photochemical Synthesis of Ethyl 1 *H*-Diazepine-1-carboxylate

By *J. Streith* and *Jean-Marie Cassal*[*]

Mesoionic pyridinium derivatives of type *(1)*, X = O, CR_2, or NR, can be considered as aromatic 1,3-dipoles[1]. Whereas pyrrole derivatives are obtained by UV irradiation of pyridine *N*-oxides or pyridinium dicyanomethylide[2], we have established that the compound *(2)* synthesized by *Hafner*[3] undergoes photochemically induced ring expansion to ethyl 1*H*-diazepine-1-carboxylate *(4)*.

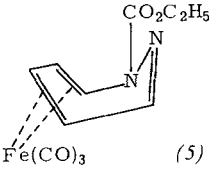
UV irradiation of a 10^{-2} M solution of the *N*-(ethoxycarbonylamino)pyridinium derivative *(2)* by means of a mercury high-pressure lamp with a Pyrex filter leads in a few hours to complete disappearance of the starting material, while the solution becomes dark red. Removal of the solvent, chromatography on silica gel and distillation of the red oil thus obtained provides a homogeneous red product (yield 95%), b.p. 50 °C/0.5 torr, $n_D^{25} = 1.5302$, whose mass spectrum[4], microanalysis, and spectral data indicate structure *(4)*.



(1) *(2)* *(3)* *(4)*

The UV spectrum of compound *(4)* in *n*-hexane [$\lambda_{max} = 217$ ($\varepsilon = 10000$), 362 nm ($\varepsilon = 230$)] is very similar to that of ethyl azepine-1-carboxylate[5]. The IR spectrum (film) contains bands at 2950, 1700, and 1600 cm^{-1}. As well as the expected ethyl multiplets at $\tau = 8.65$ (triplet) and 5.68 (quartet), the NMR spectrum contains signals for five olefinic protons, at $\tau = 2.6$, 3.42, 3.75, 3.82, and 4.25, whose chemical shifts exclude bicyclic isomeric structures.

If a solution of compound *(4)* in petroleum ether is treated with $Fe_2(CO)_9$[6] at room temperature, the carbonyliron complex *(5)*, m.p. 115–116 °C (after chromatography on silica gel and sublimation), is obtained. As is to be expected, the NMR spectrum of the complex *(5)* contains, besides signals for the ethyl protons, signals at higher magnetic field ($\tau = 6.68$, 4.90, 5.43, and 3.69) for the protons H-4, H-5, H-6, and H-7, a result that was obtained also by *E. O. Fischer* for the carbonyliron complex of ethyl azepine-1-carboxylate[7].



(5)

The conversion of *(2)* into *(4)* can be considered as a two-stage reaction, namely, 1,3-dipolar ring closure to the diaziridine *(3)* followed by valence-tautomerization to *(4)*.

Received: November 27, 1967 [Z 661 IE]
German version: Angew. Chem. *80*, 117 (1968)

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[1] *R. Huisgen*, Proc. chem. Soc. (London) *1961*, 357.

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[4] We thank Dr. *Vetter* and Dr. *Montavon*, Hoffmann-La Roche, Basel, for measuring the mass spectrum.

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[6] *E. Speyer* and *H. Wolf*, Ber. dtsch. chem. Ges. *60*, 1424 (1927).

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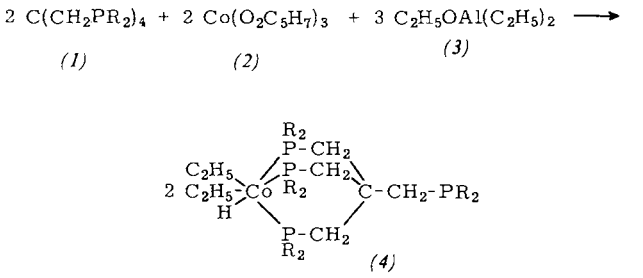
Preparation and Properties of a Bicyclic Hydridodiethylcobalt Complex [1]

By *J. Ellermann* and *W. H. Gruber*[*]

Recently we reported the synthesis of spiroheterocyclic alkylzinc complexes[2] incorporating tetrakis(diphenylphosphinomethyl)methane *(1)* that, in general, functioned as a doubly bidentate ligand[3,4]. We have now found that on reduction of tri(acetylacetonato)cobalt(III) *(2)* by ethoxydiethylaluminum *(3)*[5] in the presence of *(1)* a bicyclic hydridodiethylcobalt complex *(4)* is formed and not a spiroheterocyclic complex. The compound *(1)* thus here functions only once as a tridentate ligand[6].

Since the reaction of $P(C_6H_5)_3$ with *(2)* and *(3)* in a N_2 atmosphere leads to $N_2 \cdot Co[P(C_6H_5)_3]_3$[6a], it seems remarkable that the above reaction, which is also carried out in a N_2 atmosphere, shows no sign of the formation of an analogous N_2-containing complex.



(1) (2) (3) (4)

+ 2 C_2H_4 + 3 $C_2H_5OAl(O_2C_5H_7)_2$

R = C_6H_5

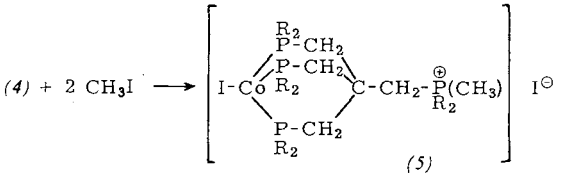
Experimental:

1 mmole each of *(1)* and *(2)* are dissolved in 10 ml of anhydrous, N_2-saturated benzene and treated with 1.5 mmoles of *(3)* slowly and with stirring at room temperature. Ethylene is evolved and the color changes within 30 min from green to dark brown. The small amounts of decomposition products that are formed during the reaction are filtered off, and the filtrate is concentrated in a vacuum to 3–5 ml and treated with 20 ml of ether. The brown crystals of 4-(diphenylphosphinomethyl)-1,1-diethyl-1-hydrido-2,2,6,6,7,7-hexaphenyl-2,6,7-triphospha-1-cobaltabicyclo[2.2.2]octane *(4)*, which separate within an hour, are filtered off, washed twice with 10 ml of diethyl ether, and dried in a vacuum. Compound *(4)* is extremely sensitive to air, soluble in benzene, acetone, or chloroform, and insoluble in petroleum ether, cyclohexane, or diethyl ether.

The composition and structure of *(4)* are proved by elemental analysis, cryoscopic determination of molecular weight in benzene, and the IR spectrum (νCo–H 1912 cm^{-1} w–m; characteristic absorptions[7] of the $Co(C_2H_5)_2$ group (cm^{-1}); νC–H 2985, 2970, 2910, 2875 (all w–m); $\delta_s CH_3$ 1169 m; ρCH_3 914 w–m, 891 s–m, 846 m, (?) 821 m; ρCH_2 647 m–st; νCoC_2 565 m, 548 w). Compound *(4)* is diamagnetic and has a UV spectrum such as is to be expected from a *cis* octahedral Co(III) complex (point group C_s)[8] [λ_{max} 28550 cm^{-1} (w–m, broad), 16750 cm^{-1} (m, broad)]. The intensity ratios of the νCoC_2 vibrations are also in accord with the assumptions.

When heated, compound *(4)* melts at 204 °C with decomposition, C_2H_6 and C_2H_4 being formed. IR spectroscopic examination of the pyrolysis residue suggests that a cobalt hydride complex is formed simultaneously.

In contrast to the hydride complexes H_3CoL_3 [L = $P(C_6H_5)_3$, $P(C_6H_5)_2C_2H_5$][9] and $H_2Co[P(C_6H_5)_3]_3$[10], compound *(4)* does not exchange its hydrogen for nitrogen. When the benzene solution of *(4)* is heated with an excess of CH_3I for one hour at 70 °C, methane, ethylene, and ethane are evolved (determined gas-chromatographically) and the pale brown cobalt(I)-phosphonium iodide complex *(5)* separates. Its



(4) + 2 CH_3I → *(5)* + CH_4 + C_2H_4 + C_2H_6

R = C_6H_5

composition and structure are proved by elemental analysis, magnetism (at 20 °C, μ = 2.5 B.M., corresponding to two unpaired electrons), conductivity in DMF (v = 1120 liter $mole^{-1}$, μ = 72 ohm^{-1} cm^2 $mole^{-1}$), and IR spectrum [$\nu\overset{\oplus}{P}-CH_3$ 660 w–m; $\nu_1\overset{\oplus}{P}-C_6H_5$ 1109 m–s; no absorption due to $HCo(C_2H_5)_2$ group]. The formation of methane is explained by reaction between hydride hydrogen and methyl carbonium ions. The simultaneous appearance of C_2H_4 and C_2H_6 is due to dismutation of the two ethyl groups[2]. Since *n*-butane is not seen to be formed, a radical mechanism is excluded.

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[1] Part 12 of Spiroheterocyclic and Biheterocyclic Compounds (Continuation of the series Spiroheterocyclic Compounds). – Part 11: *J. Ellermann* and *D. Schirmacher*, Z. anorg. allg. Chem., in press.

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[3] *J. Ellermann* and *D. Schirmacher*, Chem. Ber. *100*, 2220 (1967) and literature cited there.

[4] *J. Ellermann* and *K. Dorn*, Chem. Ber. *99*, 653 (1966).

[5] *G. Wilke*, Angew. Chem. *72*, 581 (1960); German Pat. 1191375, Studiengesellschaft Kohle; *G. Wilke* and *G. Herrmann*, Angew. Chem. *78*, 591 (1966); Angew. Chem. internat. Edit. *5*, 581 (1966).

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[6a] *A. Yamamoto*, *S. Kitazume*, *L. S. Pu*, and *S. Ikeda*, Chem. Commun. *1967*, 79.

[7] Cf. *G. E. Coates* and *D. Ridley*, J. chem. Soc. (London) *1965*, 1870; *F. Oswald*, Z. analyt. Chem. *197*, 309 (1963).

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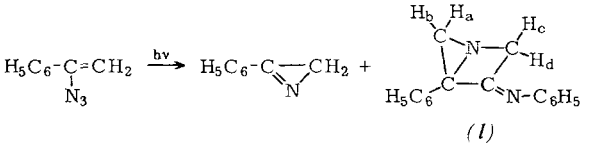
Formation of an Azabicyclopentane Derivative on Photolysis of α-Azidostyrene

By *F. P. Woerner*, *H. Reimlinger*, and *D. R. Arnold*[*]

Pyrolysis[1] and photolysis[2] of vinyl azide derivatives lead to azirine derivatives. In some cases ketene imines are formed as by-products.

After irradiating an approximately 6 % solution of α-azidostyrene in anhydrous benzene with filtered light from a mercury high-pressure lamp[3], we isolated 2-phenylazirine as main product (yield > 85 %) and a 10 % yield of 4-phenyl-3-phenylimino-1-azabicyclo[2.1.0]pentane *(1)* which is a derivative of a new heterobicyclic system.



(1)

A solution of α-azidostyrene (2.5 g) in anhydrous benzene (45 ml) was irradiated through a 2-mm thick Pyrex filter until gas evolution ceased (*ca.* 5 h), then the solvent was distilled off in a vacuum. The residue was cooled until crystals were formed. These were washed with cyclohexane [yield, 0.2 g of analytically pure *(1)*, m.p. 137–140 °C].

Elemental analysis and spectral results (NMR, mass spectrum, IR, and UV) indicate structure *(1)*. In the NMR spectrum[4] one sees two singlets with half-band width *ca.* 2 Hz at τ = 7.2 (H_a; relative intensity 1) and at τ = 8.38 (H_b; relative intensity 1). This accords with the coupling constant of the geminal protons of phenylaziridine[5]. The signals for the AB system H_c–H_d are at τ = 4.9 and 5.2 (relative intensity 2)

with a coupling constant of 16 Hz. The signal of the phenyl protons *ortho* to the imino nitrogen atom is a multiplet centered at τ = 2.4 (relative intensity 2); and that of the remaining aromatic protons is a multiplet centered at τ = 2.8 (relative intensity 8). Analogous substances[6] provide an indication of the shift of signals of the CH_2 protons on the four-membered ring to lower field owing to the neighboring nitrogen atom. Further, we also derive structure *(1)* from the mass spectrum, specifically from the appearance of the ion M−42 and of a fragment at *m/e* 42 ($H_2C{=}N{-}CH_2$). The compound is found to have molecular weight 234. The UV spectrum (in alcohol) includes an absorption band at 244 nm (ε = 12200). In the IR spectrum (KBr) the C=N absorption is at 6.2 μm and, remarkably, three absorption bands occur between 9.98 μm and 10.16 μm.

It is tempting to ascribe the formation of *(1)* to addition of ketene phenyl imine to phenylazirine. According to *Smolinsky*[1], phenylazirine and ketene phenylimine coexist after pyrolysis of α-azidostyrene. The characteristic ketene imine absorption[1] at 5 μm in the IR spectrum of our reaction mixture after photolysis can be explained by presence of a small amount of ketene phenyl imine. However, no trace of *(1)* is to be found in the gas chromatogram after pyrolysis of α-azidostyrene at 350 °C. Nor is any trace of *(1)* to be found in the mixture obtained on addition of azidostyrene to boiling phenylazirine (*ca.* 180 °C). From our results, together with the observation that *(1)* is also formed on photolysis of phenylazirine, we conclude that it is formed by photochemical and not by thermal activation. This is thus the first case of intermolecular photocycloaddition to a carbon-nitrogen double bond.

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[1] *G. Smolinsky*, J. org. Chemistry *27*, 3557 (1962).

[2] *L. Horner, A. Christmann*, and *A. Gross*, Chem. Ber. *96*, 399 (1963); *G. R. Harvey* and *K. W. Ratts*, J. org. Chemistry *31*, 3907 (1966); *A. Hassner* and *F. W. Fowler*, Tetrahedron Letters *1967*, 1545.

[3] Mercury high-pressure lamp: Philips HPK 125 W.

[4] The NMR spectra were measured with a Varian A-60 apparatus for CCl_4 solutions with tetramethylsilane as internal standard.

[5] *S. J. Brois*, J. org. Chemistry *27*, 3532 (1962).

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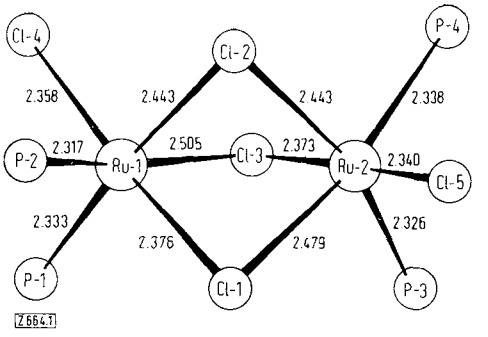
X-Ray Structure Analysis of Tri-μ-chlorobis[bis(tri-*n*-butylphosphine)-ruthenium Chloride]

By *G. Chioccola, J. J. Daly*, and *J. K. Nicholson*[*]

The synthesis of $Ru_2Cl_5[P(n\text{-}C_4H_9)_3]_4$ has been described recently and the results of chemical investigations suggest[1] the structure *(1)*. The complex has a magnetic moment of 0.75 B.M. per ruthenium atom[2] corresponding to one unpaired electron in the molecule.

The dark red crystals are monoclinic, space group $P2_1/c$ with a = 13.866, b = 16.003, c = 30.545 Å, β = 110.0°. There are four molecules in the unit cell and the observed density gives a molecular weight of 1170.7 (theoretical 1188.8). The intensities were measured on a linear diffractometer[3] and the structure was determined by Patterson and Fourier methods. A least squares refinement of 3776 planes gives a current *R*-factor of 0.083. The standard deviations of the Ru–Cl and Ru–P bond lengths are 0.0052 and 0.0054 Å respectively.



(1)

The X-ray analysis confirms the structure *(1)* and the Ru–Cl and Ru–P distances are shown in the figure. The coordination round the ruthenium atoms is approximately octahedral (the largest angular distortion is 12.4°) and the environments of these atoms are very similar. The Ru···Ru distance is 3.115 Å, and is thus much longer than that found in the metal (2.650 Å)[4]. The Ru–Cl distances fall into two groups: those *trans* to other Ru–Cl bonds are considerably shorter (2.340–2.376 Å) than those (2.444–2.505 Å) *trans* to Ru–P bonds.

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[1] *J. K. Nicholson*, Angew. Chem. *79*, 273 (1967); Angew. Chem. internat. Edit. *6*, 264 (1967).

[2] Determined by Drs. *G.* and *S. Olivé*, Zürich.

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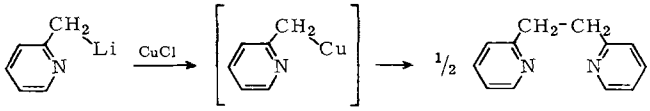
[4] *A. Hellawell* and *W. Hume-Rothery*, Philos. Mag. *45*, 797 (1954).

Dimerization of Azaallyl, Diazaallyl, and Oxaazaallyl Groups by Way of Copper-containing Intermediates[1]

By *Th. Kauffmann, G. Beissner, E. Köppelmann, D. Kuhlmann, A. Schott*, and *H. Schrecken*[*]

We are studying systematically the dimerization of organic compounds by way of organo copper derivatives, a reaction whose unusually wide applicability[2] is not yet fully recognized[3,4].

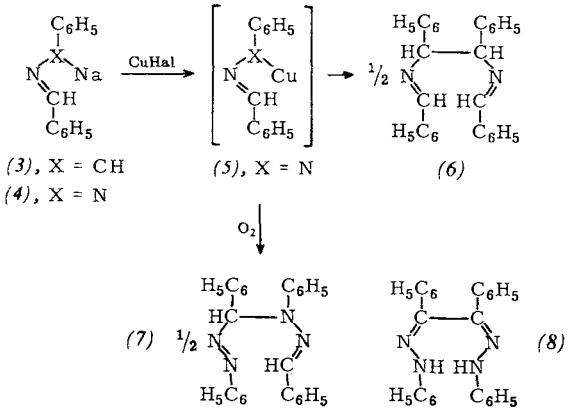
We observed dimerization of the 3-azaallyl group contained in *(1)* when treating the compound[5] with 1 molar equivalent of CuCl or $CuBr_2$ in tetrahydrofuran/ether (1:1) under nitrogen at 60 °C. The product *(2)* was formed in, respectively 72 and 78 % yield with separation of Cu or CuBr[6].



(1) *(2)*

When CuI in dimethoxyethane at 85 °C is treated with 1 molar equivalent of the deep red compound *(3)* (formed by the action of $NaNH_2$ on *N*-benzylidenebenzylamine), the 2-azaallyl group of *(3)* dimerizes analogously, yielding compound *(6)* (58 % yield) specifically in the *meso*-form (m.p. 163 °C; lit.[7], 164 °C).

The 1,2-diazaallyl group in *(4)* is also coupled by successive action of 1 molar equivalent of CuCl and oxygen in dimethoxyethane at 60 °C, to give a known[8] product of m.p.

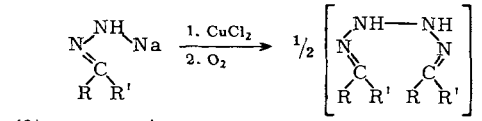


(3), X = CH
(4), X = N
(5), X = N
(6)

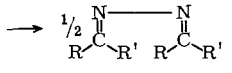
(7)
(8)

191 °C (yield 59 %), to which structure *(7)* applies[9]. Compound *(8)*, which is obtained on oxidation of benzaldehyde phenylhydrazone by iodine[10], is not formed. The Cu(I) compound *(5)* arising as intermediate is thermally stable but very sensitive to oxygen; it was isolated[11] as a colorless crystalline substance and converted into *(7)* by way of a thermally labile green Cu(II) compound.

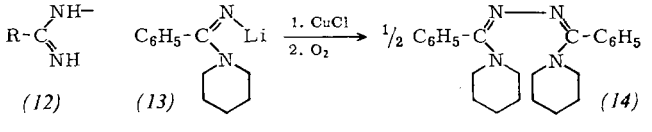
Treating compounds *(9)* and *(10)* analogously with $CuCl_2/O_2$ led to *ca.* 40 % yields of the corresponding azines. The compounds *(11)*, or the derived copper compounds, that are to be assumed as primary dimerization products apparently undergo secondary changes.



(9), R = H; R' = C_6H_5
(10), R = R' = CH_3
(11)

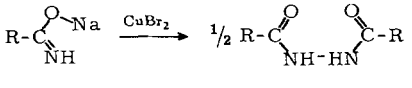


Here circumstances are thus similar to those in the case of the dimerization of 1,3-diazaallyl groups of the type *(12)* by means of $CuCl/O_2$, where substituted *s*-triazoles result from secondary reactions[3,12]. In this connection it is of interest that successive action of one molar equivalent each of CuCl and oxygen on *(13)* in dimethoxyethane at 65–75 °C affords a product *(14)* in 75 % yield.



(12)
(13)
(14)

The 1,3-oxaazaallyl group of *(15)* was not dimerized, to yield *(17)*, when *(15)* was treated with CuCl or $CuCl/O_2$ in tetrahydrofuran. However, *(17)* was obtained when *(15)* was treated with one molar equivalent of $CuBr_2$ in tetrahydrofuran, though the yield was only 26 % calculated on the benzamide taken (43 % calculated on the benzamide consumed). Addition of oxygen barely increased the yield. In the analogous dimerization of the 1,3-oxaazaallyl groups of *(16)* with $CuBr_2$, product *(18)* was formed in 30 % yield



(15), R = C_6H_5
(16), R = $(CH_2)_4$-CH_3
(17), R = C_6H_5
(18), R = $(CH_2)_4$-CH_3

calculated on the hexanamide taken (49 % calculated on the hexanamide consumed).

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[1] Part 3 of Activation of Organic Compounds by Introduction of Transition-metal Atoms. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der chemischen Industrie. – Reference [3] is considered to be Part 2 of this Series; the less comprehensive series title given there is abandoned.

[2] According to isolated observations [*H. Gilman* and *H. H. Parker*, J. Amer. chem. Soc. *46*, 2823 (1924); *K. Issleib* and *H.-O. Fröhlich*, Chem. Ber. *95*, 375 (1962)] S–S and P–S linkages by way of copper compounds are also possible.

[3] *Th. Kauffmann, J. Albrecht, D. Berger*, and *J. Legler*, Angew. Chem. 79, 620 (1967); Angew. Chem. internat. Edit. *6*, 633 (1967).

[4] *Th. Kauffmann* and *W. Sahm*, Angew. Chem. *79*, 101 (1967); Angew. Chem. internat. Edit. *6*, 85 (1967).

[5] *P. C. Campbell* and *P. C. Teague*, J. Amer. chem. Soc. *76*, 1371 (1954).

[6] Solvents used in all the reactions were anhydrous; before being further worked up, the batches were hydrolyzed by water. Unless otherwise stated, yields (which in some cases may perhaps be increased) refer to the amount of organic compound used. – In formulation of the metal compounds no attempt has been made here to represent the bonding between metal and organic group realistically.

[7] *H. Grossmann*, Ber. dtsch. chem. Ges. *22*, 2298 (1899); cf. also *W. Stürmer* and *G. Messwarb*, Arch. Pharmaz. *286*, 221 (1953).

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[9] We were unable to obtain a usable NMR spectrum owing to the insolubility and ease of decomposition of this substance. The IR spectrum is in agreement with structure *(7)*.

[10] *E. Bamberger* and *J. Grob*, Ber. dtsch. chem. Ges. *34*, 523 (1901).

[11] The molecular weight was not determined.

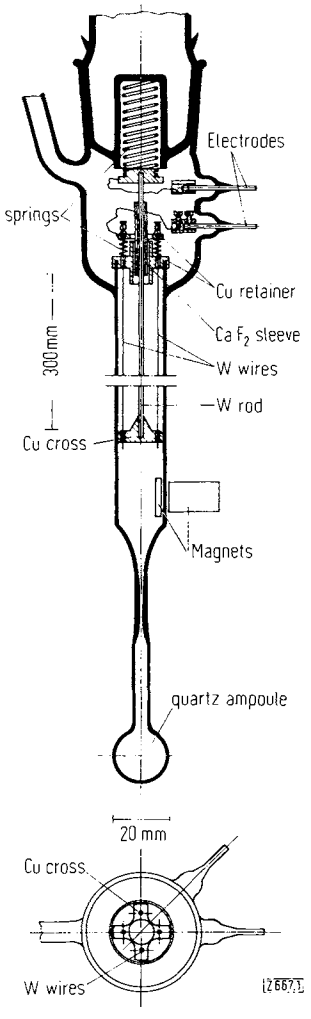
[12] *J. Albrecht*, Diplomarbeit, University of Münster (Germany) 1967.

Preparation of Tungsten Pentafluoride

By *J. Schröder* and *F. J. Grewe*[*]

Not only tungsten hexafluoride but also lower tungsten fluorides play an appreciable part in the chemical transport reactions by means of which fluorine leads to homogenization of tungsten filaments in incandescent lamps[1]. The fluorides dissociate to tungsten and fluorine on tungsten filaments whose temperatures exceed 2000 °C, and tungsten is transported from the colder to the hotter zones of the glowing body until the temperature of the hot filament is completely homogeneous. At lower temperatures, lower fluorides of tungsten are formed and these disproportionate in the gas space or on the walls of the vessel into tungsten metal and its hexafluoride. However, if the wall of the vessel is cooled, the lower fluorides can be trapped out of the gas space and can be thus isolated.

For the synthesis of tungsten pentafluoride the carefully baked out quartz apparatus (Fig.) was filled with 500 torr of WF_6 and plunged into a cooling bath at −50 to −60 °C. The WF_6 condensed in the quartz ampoule and a WF_6 vapor pressure of *ca.* 10 torr was set up in the gas space. The four tungsten wires were heated to 500 to 700 °C; WF_5 then separated on the cold quartz wall as a yellow crystalline substance; after the excess of WF_6 had been pumped off, the



pentafluoride was transferred to the ampoule by manipulation of the magnetic rod.

WF_5 can be kept undecomposed in a closed quartz vessel. At room temperature the vapor pressure amounts to *ca.* 1 torr and the substance can be sublimed from 20 to −30 °C without decomposition.

WF_5 is exceedingly hygroscopic and decomposes at once in the air. It reacts with dilute NaOH + H_2O_2 to give a clear solution of tungstate and fluoride. Analyses for fluorine and tungsten give a ratio F:W = 5:1. Determination of the oxidation number gives W^{5+} required for WF_5. Analyses of the sublimed material give the same result. At 50 to 70 °C, WF_5 disproportionates to WF_6 and a dark grey solid that also reacts with dilute NaOH + H_2O_2 to give tungstate and fluoride. Analysis of the decomposition product gives a F:W ratio of 4:1 and oxidation state W^{4+}.

The equation

$$2\ WF_5 \rightarrow WF_6 + WF_4$$

is derived from the amounts of WF_5 used, of WF_6 produced, and of the dark grey decomposition residue.

The dark grey decomposition product has the empirical formula WF_4 and is amorphous to X-rays, whereas WF_5 gives sharp X-ray diagrams with the following *d* values: 7.879 (w); 7.120 (vw); 5.205 (m^+); 4.493 (w^+); 4.218 (s^+); 3.958 (s); 3.683 (w); 3.567 (m); 3.355 (s); 3.271 (w^+); 3.112 (vw); 3.059 (s^+); 2.941 (vw); 2.867 (w); 2.772 (s); 2.731 (s); 2.652 (vw); 2.581 (vw); 2.532 (vw); 2.447 (s); 2.401 (m); 2.374 (m); 2.302 (s); 2.216 (s); 2.195 (vw); 2.130 (m); 2.009 (s^+); 1.992 (m); 1.975 (m); 1.926 (w); 1.911 (w); 1.871 (s); 1.802 (vw); 1.777 (m); 1.738 (vw); 1.723 (m^+); 1.690 (m); 1.673 (m); 1.652 (w); 1.637 (vw); 1.611 (w); 1.591 (w); 1.558 (w); 1.495 (s); 1.483 (w); 1.471 (w); 1.463 (vw); 1.428 (s^-); 1.414 (m^+); 1.397 (m^+); 1.383 (m^+); 1.368 (m^+).

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[1] *J. Schröder*, Philips techn. Rdsch. *25*, 359 (1963/64); *J. Schröder*, Chem. Engng. News *42*, 77 (1964); *A. Rabenau*, Angew. Chem. *79*, 43 (1967); Angew. Chem. internat. Edit. *6*, 68 (1967).

Preparation and Structure of Methylpotassium

By *E. Weiss* and *G. Sauermann*[*]

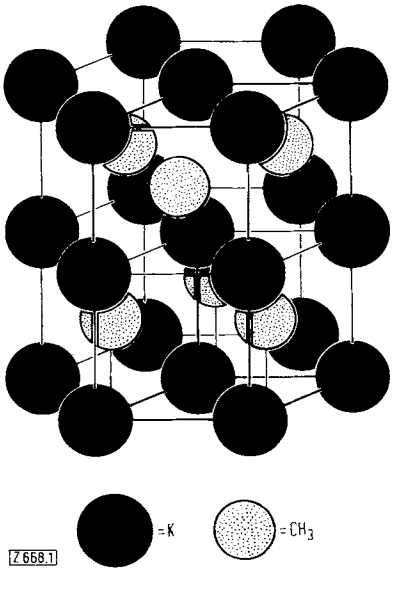
Continuing our studies of alkyl derivatives of the alkali metals[1] we have worked out new methods of preparing CH_3K and have determined its crystal structure. We obtained CH_3K (a) by reaction of dimethylmercury dissolved in pentane with a liquid K–Na alloy in excess and (b) by double decomposition of CH_3Li and K *tert*-butoxide dissolved in ether at −10 °C.

$$\text{(a)}\ (CH_3)_2Hg + K/Na \rightarrow CH_3K + Na/K/Hg$$

$$\text{(b)}\ CH_3Li + (CH_3)_3COK \rightarrow CH_3K + (CH_3)_3COLi$$

Reaction of alkyllithiums with alkali-metal *tert*-butoxides in hexane or heptane has been used previously only for preparation of organylsodiums containing rather large alkyl groups and has given impure products when applied to organylpotassiums[2]. We found that the reaction can also be effected in ether and is then suitable for, *inter alia*, the preparation of methylpotassium. It is, however, necessary to work fast and with cooling in order to avoid ether cleavage by the very reactive CH_3K. Also the CH_3Li is used in slight excess since alkyllithiums have a stabilizing effect on ethereal solutions of higher alkyl-alkali metals[3]. The products therefore contain small amounts of Li, but they give X-ray diagrams identical with those of CH_3K prepared by method (a).

When dry, the preparations are highly pyrophoric, colorless, microcrystalline powders whose X-ray diagrams can be indexed on a hexagonal structure with lattice constants $a_0 = 4.27_8$ and $c_0 = 8.28_8$ Å. The structure is of the NiAs type (space group $P6_3/mmc$) with two formula weights in the unit cell and an X-ray density of 1.37 g cm^{-3}.



Whereas CH_3Li[4], and very probably also CH_3Na[5], form tetrameric structural units with an inner metal tetrahedron surrounded by four methyl groups, CH_3K provides the first case with isolated methyl groups in the lattice, these groups being each surrounded by six nearest K atoms in trigonal-prismatic arrangement. Isolated ethyl groups occur in ethyl-sodium which forms a layer structure[5].

Since the H atoms have only feeble scattering power their location is difficult. Two ν-C–H frequencies (at 2805 and 2740 cm^{-1}) in the IR spectrum of CH_3K (KBr disks) indicate the possibility of a trigonal-pyramidal structure of the methyl groups which may then be built as methyl anions into a cation lattice.

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Preparation of *N*-Aminoaziridines and Rearrangements to Hexulose Hydrazones[1]

By *H. Paulsen* and *D. Stoye*[*]

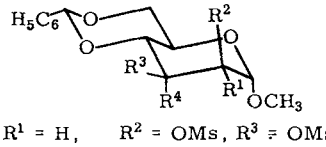
Reaction of terminal-vicinal di-*O*-mesyl groups such as are present in 3-*O*-benzyl-1,2-*O*-isopropylidene-5,6-di-*O*-mesyl-D-glucofuranose *(1)* with hot anhydrous hydrazine (4 h at 70 °C) gives the *N*-aminoaziridine *(3)*, which can be obtained as a syrup ($[\alpha]_D^{20} = -78.3°$; $c = 1.4$ in $CHCl_3$) in 80 % yield by extraction of by-products into ether and shaking of the residual solution with chloroform. The product *(3)* forms crystalline hydrazones with carbonyl compounds in the presence of a trace of acid; *e.g.* with benzaldehyde the hydrazone *(4)* [m.p. 70–73 °C, $[\alpha]_D^{20} = -103.7°$, $c = 1.0$ in $CHCl_3$; NMR of *(4)*: $\tau = 7.5$ (H-5), $\tau = 7.89$ (H-6), $\tau = 8.00$ (H-6'), $J_{5,6} = 7.5$, $J_{5,6'} = 5.0$. $J_{6,6'} = 1.0$ Hz] is formed. In *(3)* two protons are exchangeable, but in *(4)* none.

Reaction of *(3)* occurs by nucleophilic substitution on C-6 of *(1)*, leading to the 6-deoxy-6-hydrazino-5-*O*-mesylate *(2)*, which reacts further by a neighboring group reaction to give the *N*-aminoaziridine *(3)*. Grob fragmentation[2] of *(2)* occurs as a competing reaction to the extent of 16 % and affords the unsaturated sugar *(5)*[3] as olefinic fragment. Fragmentation is the main reaction of α-*O*-mesylhexurono-hydrazides and leads to sugar ketenes[4].

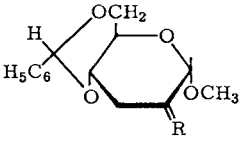
Hydrogenation of *(3)* with Raney nickel and hydrazine in ethanol at 50 °C affords a 5-amino-5,6-dideoxy-sugar *(6)* with the L-*ido*-configuration by selective ring opening at C-6. After removal of the solvent by distillation and purification by column chromatography (silica gel; benzene/ethanol = 9:1), the product *(6)* is obtained in 65 % yield as a syrup ($[\alpha]_D^{20} = -38.9°$; $c = 1.5$ in $CHCl_3$). The route *via* the *N*-amino-aziridines is thus a simple method for synthesis of 5-amino-5,6-dideoxy-sugars. If the D-*allo*-[5] or D-*gulo*-compound[6] corresponding to *(1)* is treated with hydrazine, one obtains *via* a L-*talo*- or L-*manno*-*N*-aminoaziridine the 5-amino-5,6-dideoxy-sugars corresponding to *(6)* but with, respectively, the L-*talo*-configuration (54 % yield; syrup; $[\alpha]_D^{20} = +108.3°$, $c = 1.2$ in $CHCl_3$; crystalline *N*-acetyl derivative, m.p. 106–107 °C, $[\alpha]_D^{20} = +80.3°$, $c = 0.9$ in $CHCl_3$) or the L-*manno*-configuration (syrup; $[\alpha]_D^{20} = +57.9°$, $c = 1.0$ in $CHCl_3$; crystalline *N*-acetyl derivative, m.p. 77–81 °C, $[\alpha]_D^{20} = +42.2°$, $c = 0.6$ in $CHCl_3$).

Whe *(3)* is warmed in pyridine/acetic anhydride (100 °C, 48 h) a new type of rearrangement occurs, yielding the 6-deoxy-5-ulose acetylhydrazone *(7)* (61.5 % yield, m.p. 114–118 °C, $[\alpha]_D^{20} = -72.5°$, $c = 1.1$ in $CHCl_3$). The ring opening is again selective, with migration of hydrogen from C-5 to C-6. This reaction affords a simple route to 6-deoxy-5-ulose derivatives.

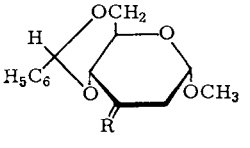
Vicinal di-*O*-mesyl groups attached to a ring (*e.g.* to the six-membered ring) behave differently in the reaction with hydrazine and do not give bicyclic *N*-aminoaziridines. All the possibilities of reaction were investigated with the methyl 4,6-*O*-benzylidene-2,3-di-*O*-mesyl-D-hexopyranosides *(8)*–*(11)*.



manno *(8)*, R^1 = H, R^2 = OMs, R^3 = OMs, R^4 = H
allo *(9)*, R^1 = OMs, R^2 = H, R^3 = H, R^4 = OMs
gluco *(10)*, R^1 = OMs, R^2 = H, R^3 = OMs, R^4 = H
altro *(11)*, R^1 = H, R^2 = OMs, R^3 = H, R^4 = OMs

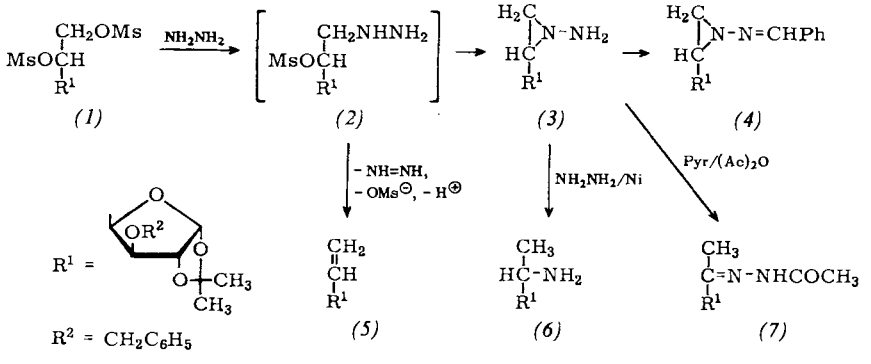


(12), R = H_3CCONH-N=
(13), R = O=



(14), R = H_3CCONH-N=
(15), R = O=

A primary *trans*-elimination is the main reaction when compounds with a hydrogen atom and an *O*-mesyl group in *trans*-diaxial relation are heated with hydrazine, even at 70 °C (4 h). In the case of the *manno*-compound *(8)*, elimination of the axial *O*-mesyl group from C-2 leads to the 2,3-enol 3-mesylate; cleavage and rearrangement thereof gives a



3-keto compound which reacts with hydrazine to give the hydrazone, which was isolated as acetate *(14)* (85 % yield; m.p. 132–135 °C, $[\alpha]_D^{20} = +135°$, $c = 0.7$ in $CHCl_3$). The *allo*-compound *(9)* eliminates the axial *O*-mesyl group from C-3, giving the 2,3-enol 2-mesylate, whose further analogous reaction and acetylation affords a 3-deoxy-2-ulose acetylhydrazone *(12)* (55 % yield; m.p. 212–214 °C, $[\alpha]_D^{20} = -23.8°$, $c = 0.9$ in $CHCl_3$).

The *gluco*- and *altro*-compounds *(10)* and *(11)* cannot undergo *trans*-elimination. Thus, in these cases, nucleophilic substitution again becomes the reaction with hydrazine (at 140 °C, 5 h). The α-hydrazino-*O*-mesylates formed with inversion as primary products contain *trans*-hydrogen atoms and *O*-mesylate groups, so that elimination follows as a secondary reaction, leading to alkenylhydrazines which can be isolated, after acetylation, as rearranged deoxy-ulose acetylhydrazones. Reaction of *(10)* and *(11)* in this way yields a mixture of *(12)* and *(14)*, wherein *(12)* preponderates since nucleophilic attack on C-2 is apparently easier than on C-3. Transhydrazonization of *(12)* and *(14)* with benzaldehyde in weakly acidified dioxane solution makes accessible the 3-deoxy-2-ulose derivative *(13)* (53.7 % yield, m.p. 112–113 °C, $[\alpha]_D^{20} = +93.8°$, $c = 1.2$ in $CHCl_3$), and the 2-deoxy-3-ulose derivative *(15)* (75 % yield, m.p. 172 to 173 °C, $[\alpha]_D^{20} = +129°$, $c = 1.2$ in $CHCl_3$ [7]).

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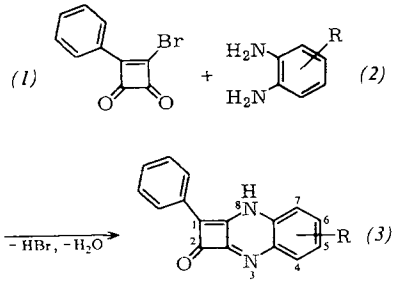
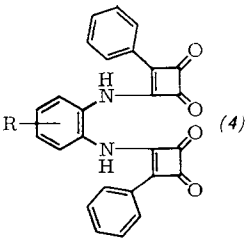
Synthesis of Cyclobuta[*b*]quinoxalines [**]

By *W. Ried* and *W. Kunstmann* [*]

1-Phenylcyclobuta[*b*]quinoxalin-2(8*H*)-ones *(3)* are formed on reaction of 1-bromo-2-phenyl-1-cyclobutene-3,4-dione *(1)* [1] with *o*-phenylenediamines *(2)*.



In no case are isomers obtained. The position of the substituents is determined by the fact that the most basic amino group in *(2)* attacks the other reactant *(1)* at position 1. Thus with symmetrical *o*-diamines (*o*-phenylenediamine, 2,3-naphthylenediamine) a by-product *(4)* is found which, on the basis of its composition, must arise from *(1)* and *(2)* in the ratio 2:1 (yield < 5 %).



R	*(4)*, m.p. (°C)	Properties	νC=O	(cm⁻¹)
H	235 (CH_3OH)	Pale red platelets	1770	1730
4,5-Benzo	259 (CH_3CN)	Pale red needles	1770	1730

No unsymmetrical *o*-diamine affords an analogous by-product.

Indications in favor of the structure of the new compounds will be adduced for the case of 1-phenylcyclobuta[*b*]quinoxalin-2(8*H*)-one *(3)*, R = H: Elemental analyses are in exact agreement with theory. A molecular weight of 246 (theor., 246.3) is found from the mass spectrum. Study of the NMR spectrum is not yet concluded; the spectrum shows only aromatic protons. It is not yet clear whether failure to find the N–H proton is due to technical causes (*e.g.* low solubility) or intermolecular association. The IR spectrum favors the latter explanation; it contains a very broad band around 3000 cm^{-1} for which the NH group is responsible. As expected, this band is not present in the spectrum of the 8-CH_3 derivative. At 1760 cm^{-1} there is a very strong carbonyl band, which is typical of comparable cyclobutenones [1,2]. The characteristic bands at 1670 cm^{-1} and 1610 cm^{-1} can be ascribed to stretching vibrations of the C=N and C=C double bond, respectively, of the four-membered ring.

The structure of the by-products *(4)* was proved by comparison with the 1-anilino-2-phenyl-1-cyclobutene-3,4-diones that are formed from *(1)* and aromatic mono- and *p*-diamines under the same conditions.

Experimental: Synthesis of compounds (3)

2.4 g (0.01 mole) of *(1)* is dissolved in 50 ml each of tetrahydrofuran and glacial acetic acid. 0.01 mole of *(2)* dissolved in 20 ml each of tetrahydrofuran and glacial acetic acid is added in one portion with stirring at room temperature.

R	*(3)*, m.p. (°C) [a]	Properties	νC=O (cm^{-1})	νC=N (cm^{-1})
H	246 (CH_3OH)	Yellow needles	1760	1670
5-CH_3	250 (CH_3OH)	Yellow needles	1755	1670
6-NO_2	300 (DMF)	Red needles	1760	1670
6-COOH	255 (Butanone)	Yellow powder	1755	1670
6-$COOCH_3$	258 (DMF/CH_3OH)	Orange needles	1770	1670
5-Cl	258 (DMF/CH_3OH)	Yellow needles	1755	1670
5-OCH_3	240 (DMF/CH_3OH)	Orange-red needles	1760	1680
5-OC_2H_5	234 (DMF/CH_3OH)	Pale brown platelets	1755	1670
6-SO_3Na	>360 (H_2O/CH_3OH)	Yellow powder	1750	1670
5-CH_3, 6-Cl	270 (DMF/CH_3OH)	Yellow needles	1755	1660
4-Cl, 6-NO_2	268 (DMF)	Red-brown needles	1755	1665
5,6-Benzo	273 (DMF)	Yellow needles	1755	1680
8-CH_3	240 (CH_3OH)	Yellow needles	1765	1675

[a] Decomposition usually occurs at the melting point of these compounds.

(Diamine salts are introduced in as concentrated aqueous solution as possible with addition of the appropriate amount of sodium acetate.) The solution immediately becomes deep red or black; after a short time it becomes turbid; a yellow precipitate is formed. The mixture is stirred for some hours further, then the product is sucked off, washed with meth-

anol, and recrystallized as indicated in the Table. Yields: 20–30 %.

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[**] Read in part at the Symposium on Heterocyclic Compounds at Reinhardsbrunn on October 11, 1967.

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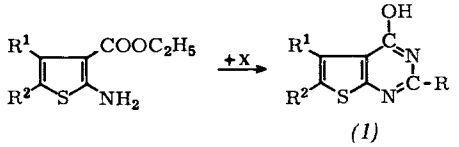
New 4-Hydroxythienopyrimidines

By *W. Ried* and *R. Giesse* [*]

Hitherto, little was known about 4-hydroxythienopyrimidines and they were accessible only by relatively complicated methods [1]. We have found that 4-hydroxythienopyrimidines can be obtained, some of them in good yield, from 2-amino-3-thiophenecarboxylic esters [2] and 3-amino-2-thiophenecarboxylic esters [3] by reaction with nitriles or their derivatives such as imidic esters, amidines, amidoximes, and acid amides; the products mostly crystallize as colorless needles.

4-Hydroxythieno[2,3-*d*]pyrimidines *(1)* are obtained from 2-amino-3-thiophenecarboxylic esters.

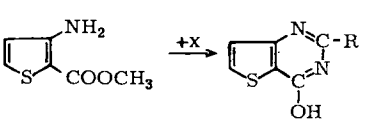


(1)

R	R^1	R^2	*(1)*, m.p. (°C)	*(1)*, yield (%)	X	Conditions
C_6H_5	H	C_2H_5	214	25	C_6H_5–C(NH)OC_2H_5	14 h/160 °C
Cl_3C	CH_3	CH_3	248	40	Cl_3C–C(NH)OCH_3	2 h/130 °C
Cl_3C	H	C_2H_5	220	50	Cl_3C–CN	8 h/50 °C
C_6H_5–CH_2	–$(CH_2)_4$–		260	30	C_6H_5–CH_2–CN	15 h/$AlCl_3$/b.p.
H	H	C_6H_5	260	95	H_2N–CHO	15 h/b.p.

4-Hydroxythieno[3,2-*d*]pyrimidines *(2)* are obtained from 3-amino-2-thiophenecarboxylic esters.

Decisive for occurrence of the reaction is sufficient basicity of the nitrogen in the aminothiophenecarboxylic ester in respect of the carbonium C atom of the nitrile or the nitrile derivatives. This condition is satisfied by use of the polar solvent pentyl alcohol and of anhydrous aluminum chloride or concentrated sulfuric acid as catalyst, or by reaction of the components without a solvent or catalyst at higher temperatures. Intermediates could not be isolated.



(2)

R	*(2)*, m.p. (°C)	*(2)*, yield (%)	X	Conditions
p-H_3C–C_6H_4	276	45	*p*-H_3C–C_6H_4–C(NH)OC_2H_5	15 h/160 °C
Cl_3C	234	90	Cl_3C–C(NH)OCH_3	12 h/165 °C
H	220	50	H_2N–CHO	12 h/b.p.

Preparation of 4-hydroxythieno[2,3-d]pyrimidines (1):

0.01 mole of 2-amino-3-thiophenecarboxylic ester and an equimolar amount or slight excess of imidic ester, nitrile, or formamide were allowed to react under the conditions stated. After the reaction had occurred, the mixture was cooled for some time (the product often crystallized from the hot mixture), added to a little ether, and filtered with suction. The product was washed with ether and then recrystallized, with addition of active charcoal, from alcohol or dioxane.

Preparation of 4-hydroxythieno[3,2-d]pyrimidines (2):

1.57 g (0.01 mole) of methyl 3-amino-2-thiophenecarboxylate and a slight excess of imidic ester or formamide were allowed to react under the stated conditions. Crystallization began even during the heating of the reaction mixture. The mixture was then cooled for a short time and the crystalline residue was filtered off. A second crop of crystals was obtained by heating the filtrate again for a couple of hours. The combined crystals were washed with ether and recrystallized from alcohol or dioxane with addition of active charcoal.

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PH_3 – A New Ligand in a Transition Metal Complex

By *E. O. Fischer, E. Louis,* and *R. J. J. Schneider* [*]

Previous experiments have shown that the binuclear complex compound $[V(CO)_4PH_2]_2$ containing two PH_2 bridges is the exclusive product when $V(CO)_6$ reacts with PH_3, hydrogen being evolved during the process [1]. We have now succeeded in incorporating PH_3 as a unidentate ligand photochemically into a metalcarbonyl compound, by exchange of CO for PH_3.

We obtained tricarbonylcyclopentadienylphosphinevanadium(I), π-$C_5H_5V(CO)_3PH_3$, by UV irradiation of a solution

of π-$C_5H_5V(CO)_4$ in tetrahydrofuran or benzene under a phosphine atmosphere for several hours at room temperature[**].

$$\underset{(1)}{\pi\text{-}C_5H_5V(CO)_4} + PH_3 \xrightarrow{h\nu} \underset{(2)}{\pi\text{-}C_5H_5V(CO)_3PH_3} + CO$$

In agreement with the low symmetry of *(2)* three sharp bands appear in the ν_{CO} region of the IR spectrum (*n*-hexane solution) at 1975 (s), 1901 (s), and 1876 (vs) cm^{-1}. The ^1H–NMR spectrum of *(2)* in C_6D_6 shows two doublets at τ = 5.72 (int. 5, C_5H_5) with $J_{P-V-C_5H_5}$ = 1.5 Hz and τ = 6.81 (int. 3, PH_3) with J_{P-H} = 324 Hz[5].

From the position of the ν_{CO} frequencies (Table 1) it follows that the d_π–d_π back-donation in the PH_3 complex must be stronger than in $P(Alkyl)_3$ or $P(Aryl)_3$ ligands. According to a recent classification of P-containing ligands of metal carbonyls according to their π-acceptor strengths[4], this would correspond approximately to that of a $PCl(Aryl)_2$ group.

Table 1. ν_{CO} bands (cm^{-1}) of $C_5H_5V(CO)_3PX_3$ complexes and of $C_5H_5V(CO)_4$ in hexane.

$C_5H_5V(CO)_3PH_3$	1975 (s)	1901 (s)	1876 (vs)
$C_5H_5V(CO)_3P(C_4H_9)_3$ [1]	1951	1874	1854
$C_5H_5V(CO)_3P(C_2H_5)_2C_6H_5$ [2]	1958	1880	1851
$C_5H_5V(CO)_3P(C_6H_5)_3$ [3]	1962	1884	1865
$C_5H_5V(CO)_4$	2031	1931	1901

The ^1H–NMR spectrum of free PH_3 in C_6D_6 shows a doublet at τ = 9.13 with a coupling constant J_{P-H} = 186.5 Hz[5]; liquid PH_3 shows J_{P-H} = 182.2 ± 0.3 Hz[6]. The considerable increase in J_{P-H} in the complex is in agreement with the decisive effect of the backdonation metal → phosphorus on linkage of PH_3 that follows from the ν_{CO} frequencies.

Preparation of (2):

All operations must be conducted with care under an inert gas. Even small amounts of oxygen yield explosive mixtures with PH_3, and these are self-inflammatory at low pressures.

One gram (4.38 mmoles) of tetracarbonylcyclopentadienylvanadium(I) *(1)* is dissolved in 30 ml of tetrahydrofuran or benzene contained in a 500 ml single-necked flask fitted with two taps. The first of these is connected *via* a three-way tap with a low-pressure and a high-pressure manometer; the second is connected with a 200 ml cold trap containing *ca.* 68 mmoles of PH_3 condensed by means of liquid N_2. While intense cooling is maintained (the reaction flask at −78 °C, the cold trap at −196 °C) the system is evacuated to water-pump vacuum and then closed. The cooling baths are then removed from the flask and trap. After complete evaporation of the PH_3 and consequent saturation of the solvent there remains a slight positive pressure (10–30 torr) in the apparatus. The solution is irradiated for 8 h with UV light from a high-pressure lamp (Q 81, Quarzlampen GmbH., Hanau). During irradiation the solution is shielded from the heat developed by the UV lamp and is subjected to vigorous magnetic stirring.

By the end of the reaction the solution has turned from orange-red to brownish-red. All the gas in the flask is removed by means of N_2, and the solution is filtered over filterwool on a G3 sinter and evaporated to dryness. The residue is purified by column chromatography (Al_2O_3 S neutral active, 5 % H_2O; Riedel) with hexane as eluant. Unchanged *(1)* (yellow zone) is followed by *(2)* as a red zone; the latter is collected separately, recovered by evaporation in a vacuum, and recrystallized from pentane. After being dried for 5 h in a high vacuum, *(2)* is obtained as red-brown platelets of m.p. 110 °C (decomp.) (yield *ca.* 45 %). The product *(2)* dissolves readily in benzene to give a red solution and moderately readily in hexane or pentane to give an orange-red solution. The solutions are decomposed by air within a few minutes.

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[**] Note added in proof: Meanwhile, by similar processes, we have obtained also a brown-red complex, $C_5H_5Mn(CO)_2PH_3$, with m.p. 72 °C [$\tau_{C_5H_5}$ = 6.30 (int. 5), τ_{PH_3} = 6.76 (int. 3), C_6D_6, $J_{P-Mn-C_5H_5}$ = 2.8 Hz, J_{P-H} = 327 Hz], a pale yellow complex, $Cr(CO)_5PH_3$, with m.p. 116 °C [τ_{PH_3} = 7.55, C_6D_6, J_{P-H} = 337.5 Hz], a light yellow complex, $Fe(CO)_4PH_3$, with m.p. 36 °C [τ_{PH_3} = 7.85 (ext. TMS), C_6D_6, J_{P-H} = 365 Hz], a colorless complex, $Mo(CO)_5PH_3$ [***], with m.p. 112 °C (decomp.) [τ_{PH_3} = 7.69, C_6D_6, J_{P-H} = 327 Hz], and a colorless, complex, $W(CO)_5PH_3$ [***], with m.p. 120 °C [τ_{PH_3} = 7.49, C_6D_6, J_{P-H} = 341 Hz].

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Deprotonation of Glycine Amide in a Ternary Copper(II)-Complex[1]

By *H. Sigel*[*]

In Cu^{2+} peptides, and presumably also in Cu^{2+} proteins, the deprotonated amide group plays an important part in binding metal ions[2a]. Deprotonation of the amide group in binary Cu^{2+} peptides and peptide-like complexes has been studied repeatedly (cf., *e.g.*[2]). We have investigated deprotonation of such a group in a ternary Cu^{2+} complex that resembles an enzyme/metal-ion/substrate complex. As ligands we chose 2,2′-bipyridyl (Bipy) and glycine amide (HL).

Three protons are liberated on titration[3] of a 1:1 solution of Cu^{2+} and glycine amide hydrochloride. The first of these is derived from the ammonium group of the protonated glycine amide, the second from the amide group, and the third from a hydrate water molecule[4]. On titration of a solution that contains the Cu^{2+}-2,2′-bipyridyl 1:1 complex (this complex is formed to the extent of more than 94 % under the titration conditions) in place of hydrated Cu^{2+} only two protons are liberated, the second being again derived by deprotonation of the amide group. Liberation of a further proton does not take place because there is no hydrate water molecule within the smaller coordination sphere of a Cu^{2+} bound in this way.

The difference in stabilities

$$\log K^{CuBipy}_{CuBipyHL} - \log K^{Cu}_{CuHL} = -0.4$$

between the ternary and the binary Cu^{2+} complex is of the order to be expected[1,5] for addition of an O–N ligand to Cu^{2+}-Bipy (the amide group coordinates first through the oxygen[2a]). The acidity of the proton of the amide group in the ternary Cu^{2+} complex is, it is true, smaller by 0.7 pK unit than that of the binary complex, which has $pK^{H}_{CuBipyHL}$ = 7.71 ± 0.06, but it is nevertheless very high. The lower acidity depends mainly on the somewhat lower stability of the ternary complex (cf. also[1]).

The important result of our investigation is thus that Cu^{2+} bound to one ligand but containing two further hydrated coordination positions can coordinate with a further ligand containing an amide group and that this group can still be deprotonated in the physiological pH range. Accordingly there is the possibility that an enzyme is at least partly coordinated by way of deprotonated proteinamide groups even in enzyme/Cu^{2+}/substrate complexes.

Stability and acidity constants of the ternary Cu^{2+}—2,2'-bipyridylglycine amide complex and of the binary Cu^{2+}-glycine amide system ($I = 0.1$; $NaClO_4$; $t = 25\,°C$) [a,b].

$Cu^{2+} + HL \rightleftharpoons CuHL$	$\log K^{Cu}_{CuHL} = 5.40 \pm 0.04$[c]
$(Cu\text{-}Bipy)^{2+} + HL \rightleftharpoons Cu\text{-}Bipy\text{-}HL$	$\log K^{Cu}_{CuBipyHL} = 5.01 \pm 0.02$
$Cu\text{-}HL \rightleftharpoons Cu\text{-}L + H^+$	$pK^{H}_{CuHL} = 7.01 \pm 0.04$
$Cu\text{-}Bipy\text{-}HL \rightleftharpoons Cu\text{-}Bipy\text{-}L + H^+$	$pK^{H}_{CuBipyHL} = 7.71 \pm 0.06$
$CuL(H_2O)_x \rightleftharpoons CuL(OH)(H_2O)_{x-1} + H^+$	$pK^{H}_{CuL(H_2O)_x} = 8.07 \pm 0.06$
$Cu^{2+} + Bipy + HL \rightleftharpoons Cu\text{-}Bipy\text{-}HL$	$\log \beta = 13.0$ [d]
$Cu(Bipy)_2 + Cu(HL)_2 \rightleftharpoons 2\,Cu\text{-}Bipy\text{-}HL$	$\log X = 2.8$ [d,e]

[a] The acidity constant of glycine amide (HL) is $pK^{H}_{H_2L} = 8.04 \pm 0.02$.

[b] The figures reported are averages from several titrations [3], evaluated as described in [1].

[c] We calculated $\log K^{Cu}_{CuHL} = 5.36$ from Cu^{2+} excess-titrations (Cu^{2+}: $GlyNH_2 = 10:1$) as described in [5].

[d] Calculated according to [5] using the values from [6].

[e] Value to be expected statistically: 0.6; cf. [5].

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[1] Part V of Ternary Complexes in Solution. – Part IV: *H. Sigel* and *B. Prijs*, Helv. chim. Acta *50*, 2357 (1967). – This work was supported by Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung.

[2] [a] *J. Peisach, P. Aisen*, and *W. E. Blumberg*: The Biochemistry of Copper. Academic Press, New York, London 1966; [b] *A. Zuberbühler* and *S. Fallab*, Helv. chim. Acta *50*, 889 (1967).

[3] Titration was carried out with 2×10^{-2} or 0.1 N NaOH under N_2. We used 20 or 25 ml of a solution that was 3×10^{-4} or 1.2×10^{-3} M in glycine amide hydrochloride and also in Cu^{2+} or Cu^{2+}-Bipy ($I = 0.1$; $NaClO_4$). A Metrohm-Potentiograph E 336 and UX glass electrodes were used in the titrations.

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Formation of 3,4-Diaza-1,3,5-hexatrienes from Alkenylamines and Diazoalkanes

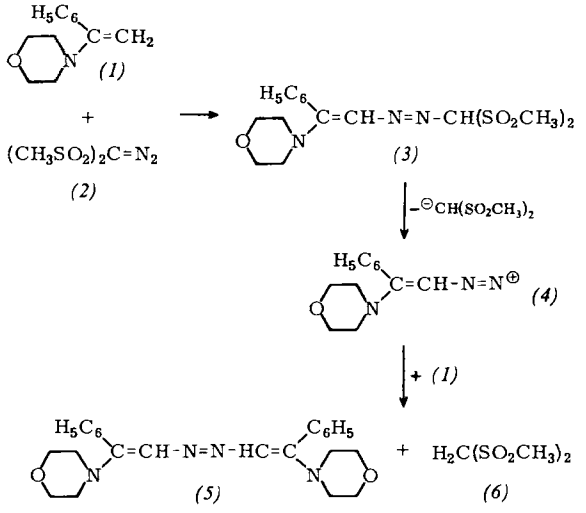
By *U. Schöllkopf, E. Wiskott*, and *K. Riedel*[*]

Reaction of alkenylamines with the usual diazoalkanes appears either not to occur or to be extremely sluggish[1]. We have now found that reaction occurs readily with those diazoalkanes that have pronounced diazonium character. Transfer of the diazo group and subsequent coupling thus lead to 3,4-diaza-1,3,5-hexatrienes.

For instance, if dimesyldiazomethane *(2)* in chloroform is allowed to react with two equivalents of α-morpholinostyrene *(1)* for 24 h at room temperature, there is formed, besides dimesylmethane *(6)* (84 % yield), a *ca.* 65 % yield of 1,6-dimorpholino-1,6-diphenyl-3,4-diazahexatriene *(5)*, m.p. 210 to 212 °C (decomp.) (after precipitation from chloroform or tetrahydrofuran by methanol); NMR ($DCCl_3$, τ): 2.6 (m, 10 H); 3.16 (s, 2 H); 6.3 (q, 8 H); 7.0 (q, 8 H); UV (λ_{max}, nm, CH_3OH or C_6H_{12}): 261 or 254 (8800), 431 or 401 (28000) [2].

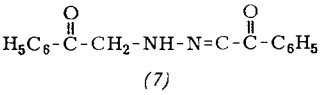
For isolation of *(5)* the mixture is evaporated to small bulk and filtered; *(5)* is then precipitated from the filtrate by methanol. Bis(phenylsulfonyl)diazomethane and ethyl nitrodiazoacetate [3] react in the same way as *(2)*, but ethyl diazoacetate itself and diphenyldiazomethane do not react.

Presumably *(1)* and *(2)* first yield the azo compound *(3)* which then reacts further with a second molecule of α-morpholinostyrene *(1)* – perhaps in a S_N1-like reaction by way of the vinyldiazonium ion *(4)* [4] – to give *(5)* and *(6)*.



As shown by the comparatively simple NMR and electron spectra, only one of the six stereoisomers theoretically possible for *(5)* is formed; but it is not yet known which.

(5) dissolves in 2 N HCl with shift of λ_{max} from 261 to 248 nm and from 431 to 346 nm. Protonation probably occurs on the nitrogen atom of the morpholine group where, according to HMO calculations [5], the π-electron density is greatest. If *(5)* is set aside in 1 N hydrochloric acid for 24 h it is hydrolyzed to the phenacylhydrazone *(7)* of phenylglyoxal.



(7)

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Mass-spectrometric Study of the Synthesis of NH_3 on Iron Tips[1]

By *W. A. Schmidt*[*]

In spite of the great importance of heterogeneous catalytic processes and of the large amount of work devoted to its study, the surface processes occurring on the catalyst are not yet satisfactorily clarified. We have attempted to apply, in the case of NH_3 synthesis, the results of field ion mass spectrometry on ionization of NH_3 and N_2/H_2 mixtures on iron to the solution of this problem. Field ionization makes it possible to ionize molecules that are interacting with a metal (tips) from the gas phase (pressure of *ca.* 10^{-4} torr) and to analyze them mass-spectrometrically. In view of the high sensitivity of the mass spectrometer, it seems reasonable to expect that even ions formed from molecules adsorbed on the metal surface will be detectable.

The apparatus used was a 60° sector field mass spectrometer[2]. The residual gas pressure was reduced to $\leq 10^{-9}$ mm; there was no disturbance from water vapor during the mass spectrometric measurements.

Table 1. Types of ions and intensities in the field ion mass spectrum of NH_3 on an iron tip.

Type of ion	Intensity (arby.) [a]	Type of ion	Intensity (arby.)	Type of ion	Intensity (arby.)
N_2^+	≤ 1.0	N_3^+	3.5	NH_3^+	2.3×10^4
N_2H^+	5.0×10^3	N_3H^+	2.5	NH_4^+	1.0×10^6
$N_2H_2^+$	3.5×10^1	$N_3H_2^+$	6.5	$NH_4^+\cdot NH_3$	2.85×10^3
$N_2H_3^+$	1.0×10^2				
$N_2H_4^+$	1.0×10^1	$N_3H_4^+$	1.5	N_4^+	1.2
$N_2H_5^+$	3.3×10^1	$N_3H_5^+$	1.0	N_4H^+	1.0
$FeN_2H_n^+$		$FeN_3H_n^+$		$FeN_4H_n^+$	
n=0,1,..,6	1.0—10.0	n=0,1,..,9	1.0—10.0	n=0,1,..12	1.0—10.0

[a] arby. = arbitrary (scale units).

Table 1 shows the types of ions and their intensities for the field ion mass spectrum of NH_3 on an iron tip. The field strength was a few 10^7 V/cm, and the NH_3 pressure was 4×10^{-4} torr; tip and gas were at room temperature.

As well as NH_3^+ (the parent molecular ion), NH_4^+ and $NH_4^+\cdot NH_3$ occurred more strongly depending on the field strength. The high intensities of NH_4^+ and $NH_4^+\cdot NH_3$ are to be explained by the fact that, since ammonia is a polar gas, ionization results from a condensed layer formed on the tip surface owing to the inhomogeneous field. This layer is thicker than a monomolecular layer. Ionization by the tunnel effect is accompanied by self-dissociation, which is promoted by the field and which leads to formation of NH_4^+ and, by association, $NH_4^+\cdot NH_3$. A similar behavior has already been observed for water vapor[2, 3].

The absence of NH_2^+, NH^+, and N^+ ions is remarkable. The observed intensity of NH_4^+ would suggest that NH and NH_2 are enriched in the absorption layer. In fact, the reactions occurring in the layer lead to structures containing molecular nitrogen as well as associates with three of four N atoms although, according to estimates and comparisons of ionization potentials, ionization of, *e.g.*, NH appears possible.

The lower part of Table 1 shows groups of ions that are analogous to those in the upper part but still contain iron. Detection of these ions permitted direct analysis of the chemisorption structures. No structures occurred containing atomic nitrogen.

Table 2 gives results of field ionization of a N_2/H_2 mixture (proportions *ca.* 1:3; pressure 5×10^{-4} torr; tip and gas at room temperature) on an iron tip at two field strengths. At the lower field strength N_2H^+ ions were found as well as the molecular ions H_2^+ and N_2^+. At the higher field strength N_2H^+ was not present, because ionization occurs before the molecules can enter into equilibrium with the metal surface.

Table 2. Field ion mass spectrum of a N_2/H_2 mixture on an iron tip at two field strengths.

Mass	Field strength 195 MV/cm		Field strength 135 MV/cm	
	Intensity (arby.)	Assignment	Intensity (arby.)	Assignment
1	10	H^+	—	—
2	75	H_2^+	0.2	H_2^+
28	3500	$^{14}N_2^+$	7.5	$^{14}N_2^+$
29	25	$^{14}N^{15}N^+$	0.5	$^{14}N_2H^+$
	$\frac{\text{Intensity mass 28}}{\text{Intensity mass 29}} = \frac{140}{1}$ [a]		$\frac{\text{Intensity mass 28}}{\text{Intensity mass 29}} = \frac{15}{1}$	

[a] The ratio $^{12}N_2^+$: $^{14}N^{15}N^+$ amounts to 138.4:1 on the basis of the natural isotope ratio.

Even if the iron tip is at a higher temperature (*ca.* 200 °C) the field ion-mass spectrum of N_2 contains only N_2^+ and no N^+ ion.

These results indicate that nitrogen enters the surface structures only in molecular form. If this result is applied to NH_3 synthesis, non-dissociative chemisorption of nitrogen should be the first step. *Shvachko et al.*[4] came to the same conclusion when they found FeN_2 adsorption complexes on iron under the conditions of NH_3 synthesis up to more than 400 °C. Furthermore, the specific adsorption of N_2 on {111} surfaces of iron, as found by *Brill, Richter,* and *Ruch*[5], also necessitates the adsorption of nitrogen in molecular form.

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[1] Read in part at the 11th Field Emission Symposium Cambridge (England) 1964; read to the GDCh General Meeting in Berlin (Germany) 1967.

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[4] *V. I. Shvachko, Ya. M. Fogel,* and *V.Ya. Kolot*, Kinetics and Catalysis *7*, 734 (1966).

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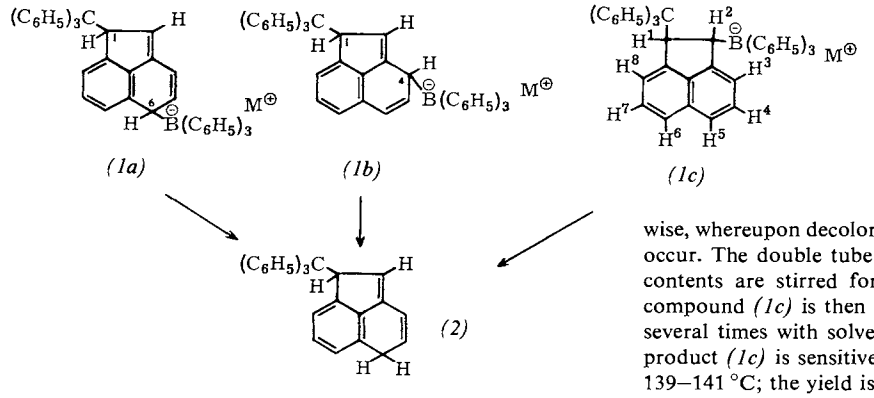
Structure and Hydrolysis of the ate-Complex from Tritylsodium, Acenaphthylene, and Triphenylborane

By *G. Wittig, W.Tochtermann,* and *B. Knickel*[*]

When polymerization of acenaphthylene is initiated by tritylsodium and terminated by triphenylborane, subsequent acid hydrolysis affords 1,5-dihydro-1-tritylacenaphthylene *(2)*[1]. It has not been possible previously to decide whether the product *(2)* arose by 1,6-addition of the Lewis base/Lewis acid pair tritylsodium/triphenylborane to acenaphthylene with subsequent hydrolysis of the complex *(1a)* in a S_E2 reaction, or whether a 1,4- or 1,2-addition to acenaphthylene occurred, leading to *(1b)* or *(1c)*, whereupon acid hydrolysis then gave rise, respectively, to a single or double allylic shift (S_E2' reaction).

In order to answer this question[2] it was essential that the ate-complex *(1)* be isolated and its structure elucidated by means of NMR spectroscopy (a method that was not available at the time of the earlier publication[1]). The product *(1)* could be isolated in either of two ways: Tetramethylammonium bromide precipitates the sparingly soluble tetramethylammonium derivative *(1)* [M = $N(CH_3)_4$, decomp. 154 to 155 °C (recrystallized from acetone/ethanol)] from an aqueous solution of the sodium salt *(1)* [M = Na[1]]; it is, however, better to prepare the complex with tritylpotassium in 1,2-dimethoxyethane[3], from which the potassium salt



(1), M = K, decomp. 139–141 °C, is precipitated directly. We have used the second method to prepare analogous complexes from 1,2-dideuterio-,4,7-di-*tert*-butyl- and 5,6-dichloro-acenaphthylene[1,4].

The ^{1}H–NMR spectrum[5] of *(1)*, M = K, shows the aromatic protons as a multiplet at τ = 2.6–3.4 and three signals at τ = 3.55 (J = 7 Hz), 3.70 (J = 8 Hz), and 4.13 (J = 7 Hz) (each 1 H, probably H^4, H^8, and H^3[6]). It contains also a broad singlet at τ = 4.29 (1 H, half-width *ca.* 5 Hz) and a structureless broad signal at τ = 6.2 (1 H)[7]. On the basis of a comparison with 1-tritylacenaphthene *(1c)*, H in place of $^{\ominus}B(C_6H_5)_3$[1] [τ (H^1) = 4.55; X part of an ABX system, *cis*-coupling J_{AX} = 7.8 Hz, *trans*-coupling J_{BX} = 2.2 Hz[8], analyzed according to AMX], we assign the singlet at τ = 4.29 to the proton H^1, and the signal at τ = 6.2 to the proton that is on the carbon atom in the α-position to the boron[9].

These results can be accounted for only by structure *(1c)*, for the following reasons:

1. In the spectrum of the complex from 1,2-dideuterio-acenaphthylene[4] there is no signal at τ = 4.29 (H^1) or 6.2. In other respects the spectrum corresponds to that of the non-deuterated complex. Thence it follows that the signal at τ = 6.2 belongs to the proton H^2 and that boron is attached to C-2 of the acenaphthene system.

2. The spectrum of the complex from 5,6-dichloroacenaphthylene[1] is very similar to that of *(1)* [multiplet at τ 2.3–3.4; doublets at τ = 3.46 (H^4), τ = 3.84 (H^8), and τ = 4.08 (H^3), J = 8 Hz in each case[6]; τ = 4.44 (H^1), τ = 6.18 (H^2)]. This is because the signals of H^5 and H^6 in the spectrum of *(1c)* appear within the broad aromatic multiplet, so that replacement of the two hydrogen atoms by chlorine does not change the appearance of the spectrum appreciably.

3. The same is true for the spectrum of the complex from 4,7-di-*tert*-butylacenaphthylene[1], in which the three doublets are merely replaced by two singlets at τ = 3.77 (3 H, presumably H^5, H^6, and H^8) and τ = 4.06 (H^3)[6]. Further signals are a multiplet at τ = 2.3–3.5, τ = 4.53 (H^1), τ = 6.25 (H^2), and *tert*-butyl resonances at τ = 8.9 and 9.0. The fact alone that such a complex is formed contraindicates 1,4- or 1,6-addition, since entry of triphenylborane in *ortho*-position to a *tert*-butyl group is not very likely.

4. The finding that the signal for H^1 in the spectrum of *(1)* does not have a large coupling constant suggests that H^1 is *trans* to H^2[8], *i.e.* *trans*-addition of the trityl group and of triphenylborane occurs, with formation of *(1c)*.

Thence it follows that acid hydrolysis of *(1)* to *(2)* and triphenylborane is a S_E2' reaction. Since it has been shown in several other cases that allylic shifts do not occur in such decompositions[10], this is the first case to our knowledge where hydrolysis of such a borate complex is to be regarded as a 1,5–S_E2' cleavage[2].

Experimental: Triphenylborane (0.9 g, 3.7 mmoles) is dissolved in benzene (30 ml) in one arm of a double Schlenk tube fitted with a sinter, and acenaphthylene (0.57 g, 3.7 mmoles) in anhydrous ether (100 ml) is added to it. After 10 minutes' stirring, a 0.175 M solution (17 ml) of tritylpotassium in 1,2-dimethoxyethane[3] is rapidly added dropwise, whereupon decoloration and deposition of *(1c)*, M = K, occur. The double tube is then sealed in a vacuum and the contents are stirred for 12 h with exclusion of light; the compound *(1c)* is then filtered off on the sinter and washed several times with solvent that is distilled on to it. The dry product *(1c)* is sensitive to light and air and decomposes at 139–141 °C; the yield is 1.6 g (63 %).

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[3] *H. O. House* and *V. Kramar*, J. org. Chemistry *27*, 4146 (1962).

[4] *B. M. Trost*, J. Amer. chem. Soc. *89*, 1847 (1967).

[5] Measured in [D$_6$]acetone with the Varian HA 100. We thank Dr. *J. C. Jochims* and Miss *G. Taigel* of the Max-Planck-Institut für Medizinische Forschung, Heidelberg, for measuring these spectra. All the complexes prepared from tritylpotassium gave also the methylene and methyl signals of 1,2-dimethoxyethane at τ = 6.54 and 6.72 since these products contain varying amounts of this solvent, *e.g.* 2 molar equivalents in *(1c)*.

[6] This assignment is based on allocation of the signal at highest field strength to H^3 because of its proximity to the boron atom. Additionally, it was shown by spin decoupling that H^3 couples with H^4.

[7] This broadening is probably to be attributed to the influence of the boron.

[8] Cf. *M. J. S. Dewar* and *R. C. Fahey*, Angew. Chem. *76*, 320 (1964); Angew. Chem. internat. Edit. *3*, 245 (1964).

[9] The tetramethylammonium salt *(1)*, M = N(CH$_3$)$_4$, prepared *via* the Na salt, gives the same signals for the ate part of the molecule. Only the signals for 1,2-dimethoxyethane are missing; in their place appears the singlet of the N(CH$_3$)$_4$ protons at τ = 6.76.

[10] *G. Wittig* and *D. Wittenberg*, Liebigs Ann. Chem. *606*, 1 (1957).

Dehydration of Gaseous [2-D]-2-Butanol over $CaSO_4$[1]

By *P. Bautista, M. Hunger*, and *H. Noller*[*]

It is usually assumed that dehydration of a gaseous alcohol over a solid catalyst involves β-elimination, but this has not previously been proved. We have studied the dehydration of 2-butanol and [2-D]-2-butanol over $CaSO_4$ (annealed at 150 °C under air (1 torr) for 11 hours) between 270 and 420 °C by microcatalysis and mass spectroscopy (catalyst volume *ca.* 0.5 cm^3 of powder; carrier gas helium; streaming velocity 40 ml/min; CEC 21–620 mass spectrometer).

In the temperature range used, the conversion of [2-D]-2-butanol was on an average 2 % less than that of the non-deuterated alcohol. The activation energy of the deuterated butanol (10.9 kcal/mole) is about 4 % greater than that of the non-deuterated butanol (10.5 kcal/mole). The low value – or perhaps complete absence – of the secondary kinetic isotope effect accords with the assumption of a β-elimination. A somewhat larger effect would perhaps be expected, but barely more than 15 %.

Distribution of the butenes formed as primary products at 270 and 406 °C, respectively, was 1-butene 23.5 and 33.5 %, *trans*-2-butene 21.5 and 26.5 %, and *cis*-2-butene 55 and 40 %. As in similar heterogeneous eliminations more 2- than 1-butene is formed (Saytzeff rule), and the *cis*-isomer predominates greatly. However, the relatively large proportion of 1-butene is divergent from previous results [2]; it even exceeds the amount of *trans*-2-butene. The thermodynamically most stable butene (*trans*-2-butene) is thus primarily the most disfavored. The deuterated and the non-deuterated alcohol give the same primary distribution of butenes.

90 % of the deuterium present in the [2-D]-2-butanol can be detected in the butenes. The deuterium loss is distributed as follows among the three butenes: *cis*-2-butene 15 %; *trans*-2-butene 8 %; 1-butene 0 %. Thus 1-butene arises by a pure β-elimination

$$H_3C{-}CDOH{-}C_2H_5 \rightarrow H_2C{=}CD{-}C_2H_5 + H_2O$$

Partial α-elimination (with subsequent migration of hydrogen) cannot be excluded for the 2-butenes

$$H_3C{-}CDOH{-}CH_2CH_3 \rightarrow H_3C{-}CH{=}CH{-}CH_3 + HDO.$$

Presumably, however, the loss of deuterium is due to the structure of the intermediate carbonium ion, which then should not be considered as a classical carbonium ion.

The differences can perhaps be interpreted as follows: the formation of 1-butene occurs in a pure concerted reaction, whereas elimination to yield 2-butene has some E-1 character caused by the differing acidities of the protons at the end and in the middle of the chain. Furthermore, the elimination to give *cis*-2-butene must have more E-1 character than that leading to the *trans*-isomer. This could indicate that the probability of conversion into the *cis*-isomer increases with the lifetime of the carbonium ion; but then chance of losing deuterium must increase correspondingly.

Butenes with two or more deuterium atoms were not detectable.

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[1] Part XVI of Mechanism of Contact Eliminations. – Part XV: *A. Correa, M. Hunger,* and *H. Noller,* Z. Naturforsch., Part b, in the press.

[2] See previous communications, *e.g. P. Andréu, M. Rosa-Brusin, C. Sánchez,* and *H. Noller,* Z. Naturforsch. *22b*, 814 (1967).

Passivation of Raney Nickel by Nitriles. – Hydrogenation in Acid Solution

By *P. Tinapp* [*]

In connection with a study of the possibilities of hydrogenating nitriles at various pH values it has been found that dissolution of Raney nickel in dilute non-oxidizing mineral acids can be prevented by addition of a nitrile. The activity of the Raney nickel is retained in this very acid medium. Contrary to previous assumption, hydrogenations with Raney nickel are thus, in general, possible in the presence of dilute mineral acid.

Experimental:

Benzonitrile (51.5 g, 0.5 mole) was dissolved in a mixture of tetrahydrofuran (180 ml), water (20 ml), and 96 % sulfuric acid (50 g) and, after addition of *ca.* 10 g of Raney nickel, was hydrogenated at room temperature and normal pressure. Uptake of hydrogen had ceased after about 5 h. Without having been filtered from the catalyst, the mixture was poured into water (*ca.* 600 ml), and the benzaldehyde formed was extracted with ether. The combined extracts were washed once with water and dried over sodium sulfate. Subsequent distillation gave 41 g (79 %) of benzaldehyde.

The procedure can be applied to other aromatic nitriles. To what extent the influence of solvent or substituents must be taken into account is the subject of further study.

Nothing is yet known about the origin of the passivation effect. The amount of nitrile necessary for passivation depends on the amount of Raney nickel and on the nature of the nitrile. α,β-Unsaturated and aromatic nitriles hinder most strongly the dissolution of the Raney nickel. Passivation may thus perhaps arise by π-complex formation at the CN group. Complexes of this type have already been described [1].

Table 1. Passivation of Raney nickel by nitriles. 1 g of Raney nickel was suspended in 25 ml of 25 % aqueous-ethanolic sulfuric acid, and the nitrile was added dropwise until evolution of hydrogen had ceased. The value found for benzonitrile was taken as unity and the values for the other nitriles were referred to this on a molar basis.

Nitrile	Activity of nitrile referred to benzonitrile = 1 (average value)
Cinnamonitrile	0.7
Acrylonitrile	1.03
m-Tolunitrile	1.1
o-Tolunitrile	1.18
n-Hexyl cyanide	1.69
Acetonitrile	1.75
Benzyl cyanide	1.34

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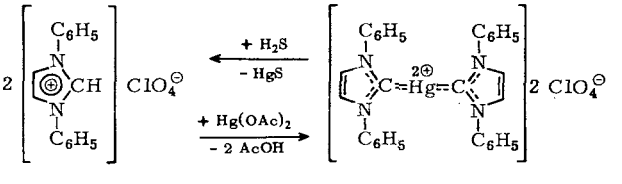
Direct Synthesis of a Mercury Salt-Carbene Complex [1]

By *H.-W. Wanzlick* and *H.-J. Schönherr* [*]

Transition-metal-carbene complexes have hitherto been obtained only indirectly: suitable ligands are converted into carbene ligands with retention of the existing bond to the central atom [2,3]. Nucleophilic carbenes, which are similar to isocyanides [4], should be suitable for direct synthesis of such complexes. That is the case, as we have shown by a first example: In view of the results obtained by *Schöllkopf et al.*, with Hg^{2+} as central atom [3,3a], we treated 1,3-diphenylimidazolium perchlorate *(1)* with mercury(II) acetate in dimethyl sulfoxide (DMSO) and obtained the carbene complex *(3)* [5]. It was unnecessary to add a base to produce the carbene *in situ*. Bis(1,3-diphenylimidazolio)mercury diperchlorate *(3)* [crystallizes from DMSO as colorless plates, m.p. *ca.* 370 °C (decomp.), which darken above *ca.* 250 °C] is formed with liberation of acetic acid in almost quantitative yield. It is stable to acids but is immediately reconverted into



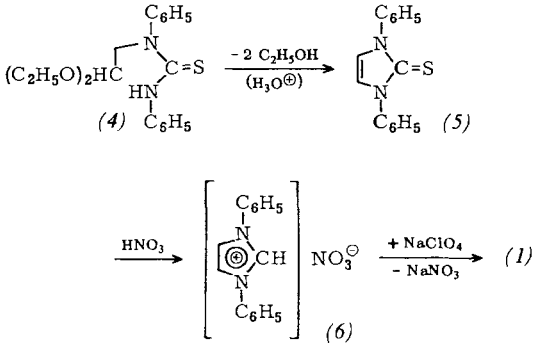
(1) *(3)*

(1) by hydrogen sulfide (in DMSO) with separation of mercury sulfide. The carbene fragment forms the base peak (m/e = 220) in the mass spectrum[6].

The NMR spectra (measured in [D_6]-DMSO as solvent) of *(1)* and *(3)* prove the structure of *(3)*. The "*meta*-coupling" shown by the salt *(1)*[7] naturally is absent for the complex *(3)*. The signals of the phenyl protons, and particularly of the protons on C-4 and C-5, are shifted upfield on conversion of *(1)* into *(3)*.

	H(1)	H(4), H(5)	H_{phenyl}
(1)	τ = −0.29 (t) (J = 1.5)	τ = 1.47 (d) (J = 1.5)	τ = 1.95–2.5 (m)
(3)	—	τ = 1.71 (s)	τ = 2.2–2.7 (m)

The salt *(1)* was prepared as follows:



Experimental:

A mixture of *N*-(2,2-diethoxyethyl)aniline and phenyl isothiocyanate (molar ratio 1:1.1), when kept for 4 days at room temperature, gave the thiourea derivative *(4)*, m.p. 94 °C (yield 88 %), which afforded the thione *(5)*, m.p. 161 °C (yield 66 %), when heated with conc. hydrochloric acid. Heating *(5)* with 36 % nitric acid (d = 1.220) gave an almost quantitative yield of the nitrate *(6)* (very hygroscopic), which was converted into *(1)*, m.p. 169 °C (yield 94 %), by dissolution in dilute nitric acid and addition of alcoholic sodium perchlorate solution.

Complex salt (3): 4 g of the salt *(1)* and 2 g of mercury(II) acetate were shaken in *ca.* 7.5 ml of DMSO at 80 °C for 10 min. When the solution cooled to room temperature crystals separated; crystallization was completed by addition of *tert*-butyl alcohol. When recrystallized from a little DMSO the complex is obtained in well-formed rectangular plates.

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[1] Part XIV of Chemistry of Nucleophilic Carbenes. – Part XIII: *H.-W. Wanzlick* and *H. Steinmaus*, Chem. Ber. *101*, 244 (1968).

[2] *E. O. Fischer* and *A. Maasböl*, Chem. Ber. *100*, 2445 (1967), where previous literature is cited.

[3] *U. Schöllkopf* and *F. Gerhart*, Angew. Chem. *79*, 819 (1967); Angew. Chem. internat. Edit. *6*, 805 (1967), where previous literature is cited.

[3a] *U. Schöllkopf* and *F. Gerhart*, Angew. Chem. *79*, 990 (1967); Angew. Chem. internat. Edit. *6*, 970 (1967).

[4] Cf. *W. Kirmse*: Carbene Chemistry. Academic Press, New York, London 1964.

[5] Formulation of the complex by analogy with the symbolism used for other carbene-metal complexes [2, 3].

[6] We thank Dr. *D. Schumann* for the measurement of the spectrum. Apparatus: AEI MS 9, 70 eV, 350 °C.

[7] Cf. *G. S. Reddy*, *R. T. Hobgood*, and *J. H. Goldstein*, J. Amer. chem. Soc. *84*, 336 (1962).

Compounds with Si–Ti Linkages

By *E. Hengge* and *H. Zimmermann*[*]

We have obtained compounds with the hitherto unknown Si–Ti linkage by treatment of triphenylsilylpotassium with titanium halides. The stability of the Si–Ti bond is appreciably increased by neopentane structures, which are particularly stable in compounds of elements of the fourth main group, or by substituents that are π-bonded to the titanium.

A characteristic example is the formation of tetrakis(triphenylsilyl)titanium from $TiCl_4$ and $(C_6H_5)_3SiK$:

$$TiCl_4 + 4\ (C_6H_5)_3SiK \rightarrow Ti[Si(C_6H_5)_3]_4 + 4\ KCl$$

Ethereal solutions of $(C_6H_5)_3SiK$ and $TiCl_4$ are simultaneously added dropwise to ether at 0 °C with stirring. Stirring is continued overnight, then the mixture is poured on ice plus 2 N HCl; the water and ether are then separated off and the precipitate is washed with methanol/water and ether and recrystallized from xylene (yield 44 %).

Tetrakis(triphenylsilyl)titanium is a pale yellow substance that melts at 395–400 °C with decomposition. It is very sparingly soluble in xylene, toluene, or benzene, and insoluble in all other solvents. Its particular stability may depend above all on the strong shielding of the phenyl groups in the neopentane structure, and on the high symmetry. Aqueous alkali decomposes the compound slowly, causing evolution of hydrogen:

$$Ti[Si(C_6H_5)_3]_4 + 8\ H_2O \rightarrow Ti(OH)_4 + 4\ (C_6H_5)_3SiOH + 4\ H_2$$

The amount of hydrogen evolved corresponds to theory ($Si:H_2$ = 1:1).

The IR spectrum shows, besides the usual CH, phenyl, and Si-phenyl bands, a new band at 900–940 cm^{-1}. This vibration may be associated with the neopentane skeleton since similar bands appear for similar compounds such as $[(CH_3)_3Si]_4Si$.

$(C_6H_5)_3SiK$ reacts also with $Cl_2Ti(\pi\text{-}C_5H_5)_2$ forming a Si–Ti bond:

$$(\pi\text{-}C_5H_5)_2TiCl_2 + 2\ KSi(C_6H_5)_3 \rightarrow (\pi\text{-}C_5H_5)_2Ti[Si(C_6H_5)_3]_2$$

The reaction is carried out in diglyme (diethylene glycol dimethyl ether) with ice cooling. The resulting reddish-brown solution is evaporated and the resulting residue is extracted with chloroform. On addition of pentane to the extract, yellow bis(triphenylsilyl)di(π-cyclopentadienyl)titanium is precipitated and is purified by sublimation at 280 °C (yield 35 %).

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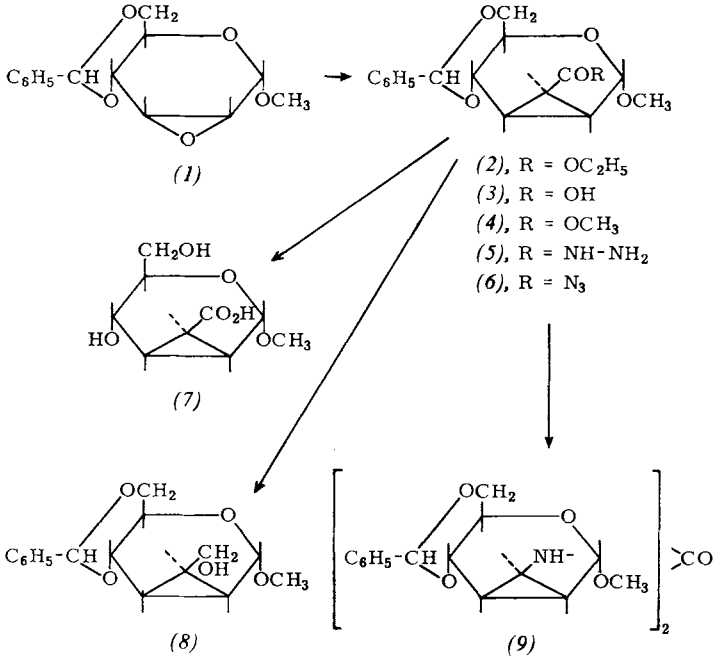
Synthesis of Methyl 4,6-*O*-Benzylidene-2,3-(2′-hydroxyethylidene)-α-D-mannopyranoside, a Cyclopropane Sugar

By *W. Meyer zu Reckendorf* and *U. Kamprath-Scholtz*[*]

PO-Activated olefination, as described by *Horner*[1], has seldom been used for the preparation of sugars with a branched carbon skeleton. Its application to the preparation of cyclopropane derivatives from epoxides of the sugar series has not previously been described.

We treated the epoxide *(1)*[2] with ethyl diethoxyphosphorylacetate[3], $(C_2H_5O)_2PO\text{–}CH_2COOC_2H_5$, and NaH in di-

oxane. After a sufficiently long reaction time (3 days at 80 °C) most, but not all, of the compound *(1)* was consumed Since separation of the product was difficult we hydrolyzed the mixture *(1)* + *(2)* cautiously (1 N NaOH/acetone at room temperature), whereupon the unchanged epoxide *(1)* remained unattacked and we obtained the acid *(3)* in 46 % yield; it has m.p. 191–192 °C and $[\alpha]_D^{20} = +57°$ (c = 1 in $CHCl_3$). Esterification with diazomethane gave the methyl ester *(4)* (> 90 % yield), m.p. 164–166 °C, $[\alpha]_D^{20} = +57°$ (c = 1 in $CHCl_3$). The configuration assigned follows from the NMR spectrum[4] (100 MHz, in $CDCl_3$, ppm with reference to TMS): H-1, δ = 4.83 (singlet, $J_{1,2} = 0$[5]); H-2, δ = 1.83; H-3, δ = 2.12 ($J_{2,3}$ = 9.1 Hz, *cis*); H-4, δ = 3.50 ($J_{3,4}$ = 1.9 Hz); H-7, δ = 1.68 ($J_{3,7}$ = 4.6 Hz, *trans*; $J_{2,7}$ = 5.0 Hz, *trans*). In C_6D_6: H-4, δ = 3.14; H-5, δ = 3.75 ($J_{4,5}$ = 9.0 Hz, diaxial).



Of the wealth of reactions that are possible with *(3)* and *(4)* we have investigated the following: Treating *(4)* with hydrazine hydrate in ethanol (16 h, reflux) gives the hydrazide *(5)* [quantitative yield, m.p. 236–238 °C, $[\alpha]_D^{20} = +42°$ (c = 1 in $CHCl_3/CH_3OH$ 9:1)]. Reaction of *(3)* with chloroformic ester, triethylamine, and sodium azide[6] afforded the azide *(6)* [85 % yield, m.p. 100–101 °C, $[\alpha]_D^{20} = +52°$ (c = 1 in $CHCl_3$)], which yielded the urea derivative *(9)* [91 % yield, m.p. 241–245 °C, $[\alpha]_D^{20} = +59.5°$ (c = 1 in $CHCl_3$)], when heated in anhydrous toluene for 1 h, treated with water, and boiled for a further 16 h. Further hydrolysis of the acid *(3)* proceded only as far as compound *(7)* [yield 80 %, m.p. 133–134 °C, $[\alpha]_D^{20} = +5°$ (c = 1 in CH_3OH)]. The glycosidic linkage is stable to 5 N HCl. Reducing the ester *(4)* with $LiAlH_4$ in tetrahydrofuran (1.5 h, reflux) gave the alcohol *(8)* [74 % yield, m.p. 140–142 °C, $[\alpha]_D^{20} = +72°$ (c = 1 in $CHCl_3$)].

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[1] *L. Horner*, Fortschr. chem. Forsch. *7*, 1 (1966).

[2] *N. K. Richtmyer* in *R. L. Whistler* and *M. L. Wolfrom*: Methods in Carbohydrate Chemistry. Academic Press, New York, London 1962, Vol. I, p. 106.

[3] *W. S. Wadsworth* and *W. D. Emmons*, J. Amer. chem. Soc. *83*, 1733 (1961).

[4] We thank Dr. *J. C. Jochims*, Max-Planck-Institut für Medizinische Forschung, Heidelberg, for measurement and interpretation of the 100 MHz spectra.

[5] The *manno*-configuration thus made probable was confirmed by comparison with *(1)* (H-1, δ = 5.0 ppm, doublet, $J_{1,2}$ = 2.5 Hz) and the corresponding *manno*-epoxide (H-1, δ = 4.9 ppm, singlet), which, having a configuration analogous to that of *(4)*, also shows no coupling between H-1 and H-2.

[6] *J. Weinstock*, J. org. Chemistry *26*, 3511 (1961).

CONFERENCE REPORTS

Chemistry of Organic Peroxides

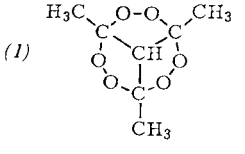
The International Symposium on "The Chemistry of Organic Peroxides" was held in Berlin-Adlershof during 13–15th September 1967. It was arranged by the Institut für Organische Chemie of the Deutsche Akademie der Wissenschaften zu Berlin and by the Chemische Gesellschaft in der DDR. Thirty-two papers were read and 250 participants from 20 countries were present.

Peroxide Synthesis

In a review paper *A. Rieche* (Berlin-Adlershof) reported the synthetic principles used by the Adlershof school for the preparation of numerous peroxy compounds.

1. Addition of hydrogen peroxide or alkyl hydroperoxides to carbonyl compounds, nitriles, Schiff's bases, or ketene acetals. With hydrogen peroxide in the presence of mineral acid, triacetylmethane affords triacetylmethane peroxide *(1)*, which formed the symbol of the peroxide symposium.

(1)



2. Reactions of mesomerically stabilized carbonium ions with H_2O_2 or HOOR. They lead particularly smoothly to peroxides containing α-situated N or O functional groups.

3. Reactions of electrophilic agents such as halogens or Hg(II) acetate with olefins in the presence of hydrogen peroxide.

4. Substitution of $R-OO^{\ominus}$ for functional groups (Cl, OR, OH, NH_2) in organometallic compounds of Sn, Ge, Pb, As, or Sb.

Bond-breaking Reactions; Trioxides, Tetroxides

According to *P. D. Bartlett* (Cambridge, Mass.) *t*-butyl hydroperoxide and lead(IV) acetate at −95 °C give a solution of di-*t*-butyl tetroxide *(2)*, which is in equilibrium with the hydroperoxy radical ($K = 5 \times 10^{-5}$ at −95 °C, heat of dissociation 6 kcal/mole). At higher temperatures the tetroxide

evolves oxygen, and radical recombination leads to di-*t*-butyl trioxide *(3)*, which is stable up to −35 °C.

$$Bu{-}OOH \rightarrow BuOO\cdot \rightleftarrows Bu{-}O{-}O{-}O{-}O{-}Bu \quad (2)$$

$$Bu{-}O{-}O{-}O{-}O{-}Bu \rightarrow 2\,BuO\cdot + O_2 \quad (2)$$

$$BuO\cdot + \cdot O{-}O{-}Bu \rightleftarrows Bu{-}O{-}O{-}O{-}Bu \quad (3)$$

Above −35 °C oxygen and di-*t*-butyl peroxide are formed as stable end products. Following the radical concentration by ESR spectroscopy over the whole temperature range shows minima in the region where the tetroxide and trioxide exist.

N. A. Milas (Cambridge, Mass.) found that iodobenzene is formed without evolution of oxygen on reaction of diacetoxy iodobenzene with *t*-butyl hydroperoxide at −80 °C, so that the tetroxide *(2)* must be present in these solutions. Cautious warming leads at −70 °C to evolution of oxygen and formation of the trioxide *(3)*, whence oxygen is again evolved between −45 and −20 °C.

$$C_6H_5{-}I(O{-}Ac)_2 \xrightarrow[-80°C]{Bu{-}OOH} C_6H_5I + Bu{-}O{-}O{-}O{-}O{-}Bu \quad (2)$$

$$\xrightarrow{-70°C} Bu{-}O{-}O{-}O{-}Bu + {}^1/_2\,O_2 \xrightarrow{-45/-20°C} {}^1/_2\,O_2$$
$$(3)$$

The temperature ranges in which the tetroxide and trioxide appear agree well with those found by *P. D. Bartlett*.

In the discussion there were various references to the importance of spin conservation for reaction mechanism. For instance, a one-stage decomposition of the tetroxide *(2)* must produce the O_2 molecule as a singlet. However, *T. G. Traylor* (San Diego, California) was able to exclude this one-stage mechanism by comparison with the decomposition of di-*t*-butyl hyponitrite *(4)*. Compound *(4)* exists in the *trans*-form and cannot yield an O–O bond in one step; yet the almost identical proportion of Bu–O–O–Bu among the decomposition products from *(2)* and *(4)* indicates analogous decomposition mechanisms.

$$(2)\quad BuO(O{-}O)OBu \xrightarrow{?} Bu{-}O{-}O{-}Bu \;(O{=}O)$$

$$(4)\quad BuO{-}N{=}N{-}OBu \rightarrow\rightarrow Bu{-}O{-}O{-}Bu + N_2$$

In the papers by *Bartlett*, *Traylor*, and *Hiatt* formation of O_2 and a radical pair was assumed in place of a one-stage decomposition of the tetroxide *(2)*. Here the spin conservation rule permits formation of singlet O_2 with a singlet radical pair or formation of (normal) triplet O_2 and a triplet radical pair:

$$(2)\ Bu{-}O{-}O{-}O{-}O{-}Bu \rightarrow \begin{cases} BuO\cdot\downarrow\ O{=}O\ \uparrow\cdot OBu \\ BuO\cdot\downarrow\ O{=}O\ \downarrow\cdot OBu \end{cases}$$

P. D. Bartlett pointed out that an experimental decision between the two possibilities was not yet possible, since reversal of spin in the radical pairs is faster than coupling of the radicals or their diffusion away, as shown by the identical cage effects of "singlet" and "triplet" pairs of methyl or cumyl radicals.

G. A. Russell (Ames, Iowa) pointed out in his paper that oxygen in the triplet ground state cannot add to a carbanion in a one-stage reaction, since this would break the spin conservation rule. His observation that triphenylmethyl and diphenylmethyl anions nevertheless add oxygen very rapidly requires a multistage mechanism for its interpretation:

Electron transfer $\quad R{:}^{\ominus} + O_2^{\uparrow\uparrow} \rightarrow R^{\cdot\uparrow} + O_2{\cdot}^{\ominus\uparrow}$

Spin reversal $\quad R^{\cdot\uparrow} + O_2{\cdot}^{\ominus\uparrow} \rightarrow R^{\cdot\uparrow} + O_2{\cdot}^{\ominus\downarrow}$

Coupling $\quad R^{\cdot\uparrow} + O_2{\cdot}^{\ominus\downarrow} \rightarrow R{-}OO{:}^{\ominus\uparrow\downarrow}$

According to the acidity of the hydrocarbon, either the anion formation (*e.g.* diphenylmethane) or the reaction of the anion with O_2 (fluorene) is rate-determining.

Owing to spin conservation, the occurrence of singlet oxygen would be expected in reactions where oxygen is evolved, which involve a polar mechanism. For instance, the singlet oxygen ("doubly bonded" O_2) that is evolved on reaction of bromine with hydrogen peroxide as reported by *W. A. Waters* (Oxford, England) could attack olefins with shift of the double bond or undergo 1,4-addition to 1,3-dienes or to hydrocarbons of the anthracene type. Singlet oxygen is thus

$$H{-}\overset{\curvearrowright}{O}{-}O{-}\overset{\curvearrowright}{H}\quad Br{-}\overset{\curvearrowright}{Br} \rightarrow O{=}O$$

to be considered the key compound in the photosensitized reactions of O_2 discovered by *G. O. Schenck*.

Connections with co-carcinogenesis were also referred to.

Mrs. *S. K. Maizu*, (Moscow, USSR) dealt with the role of alkyl hydroperoxides and peroxy radicals in the liquid-phase oxidation of organic compounds. For the process yielding radicals, not only the decomposition of an alkyl hydroperoxide must be considered, but also the reaction

$$RH + ROOH \rightarrow R\cdot + RO\cdot + H_2O$$

as indicated by the dependence of the decomposition of the hydroperoxide on the strength of the C–H bond in RH. The influence of the reaction medium and of homogeneous catalysts (salts of metals of variable valence) was discussed. Complexes of alkyl hydroperoxides with other components of the reaction mixture play an important part. Studies of the formation of epoxides in co-oxidation of olefins and organic compounds showed that acylperoxy radicals are the epoxidizing agents.

W. Pritzkow (Merseburg, DDR) deduced from competition experiments that tertiary C–H bonds on the cyclohexane ring are autoxidized faster by a factor of at least 2 when in equatorial than in axial positions. *L. Novotný* (Prague, CSSR) discussed the formation, by way of peroxidic intermediates, of α,β-unsaturated five-membered ring lactones in plants (various *Petasites* species).

According to *A. G. Davies* (London, England), autoxidation of organometallic compounds occurs by way of a radical chain:

$$ROO\cdot + M{-}R \rightarrow R{-}OO{-}M + R\cdot$$
$$R\cdot + O_2 \rightarrow R{-}OO\cdot$$

When R is optically active α-methylbenzyl and M is boron complete racemization results, which makes direct introduction of O_2 unlikely. An addition-elimination mechanism was proposed.

In a review paper *G. A. Razuvayev* (Gorki, USSR) gave an insight into his own, very numerous, investigations of new homolytic reactions of peroxy compounds. Many organometallic compounds react with diacyl peroxides even below the decomposition temperature of the peroxides, the acylperoxy radical then not undergoing decarboxylation.

$$R_nM + (R'COO)_2 \rightarrow R_{n-1}M{-}O{-}CO{-}R' + R'COOR$$

$$2\,R_nM + (R'COO)_2 \rightarrow 2\,R_{n-1}M{-}O{-}CO{-}R' + 2\,R\cdot$$

(M = Al or Tl)

Metal-metal bonds are cleaved by diacyl peroxides.

$$R_3M{-}MR_3 + (R'COO)_2 \rightarrow 2\,R_2M{-}O{-}CO{-}R'$$

(M = Sn or Pb)

$$(R_2M)_2M' + (R'COO)_2 \rightarrow 2\,R_3M{-}O{-}CO{-}R' + M'$$

(M = Si or Ge; M' = Hg, S, Se, or Te)

Dialkyl peroxides have appreciably greater difficulty in reacting with organometallic compounds; at room temperature only the following reaction with trialkylaluminum occurs:

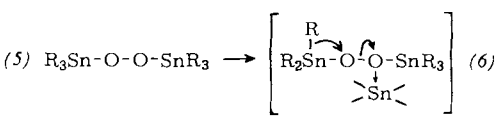
$$2\,Alk_3Al + t\text{-}Bu_2O_2 \rightarrow 2\,Alk_2Al{-}O{-}Bu\text{-}t + 2\,Alk\cdot$$

Stable organometallic compounds such as tetraalkyl compounds of silicon and germanium react with dialkyl or diacyl peroxides or peresters only above the decomposition temperatures of the latter. Then a reaction of the alkyl groups with the free radicals occurs that involves attack on the C–H bonds.

Peresters of the type $R_3M{-}CH_2{-}CH_2{-}CO{-}OOBu\text{-}t$ were prepared with M = Si or Ge, and the reactions of the radicals formed on their thermal decomposition were studied. Further, peroxides of composition $RHgOOR'$ and R_2TlOOR' have been synthesized for the first time and studied.

For organic peroxy derivatives of tin and lead, *V. A. Shushunov* (Gorki, USSR) showed that alkylperoxy derivatives of the type $R_3M{-}OO{-}R'$ decompose homolytically only above 100 °C. However, heterolytic decomposition of acylperoxy derivatives of type $R_3M{-}OO{-}CO{-}R'$ (M = Sn or Pb) is rapid even at room temperature. Both reactions follow a kinetic law of the first order. The influences of the substituent, the metal, and the solvent on the decomposition reactions were studied.

J. Dahlmann (Berlin-Adlershof, DDR) reported the synthesis and decomposition of bis(organometallyl) peroxides $R_3M{-}OO{-}MR_3$ (M = Ge, Sn, or Pb). In the decomposition of tin peroxides, which occurs even below room temperature, the kinetics and the influences of substituents, solvent, and added tin compounds show that the decomposition is induced by diorganotin oxides formed in the decomposition.

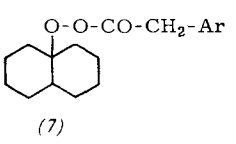


$$\rightarrow R_2SnO + R_3SnOR$$

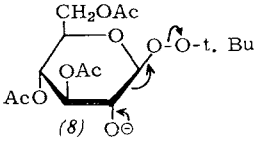
W. P. Neumann (Giessen, Germany) reported the reaction of diacyl peroxides with organotin hydrides. It results from attack of R_3Sn radicals on the peroxidic oxygen and chain propagation by the acyloxy radicals thus formed. The stannyl radical is nucleophilic and always attacks the electron-poorer peroxidic oxygen.

A kinetic study of the reaction of amines with dibenzoyl peroxide (*O. A. Tschaltykjan*, Jerewan, USSR) showed that amines are of two types, namely, those that react with the O–O bond either mainly heterolytically or mainly homolytically.

C. Rüchardt (München, Germany) studied the thermal decomposition of substituted 9-decalyl perphenylacetates *(7)* in polar and apolar solvents. By following the consumption of the perester and the formation of radicals (trapping by galvinoxyl) kinetically, he found that heterolysis and homolysis of the O–O bond of *(7)* are truly competitive reactions. Radical formation is favored by electron-donor substituents (*e.g.* $p\text{-}OCH_3$).



(7)

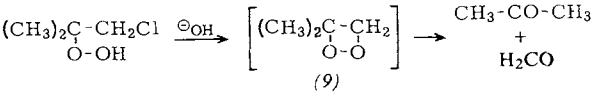


(8)

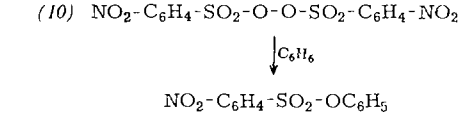
M. Schulz (Berlin-Adlershof, DDR) studied fragmentation of the system *(8)*, his examples being the base-catalyzed decomposition of acylated *t*-butyl peroxyglycosides, sugar azohydroperoxides, and acetylated sugar peroxy esters. The five-center fragmentation of peroxyglycosides has preparative importance as a sugar degradation reaction.

E. Schmitz (Berlin-Adlershof, DDR) gave several examples of heterolysis of nitrogen-containing peroxides, whose fragmentation is started by presence of a basic N atom or a deprotonated amide nitrogen in the γ-position to the peroxy group.

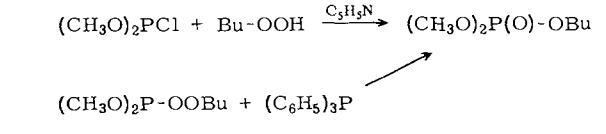
W. H. R. Richardson (San Diego, California) discussed the decomposition of monochlorinated *t*-butyl hydroperoxide by bases to yield acetone and formaldehyde by way of an intermediate *(9)* containing a four-membered ring. Kinetic data were adduced in favor of neighboring group participation by the peroxide group.



R. L. Dannley (Cleveland, Ohio) studied electrophilic substitution of aromatic compounds by nitrobenzenesulfonyl peroxides *(10)*. The reaction leads to phenols, in good yield, by way of sulfonic esters.



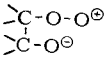
According to *G. Sosnovsky* (Milwaukee, Wisconsin) reaction of monochloro derivatives of tervalent phosphorus with *t*-butyl hydroperoxide in pyridine gives a phosphate ester, which is also obtained from the perphosphate ester and triphenylphosphine.

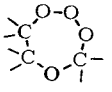


Reactions of Ozone; Ozonides

P. S. Bailey (Austin, Texas) reviewed reactions of ozone with organic compounds. Four types of reaction were distinguished: 1. Cycloaddition to olefins, yielding primary ozon-

ides; 2. electrophilic attack, for instance on phosphines and amines; 3. nucleophilic attack, for instance on Schiff's bases; and 4. 1,3-dipolar insertions into C–H bonds, for instance with benzaldehyde. *R.W. Murray* (Murray Hill, New Jersey) discussed the route from primary ozonide to ozonides on the basis of extensive experimental material. The Criegee mechanism needs some extensions. The intermediate stages *(11)* and *(12)* were brought into the discussion on the basis of stereochemical and crossing experiments, as well as labeling experiments with deuterium or ^{18}O.

(11) 

 *(12)*

R. Criegee (Karlsruhe, Germany) showed that aldozonides from styrene and substituted styrenes are cleaved to aldehyde and acid by some solvents, particularly rapidly by methanol. A diozonide isomerizes under acid catalysis to a compound that contains two peroxide groups and two acetal oxygen atoms.

[VB 104 IE]

German version: Angew. Chem. *80*, 125 (1968)

The Kinetic Principle of Excitable Systems

By *W. Seidel*[*]

About 70 years ago *W. Ostwald*[1] noted in the behavior of the system Fe/HNO_3 remarkable analogies to phenomena that were known in excitation physiology. This finding suggested that a chemical kinetic principle exists that is capable of generalization and is not confined to living systems. In fact, many such, so-called "kinetic" model systems are known, and the analogies of their functioning to that of living systems that can undergo excitation is so astonishingly extensive that "no biological phenomenon of excitation is known that cannot be simulated by a kinetic model"[2].

The most obvious characteristic of all these systems is an "either-or" behavior that results from the ability of the system to exist in two different (stationary) states. Like the living systems, the models are open systems in the thermodynamic sense; a stationary state arises only if an inward flow from the environment compensates the outward flow from the system. These flows are caused by driving forces that originate from an energy or a potential difference. A superposition of the relations between flow and driving force for the system and for its surroundings should make it possible to interpret the behavior observed.

It can be clearly shown[3] how, for instance, superposition of a "load line" on a non-monotonic N-shaped characteristic of a system leads to the existence of two stable stationary states which are separated by an unstable one. If the characteristic of the system can shift relative to the characteristic of the evironment, because of the chemical kinetics, then an "either-or" behavior can be explained.

In the nerve-cell membrane the phenomenon of excitability is of electrochemical nature[4]. Like most model systems, the Fe/HNO_3 system, later called the Ostwald-Lillie nerve model, also belongs to electrochemistry[5]. As a typical electrode having a passivating film, iron shows the requisite non-monotonic course in its current-potential characteristic. The Fe/HNO_3 model can be used to simulate the most varied biological excitation phenomena[6]. In all other cases a non-monotonic characteristic of the system is found to be significant. Doubtless, occurrence of such characteristics is not confined to the particular set, "current-potential". On the contrary, excitable systems are to be expected whenever a non-monotonic course of any flow-driving force relation is the kinetic principle.

Lecture at Kiel (Germany), on October 19, 1967 [VB 105 IE]

German version: Angew. Chem. *80*, 156 (1968)

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[1] Cf. *H. L. Heatcoat*, Z. physik. Chem. *37*, 368 (1901).

[2] *U. F. Franck*, Ber. Bunsenges. physik. Chem. *68*, 876 (1964).

[3] *U. F. Franck*, Z. physik. Chem. N.F. *3*, 183 (1955).

[4] *A. L. Hodgkin*, *A. F. Huxley*, and *B. Katz*, J. Physiology *116*, 424 (1952).

[5] *K. F. Bonhoeffer*, Naturwissenschaften *40*, 301 (1953), and further literature cited there.

[6] *U. F. Franck*, Z. Elektrochem. angew. physik. Chem. *55*, 535 (1951); Chem.-Ing.-Techn. *38*, 612 (1966); and further literature cited there.

Condensation of D-Glucose with Aromatic Systems in Liquid Hydrogen Fluoride

By *F. Micheel*[*]

High polymers are formed by condensation, in nucleophilic reactions, of polycyclic aromatic hydrocarbons[1] with aldoses in liquid HF at room temperature. The site of substitution can be determined by condensation with [1-^{14}C]-D-glucose and oxidation to carboxylic acids. Carbazole gives a polymer-homologous series of condensation products; C–C bonds occur in all of these, and the OH groups of the sugar residue can be acetylated.

Being aromatic systems, coals of various ages also give condensation products (labeling with [1-^{14}C]-D-glucose; glycosidically bound D-glucose is removed by hydrolysis)[2]. Moreover, very pure graphite (99.999 % of C) condenses with formation of covalent bonds (0.6–1.8 % of [1-^{14}C]-D-glucose)[3]. All the condensation products are free from water-soluble self-condensation products of D-glucose. Benzene and [1-^{14}C]-D-glucose afford, amongst other condensation products, triphenylmethane whose labeled tertiary C atom is derived from the D-glucose (yield: 15 %, calc. on D-glucose). Toluene and [1-^{14}C]-D-glucose yield, as well as a methylanthracene, a hydrocarbon $C_{24}H_{24}$, $[\alpha]_D = -44°$ (in benzene), which fluoresces blue in solution and contains aliphatic groups (yield: *ca.* 4 %, calc. on D-glucose).

Lecture at Clausthal-Zellerfeld (Germany), on October 27, 1967 [VB 106 IE]

German version: Angew. Chem. *80*, 156 (1968)

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[1] *F. Micheel* and *L. Rensmann*, Makromolekulare Chem. *65*, 26 (1963); *A. H. Haines* and *F. Micheel*, *ibid.* *80*, 74 (1964); *F. Micheel* and *H. Licht*, Tetrahedron Letters *1965*, 3701; Makromolekulare Chem. *103*, 91 (1967).

[2] *F. Micheel* and *D. Laus*, Brennstoff-Chem. *47*, 345 (1966).

[3] *F. Micheel*, Lecture at the International Symposium on Carbohydrate Chemistry, Kingston (Ontario), July 1967; Lecture at Osaka on October 13, 1967.

Individual Steps in the Chemisorption of Gases on Metals

By *W. M. H. Sachtler*[*]

The chemisorption of gases on metals is determined primarily, not by the collective parameters of the metallic state – Fermi level, holes in the d-band, *etc.* – but by the chemical

properties of the individual surface atoms and by those of the atoms of the gaseous molecule. Just as in complex chemistry, the chemical properties of an adsorbing atom are modified by its neighbors. A study has been made of the role played in chemisorption by the geometry (*e.g.* the size of the adsorbed atoms, number of adsorption sites on the surface) in comparison with the stoichiometry, *i.e.* the number of valence electrons of the surface atoms.

Chemisorption of gases of the type H_aX on pure Ge or Si surfaces follows stoichiometric laws[1]; each molecule dissociates into a H atoms and one X atom, each H atom saturates one surface atom, and each X atom saturates a surface atoms; thus, in sum, $2a$ surface atoms are saturated per H_aX molecule. The surface atoms behave as univalent species, since of each four valence electrons of each Ge atom three electrons are used for covalent bonding to the three nearest neighbors; the fourth electron is available for chemisorption, as a "dangling bond".

Stoichiometry also determines chemisorption by typical metals. However, in contrast to covalent crystals (such as Ge) metals do not confine themselves to the "dangling bonds"; instead, all the valence electrons are available for bonding with the adsorbate.

As a result chemisorption causes marked demetalization of the surface atoms and is therefore dissociative in two respects: the bonds within the gas molecule and also those within the surface can be broken. By using the field ion microscope it has been shown[2] that the surface atoms can even leave their original positions in the lattice and move to more favorable positions between or even above the adsorbate atoms. Such rearrangements can occur even at the temperature of liquid nitrogen. Since each atom that leaves its position in the lattice leaves a vacancy, which can then move into the interior of the crystal, the injection of vacancies caused by chemisorption is an additional phenonemon which has been verified experimentally.

Chemisorption often occurs in three successive stages:

1. Chemi-adsorption (surface atoms remain in their original places in the lattice).

2. Corrosive chemisorption (rearrangement of the atoms of the surface and of the adsorbate).

3. Ligand chemisorption (the metal atoms or ions that have migrated in process (2) complete their coordination number by further chemisorption).

Lecture at Berlin (Germany), on November 3, 1967 [VB 107 IE]
German version: Angew. Chem. *80*, 155 (1968)

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[1] *A. H. Boonstra*, Dissertation, TH Eindhoven, 1967.

[2] *A. A. Holscher* and *W. M. H. Sachtler*, Discuss. Faraday Soc. *41*, 29 (1966).

Formation and Properties of Molecular Complexes in the Excited State

By *A. Weller*[*]

The fluorescence spectrum of a solution that contains electron-acceptor (A) as well as electron-donor molecules (D) can disclose the formation of excited charge-transfer complexes A^-D^+ (heteroexcimers) by the appearance of a long-wave fluorescence emission that is structureless and unaccompanied by a corresponding change in the absorption spectrum. The molecular complexes, which are unstable in the ground state, are formed in accord with

$$\overset{*}{A} + D \rightarrow A^-D^+ \text{ or } \overset{*}{D} + A \rightarrow D^+A^-$$

in diffusion-controlled reactions between an excited and an unexcited molecule with an enthalpy of formation ($-\Delta H$) of several kcal/mole; at higher temperatures this enthalpy can be measured from the temperature-dependance of the relative fluorescence intensities, if back-reaction occurs.

The wave number of the maximum of the complex emission is governed by the simple energy relationship:

$$h\nu_{max} = IP_D - EA_A - (C + U) - H^{solv}_{A^-D^+} - E_{rep}$$

where IP_D is the ionization energy of the donor molecules, EA_A is the electron affinity of the acceptor molecules, $C + U$ is the Coulomb + resonance energy in the complex, $H^{solv}_{A^-D^+}$ is the solvation energy of the complex and E_{rep} is the repulsion energy between A and D in the ground state of the complex. The validity of this relation has been tested for a large number of acceptor-donor systems by using substituted and unsubstituted aromatic compounds and numerous solvents; this work confirms the assumptions made about the charge-transfer character of the excited molecular complexes. Moreover, it now becomes possible to estimate the resonance energy U, which can be ascribed to participation of localized excited structures

$$\overset{\bullet}{A}D \leftrightarrow A^-D^+ \leftrightarrow A\overset{\bullet}{D}$$

in the complex.

In the system naphthalene (D)/*p*-dicyanobenzene (A) at high concentrations, formation of excited triple complexes $(DD)^+A^-$ can be observed, which dissociate partly when the temperature is increased, yielding D and D^+A^- (excited).

The significance of these studies lies on the one hand in the possibility of studying the diffusion-controlled kinetics of molecular complex formation in relation to various parameters (solvent, temperature, pressure, *etc.*), and on the other in the fact that the heteroexcimers, which are readily detected by means of their characteristic properties, can appear as intermediates in redox reactions.

Lecture at Braunschweig (Germany), on November 6, 1967 [VB 108 IE]
German version: Angew. Chem. *80*, 156 (1968)

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Fine Structure of Ruthenium(III) Bromide

By *K. Brodersen*[*]

$RuBr_3$ crystals are rhombic (space group D^{13}_{2h})[2] and not, as hitherto assumed[1], hexagonal with the TiI_3 structure (space group D^3_{6h}). The unit cell (a = 6.47 Å, b = 11.205 Å, c = 5.855 Å) contains 4 formula units ($D_{X\text{-ray}}$ = 5.34 g cm^{-3}; $D_{pycn.}$ = 5.42 g cm^{-3}).

X-ray determination of the structure by Patterson and Fourier syntheses (refinement of the parameters by the method of least squares) shows characteristic $(Ru_2Br_3)Br_{6/2}$ groups as the structural unit with the Ru atoms in an approximately octahedral environment. The points in space group D^{13}_{2h} are occupied as follows:

4 Ru in 4 (e) with $x = 0.254_5$ and $z = 0.016_5$
4 Br_I in 4 (f) with $x = 0.587$ and $y = 0.599$
4 Br_{II} in 4 (f) with $x = 0.089$ and $y = 0.405_5$
2 Br_{III} in 2 (a) with $x = 0.571$
2 Br_{IV} in 2 (b) with $x = 0.945$

The magnetic moment is much depressed (to $\chi_{mol} = 108 \times 10^{-6}$ at 20 °C, temperature-independent) by the formation of Ru_2 groups. The interatomic distances are: Ru–Ru = 2.73 Å (shortest distance between two Ru_2 pairs in the chain = 3.12

Å); Ru–Br (within the Ru_2Br_3 group) = 2.46 Å; Ru–Br (to the 6 linking Br atoms) = 2.52 and 2.54 Å; Br–Br (shortest separations) = 3.38, 3.47, and 3.53 Å.

$RuBr_3$ with the grouping $(M_2X_3)X_{6/2}$ contributes to completion of the scheme set up by *Schäfer* and *Schnering* for the structures of transition-metal halides [3].

Lecture at Aachen (Germany), on October 24, 1967 [VB 109a IE]
German version: Angew. Chem. *80*, 155 (1968)

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[1] *H. G. Schnering, K. Brodersen, F. Moers, H. K. Breitbach,* and *G. Thiele,* J. Less-common Metals *11*, 288 (1966).

[2] *H. K. Breitbach,* Dissertation, Universität Erlangen-Nürnberg 1967.

[3] *H. Schäfer* and *H. G. Schnering,* Angew. Chem. *76*, 833 (1964).

Structure of β-$RuCl_3$, RuI_3, $IrBr_3$, and IrI_3

By *K. Brodersen* [*]

Comparison of powder diagrams shows that RuI_3 and β-$RuCl_3$ have the same structure as $RuBr_3$ [1]. Calculation of the intensities on the X-ray diagrams of RuI_3 and β-$RuCl_3$ gives good agreement between the calculated and the expermental intensities if the atomic parameters of the $RuBr_3$ structure are used [$(Ru_2X_3)X_{6/2}$ units]. The structure given by *Fletcher* [2] for β-$RuCl_3$ must therefore be refined analogously to the $RuBr_3$ structure; this is also supported by the splitting of the Ru–Cl bands in the IR spectrum [2], which is in agreement with the D_{2h} symmetry found by us [1]. The molar susceptibilities [1,2] correspond only to a temperature-independent paramagnetism, and not to the temperature-dependent paramagnetism expected for the d_ε^5-configuration of Ru^{3+}.

$IrBr_3$ and IrI_3 (single crystals obtained by "chemical transport": 900 → 450 °C or 1000 → 400 °C [3]) crystallize in the monoclinic form with lattice constants: $IrBr_3$, a = 6.30 Å, b = 10.98 Å, c = 6.34 Å, and β = 108.7 °; IrI_3, a = 6.74 Å, b = 11.75 Å, c = 6.80 Å, and β = 108 °.

$IrBr_3$ has the $AlCl_3$ structure, but strongly disordered [3]. Model calculations indicate that these dislocations are to be attributed to shift of complete Br–Ir–Br layers, the cubic close packing of the Br atoms being retained during the shift. The $AlCl_3$ and $CrCl_3$ types now appear to be only special cases of a type of structure having cubic close packing of anions and an ordered distribution of the cations within one layer [3].

Lecture at Giessen on November 14, 1967 [VB 109b IE]
German version: Angew. Chem. *80*, 155 (1968)

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[1] *H. K. Breitbach,* Dissertation, Universität Erlangen-Nürnberg 1967.

[2] *J. M. Fletcher, W. E. Gardner, A. C. Fox,* and *G. Topping,* J. chem. Soc. (London) *A 1967*, 1038.

[3] *H. Ohnsorge,* Dissertation, Universität Erlangen-Nürnberg, 1967.

SELECTED ABSTRACTS

The H/D isotope effect of salt-like hydrides must lead to a decrease in the lattice constants of the crystal on H → D exchange, according to the potential curves. (The lattice constants increase for homopolar bonds.) *V. Subrtová* found the values given in the table for salt-like hydrides by X-ray measurements on powders under nitrogen.

Compound	Crystallographic class	Lattice constants
NaH/NaD	cubic NaCl type	a = 4.885 ± 0.001/ 4.871 ± 0.001
$NaBH_4/NaBD_4$	cubic NaCl type	a = 6.163 ± 0.001/ 6.146 ± 0.001
$NaAlH_4/NaAlD_4$	tetragonal scheelite type $I\,4_1/a$	a = 5.024 ± 0.001/ 5.011 ± 0.001 c/a = 2.259
$LiBH_4/LiBD_4$	rhomb. Pcmn	a = 6.827 ± 0.002/ 6.769 ± 0.002 c/a = 1.052

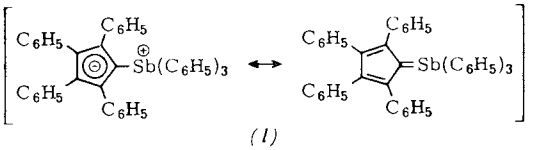
/ Z. anorg. allg. Chem. *350*, 211 (1967) / –Jg. [Rd 748 IE]

The resolution of racemates on optically active polymers has been studied by *G. Manecke* and *W. Lamer.* Chlorosulfonyl-substituted polystyrene (bead polymer, 200–400 mesh; with 2% of divinylbenzene) was first linked to L-arginine, L-α-phenylethylalanine, or L-ephedrine in dioxane or dioxane/water *via* sulfonamide bridges. 50 to 500 mg of DL-mandelic acid or DL-α-aminophenylacetic acid could be partially resolved on these polymers on columns 80 cm long and 1 cm in diameter (elution rate 6 to 12 ml/h; 1.5 ml fractions). Fractions containing an excess of the D-antipode are always eluted first; the results obtained on resolution of 70 mg of DL-mandelic acid on resin containing L-arginine are shown in the table.

ml of eluate after breakthrough	Concentration (mg/ml)	Specific rotation $[\alpha]_{313}$ (°)	Activation (%)
1.5	0.51	–55	6
4.5	3.07	–39	4.3
7.5	6.83	–24	2.7
10.5	10.69	+21	2.3
13.5	0.27	+89	9.8

/ Naturwissenschaften *54*, 140 (1967) / –Jg. [Rd 731 IE]

A crystalline antimony ylide, tetraphenylcyclopentadienylidene triphenylstiborane *(1)* has been synthesized for the first time by *D. Lloyd* and *M. I. C. Singer* by heating diazotetraphenylcyclopentadiene in molten triphenylstibine under N_2 at 140 °C (isolation by the addition of ether); m.p. 196–198 °C, ochre crystals, soluble in mineral acids, λ_{max} = 349 nm



(1)

(benzene). *(1)* is converted by prolonged heating mainly into tetraphenylcyclopentadiene. / Chem. and Ind. *1967*, 787 / –Ma. [Rd 721 IE]

The preparation and properties of boranocarbonates have been investigated by *L. J. Malone* and *R. W. Parry*. The structure of the anion corresponds to that of a carbonate in which one oxygen atom is replaced by the isoelectronic H_3B group. Potassium and calcium boranocarbonates are obtained in good yields as air-stable, water-soluble salts by the following reactions:

$$H_3BCO + 2\,KOH \xrightarrow{\text{alcohol}} K_2H_3BCO_2 + H_2O$$

$$H_3BCO + CaO \xrightarrow[H_2O\ (\text{trace})]{25\,^\circ C} CaH_3BCO_2$$

The H_3BCO, which may be prepared from the two condensed components B_2H_6 and CO, is not isolated in the pure state, but is introduced into the reaction in the form of an $H_3BCO/CO/B_2H_6$ mixture. IR investigations show the boranocarbonate ion to possess the symmetry of the acetate ion; the acid $H_2(H_3BCO_2)$ is rather weaker than carbonic acid. When treated with 85 % H_3PO_4, the boranocarbonates give H_3BCO of extremely high purity. / Inorg. Chem. *6*, 817 (1967) / –Sch. [Rd 761 IE]

The preparation of aziridines by reduction of α-chloronitriles with $LiAlH_4$ is reported by *K. Ichimura* and *M. Ohta*. The procedure is simple and leads to good yields. Rather more than one equivalent (≈ 1:1.3) of a suspension of $LiAlH_4$ in ether is added dropwise at −5 to 0 °C to a solution of α-chloronitrile in ether. After a few hours, the excess of $LiAlH_4$ is decomposed with alkali. No piperazines (which occur as by-products when Grignard compounds are used instead of $LiAlH_4$) or β-chloroamines are formed.

$$R\text{-}CHCl\text{-}CN \xrightarrow{LiAlH_4} RHC\!-\!CH_2 \quad (N\text{–}H)$$

R	B.p. (°C/mm)	Yield (%)
n-C_3H_7	114–118/760	82
i-C_3H_7	104–106/760	72
n-C_6H_{13}	100/40	62
C_6H_5–CH_2	117.5–118/22	58
C_6H_5	97–99/13	46

/ Bull. chem. Soc. Japan *40*, 432 (1967) / –Jg. [Rd 750 IE]

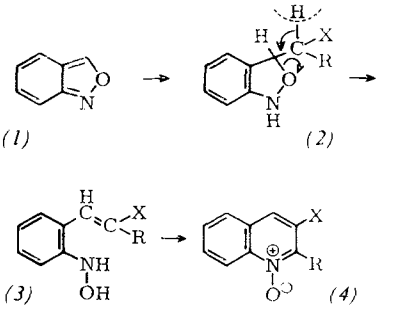
A one-stage synthesis of aliphatic nitriles was achieved by *J. A. Findlay* and *C. S. Tang*, starting from aldehydes. If a solution of aliphatic aldehydes, aldehyde trimers, or aldehyde-bisulfite compounds is boiled with hydroxylamine hydrochloride and a few drops of hydrochloric acid in 95 % ethanol for six hours under reflux, the corresponding nitrile is obtained in a practically quantitative yield. For example:

n-octanal	→	octanenitrile (83% yield)
n-tetradecanal	→	n-tetradecanenitrile (90% yield)
n-octadecanal bisulfite	→	n-octadecanenitrile (89% yield)
octadecanal trimer	→	n-octadecanenitrile (87% yield)

/ Canad. J. Chem. *45*, 1014 (1967) / –DK. [Rd 758 IE]

The use of dipotassium tetraisothiocyanatocobaltate(II) enables the detection of oxygen-containing organic molecules to be carried out more comprehensively and simply than previously (*e.g.* with iron(III) thiocyanate, or with CO formation at 1100–1500 °C over carbon). According to *F. Buscaróns* and *M. Pareira*, the microtest (mg range) depends upon the fact that $K_2Co(SCN)_4 \cdot 4H_2O$ rapidly turns blue on contact with a large number of liquid organic compounds (or solid compounds that can be heated up to the melting point without decomposition). Investigations conducted with 500 compounds showed that the test is negative for hydrocarbons and halogenated hydrocarbons of all types, and for mercaptans, thioethers, thiones, amines, heterocycles, and azo compounds. Positive reactions were obtained with ethers, alcohols and phenols, aldehydes and ketones, carboxylic acids and their esters, carboxylic amides halides, and anhydrides, quinones, and nitro compounds. Nitriles although oxygen-free, also react, while thymol, furan, and compounds that themselves are reagents for Co, such as imidodioxines and α-nitroso-β-naphthol do not react. / Analyt. chim. Acta *37*, 490 (1967) / –Jg. [Rd 784 IE]

The ring expansion of benzoxazole to form quinoline 1-oxides *(4)* in reactions with a number of active methylene compounds, such as $NC\text{–}CH_2\text{–}R$ and $C_2H_5O_2C\text{–}CH_2\text{–}R$, has been observed by *E. C. Taylor* and *J. Bartulin*. Thus the reaction of benzoxazole *(1)* with malonodinitrile in the presence of a catalytic quantity of piperidine is exothermic and leads to 2-amino-3-cyanoquinoline 1-oxide (yield 99 %). Less reactive methylene compounds are best used in the form of their alkali metal salts. The reaction probably proceeds



(1) *(2)* *(3)* *(4)*

via (2) and *(3)*. Examples: ethyl cyanoacetate → 3-cyano-1-hydroxy-1,2-dihydroquinolin-2-one (97 %); phenylsulfonylacetonitrile → 2-amino-3-phenylsulfonylquinoline 1-oxide (82 %). / Tetrahedron Letters *1967*, 2337 / –Ma. [Rd 723 IE]

A new type of compound of sulfuryl diamide was reported by *D. Zoellner* and *A. Meuwsen*. When dry HCl is passed into a cold suspension of sulfuryl diamide in acetonitrile, compound *(1)* is obtained as odorless, non-hygroscopic crystals (m.p. 160–162 °C (decomp.), 64 % yield). Compound *(1)* may be

$$CH_3\text{–}CN + (H_2N)_2SO_2 + HCl \rightarrow CH_3\text{–}C(=NH_2^{\oplus}Cl^{\ominus})\text{–}NH\text{–}SO_2\text{–}NH_2 \quad (1)$$

recrystallized from hot glacial acetic acid, and is readily soluble in cold anhydrous methanol but practically insoluble in ether, ethyl acetate, acetone, $HCCl_3$, CCl_4, C_6H_6, and boiling CH_3CN. The reaction of a cold methanolic solution of *(1)* with a similar solution of KOH gives a 55 % yield of

$$(1) + KOH \rightarrow CH_3\text{–}C(=NH)\text{–}NH\text{–}SO_2\text{–}NH_2 + KCl + H_2O \quad (2)$$

(2) in the form of crystals which are stable in air, melt at 125–130 °C (decomp.), and can be recrystallized from boiling CH_3CN. Compound *(2)* is soluble in cold methanol or ethanol; in water it is slowly hydrolyzed to acetamide and sulfuryl diamide. / Z. anorg. allg. Chem. *349*, 19 (1967) / –Sch. [Rd 764 IE]

Complexes of trivalent manganese have been prepared by *H. Funk* and *H. Kreis* by slow addition of fresh, anhydrous, ethereal $MnCl_3$ solutions (from manganese dioxide + HCl) to the other component at −40 and −5 °C. The complexes are

Complex	Color/stable up to (°C)	Remarks
$MnCl_3$·3 amine	brown/20	amine = NH_3; $C_nH_{2n+1}NH_2$ (n = 1 to 4; $(CH_3)_2NH$; $(C_2H_5)_2NH$
$MnCl_3$·3 R_3N	dark brown or dark green	R = C_2H_5; $C_6H_5CH_2$
$MnCl_3$·3 Z	green/100	Z = pyridine, quinoline
$MnCl_3$·2 Z	brown	Z = H_2N-CH_2-CH_2-NH_2; piperidine
$MnCl_3$·Z	green/−10	Z = pyridine,quinoline
$MnCl_3$·A	dark red or dark brown/180	A = α,α'-bipyridyl; o,o'-phenanthroline
$MnCl_3$·5 THF·HCl	red brown/−40	Probably as $MnCl_4^{\ominus}$onium salt
$MnCl_3$·4 THF	brown-violet/5	
$MnCl_3$·2(1,4-dioxane)	red violet/20	
$MnCl_2$(acac)	green/−30	acac = acetyl acetonate
$MnCl(acac)_2$	green-brown/≈10	

nearly all sensitive to water, but are much more stable in the dry state than "free" $MnCl_3$ (decomposes above −35 °C). / Z. anorg. allg. Chem. *349*, 45 (1967) / −Jg. [Rd 734 IE]

The diazotizability of aminophenols in concentrated tetrafluoroboric acid has been studied by *O. Daněk*, *D. Šnobl*, *I. Knížek*, and *S. Nouzová*, since fluorophenols had already been obtained in this way. 1.4 mole of 40 % HBF_4 is added to 0.5 mole of the aminophenol at −5 to −10 °C, and the aminophenol is diazotized with 0.5 mole of aqueous $NaNO_2$ solution at a temperature not exceeding 0 °C. The compounds listed in the table, which crystallize out at −10 °C, are formed as intermediates, and can be converted into fluorophenols by heat.

Intermediate [a]	Decomp. temp. (°C)	Fluoro-phenol	B.p. (°C/mm)	Yield (%)
2Hydrb. BF_4Z	99	*ortho*	49—50/14	37.4
3Hydrb. BF_4	78	*meta*	75/15	34.8
4Hydrb. BF_4Z	128	*para*	83—84/15	69.5

[a] Hydrb = hydroxybenzenediazonium; Z = 2,2-diazidocyclohexadienone; bound by N....OH bridges, according to NMR- and IR-spectroscopic results.

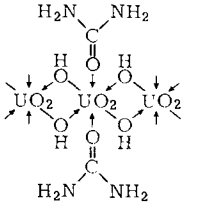
/ Collect. czechoslov. chem. Commun. *32*, 1642 (1967) / −Jg. [Rd 753 IE]

The cofactor requirement of collagen-proline hydroxylase has been determined by *J. J. Hutton*, *A. L. Tappel*, and *S. Udenfriend*. It was found that iron(II) ions, α-ketoglutarate, and ascorbate are required in addition to oxygen. The Michaelis constants were 3×10^{-5}, 3×10^{-6}, and 2×10^{-4} in a standard mixture containing 10^{-4} M iron(II) ion, 10^{-4} M α-ketoglutarate, and 5×10^{-4} M ascorbate. The α-ketoglutarate is assumed to have a regulating function. Though α-ketoglutarate was consumed in the tests, no correlation could be detected between this consumption and the formation of hydroxyproline. The enzyme from chick embryo was purified to such an extent that the cofactor requirement was "absolute", but this gave only a small increase in specific activity; moreover, the purity was not sufficient to explain the stoichiometry. The enzyme catalyzes the hydroxylation of certain proline residues in polypeptides that are rich in proline but poor in hydroxyproline and which can be broken down by collagenase.

$$\text{Peptidylproline} + \text{ascorbate} + O_2 \xrightarrow[Fe^{2+}]{\text{α-ketoglutaric acid}} \text{peptidylhydroxyproline} + \text{dehydroascorbate} + H_2O.$$

The measurement of the hydroxylase activity is based on the determination of tritium in the water of the reaction mixture on hydroxylation of [3,4−T_2]-proline in peptides. These peptides are obtained from chick embryos or are synthesized. The triple-helix structure of collagen is not essential to its suitability as a substrate for the hydroxylase. / Arch. Biochem. Biophysics *118*, 231 (1967) / −Hö. [Rd 708 IE]

The structure of the dihydroxyuranyl-urea complex, which was first prepared in 1958 and isolated as the urea uranate, has been elucidated by *W. Dembiński* and *A. Deptuła*. Whereas true uranates (polyuranates) are precipitated from uranyl salt solutions by strong bases such as NaOH or $Ba(OH)_2$, urea (the tendency of $UO_2^{2\oplus}$ to assume a coordination number of 6 and to form O and HO bridges is well known) gives the dihydroxyuranyl complex *(1)*, for the following reasons: a) the IR region around 3000 cm^{-1} is so little wider than that of free urea that only OH−NH_2 bridges are conceivable; there are no $-NH_3^{\oplus}$ bands at about 1050 cm^{-1}; the C=O band, which normally occurs at about 1680 cm^{-1}, is displaced by 55 cm^{-1} toward longer wavelengths,

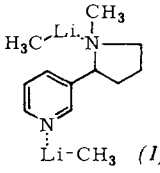


(1)

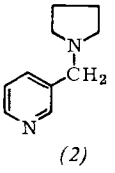
indicating CO−U coordination (Cr(III)- or Ti(IV)-urea complexes behave similarly). b) Thermal decomposition begins only 30 °C above the melting point of free urea; numerous decomposition products point to covalent bonding of the components. c) Even bases 10^4 times as strong, such as aniline or quinoline, do not form salts, but precipitate $UO_3\cdot2H_2O$. d) NH_3 is displaced from its complexes by the weaker base urea. e) The "cation": U ratio is only 1:1 even for stronger bases, but is 2:1 in this case. f) The molar volumes of $UO_2(OH)_2$, $UO_2(OH)_2\cdot H_2O$, $UO_2(OH)_2\cdot[CO(NH_2)_2]_2$, $UO_2(OH)_2\cdot[CONH_2NHCH_3]_2$ are linearly related to the molar volumes of their components. / J. inorg. nuclear Chem. *29*, 799 (1967)/− Jg. [Rd 742 IE]

The synthesis of *N*-(*t*-butyloxycarbonyl)amino acids, which are important components for peptide syntheses, has been optimized by *E. Schnabel* with respect to reaction rate and yield by the use of the correct pH value (pH-stat reaction; autotitrator). Free as well as sterically hindered or *N*-benzyl- and *N*-carbobenzoxy-substituted amino acids (Ala, Arg(NO_2) Arg(Tos), Asp (NH−NH−Boc), Glu(NH_2), Ile, Lys(Z), Met, Sar, Thr(Bu^t) *etc.*) react smoothly and in yields of 80 to 100% with a 10 % excess of *t*-butyl azidoformate in dioxane/water (1:1), water, or acetone within a few hours; examples of suitable bases are Na_2CO_3, $NaHCO_3$, $N(C_2H_5)_3$, NaOH, or MgO (pH = 8.5 to 12, generally 9.8). The *N*-(*t*-butyloxycarbonyl = Boc)amino acids or their Na salts are generally obtained in a very pure and crystalline state; they can be purified *via* the dicyclohexylammonium salts. / Chem. Ber. *702*, 188 (1967) / −Jg. [Rd 743 IE]

***para*-Substitution on Ziegler-Zeiser alkylation** was observed for the first time by *F. Haglid* and *J. O. Norén*. In contrast to pyridine, nicotine and *N*-(3-picolyl)-pyrrolidine *(2)* were also methylated in position 4 by methyllithium in ether/toluene. The ratio of substitution in positions 2, 4, and 6 was trace:1:5 in the case of nicotine and 5:1:2.75 in the case of *(2)*; different values were obtained with other solvents.



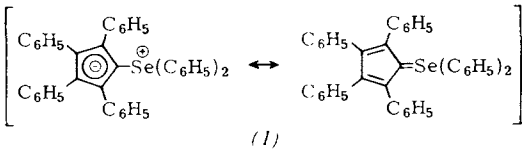
(1)



(2)

It is assumed that 4-alkylation occurs with nicotine and *(2)* *via* a methyllithium primary complex, as shown in *(1)* for nicotine. The preference for position 2 in *(2)* may be explained by the low steric hindrance for this position in comparison with nicotine. / Acta chem. scand. *21*, 329, 335 (1967) / –WG.
[Rd 766 IE]

The synthesis of a selenium ylide has been described for the first time by *D. Lloyd* and *M. I. C. Singer*. When diazotetraphenylcyclopentadiene was heated at 140 °C (10 min) in diphenylselenide under N_2, dilution of the cooled green solution with ether/petroleum ether gave yellow crystals of

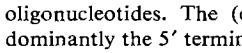


(1)

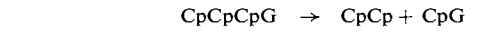
diphenylselenonium-tetraphenylcyclopentadienylide *(1)*, m.p. 188–190 °C (decomp.), in 93 % yield. The IR spectrum is very similar to that of the sulfonium analog. *(1)* is stable in air in the absence of light, is only weakly basic, and is insoluble in HCl. / Chem. Commun. *1967*, 390 / –Ma.
[Rd 730 IE]

The monomer of the fd phage coat protein has a molecular weight of only 5163 and consists of 49 amino acid units, according to *G. Braunitzer et al.* The protein coat of the phage is built up of approximately 1900 of these units. The protein sequence has been almost completely determined. Because of the particularly high proportion of helical structures, the protein is highly resistant to attack by peptidases. The chain contains no cysteine, histidine, or arginine. At the carboxyl end there are five lysine units next to one another. The only proline unit is at position 6 from the amino end. Apart from the peptide hormones, the phage protein is the smallest functional protein yet known. In view of its small size, the methods now available (*e.g.* the Merrifield synthesis) make its total synthesis, and thereby the partial synthesis of a phage, appear possible. / Hoppe-Seylers Z. physiol. Chem. *348*, 725 (1967) / –Hö.
[Rd 773 IE]

Micrococcus nuclease has been investigated by *H. Feldmann* with regard to its suitability for the sequence analysis of oligonucleotides. The (crystallized) enzyme splits off predominantly the 5′ terminal dinucleoside diphosphate and the 3′terminal dinucleoside phosphate.



For this reason, tetranucleotides are mainly cleaved at the middle.

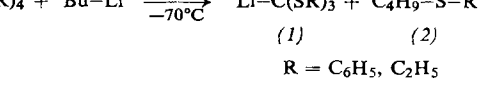


Pentanucleotides give the central nucleotide and the two terminal dinucleotides. In certain combinations of nucleotides other bonds are attacked, *e.g.* the internucleotide bonds in ApAp, CpCp, and CpG appear to be particularly labile. Clear results appear to be obtained only from pentanucleotides downward; for example, it appears that the bonds of heptanucleotides are first attacked endonucleolytically, and then the shorter oligonucleotides are degraded according to the above scheme. Once formed, dinucleotides appear to be stable. Despite these limitations the enzyme promises to be a useful tool for sequence analysis. / European J. Biochem. *2*, 102 (1967) / –Hö.
[Rd 774 IE]

Hexagonal diamond, a new modification of carbon, is formed from graphite at a static pressure of over 130 kbar and at a temperature greater than 1000 °C. As *F. B. Bundy* and *J. S. Kasper* show, it is necessary to start from well-crystallized graphite, in which the *c* axes of the crystallites are parallel to one another and to the direction of compression. During the conversion, the electrical resistance in the direction of the graphite *c* axis increases by a factor of about 4, and at right angles to this it increases by a factor of 10 to 200, depending on the completeness of the graphite lattice. The crystal structure of the product is hexagonal, with $a = 2.52$ Å and $c = 4.12$ Å. / J. chem. Physics *46*, 3437 (1967) / –Hz.
[Rd 782 IE]

The distortions of IR bands as a result of finite spectral slit width are corrected by *R. N. Jones*, *R. Venkataraghavan*, and *J. W. Hopkins* with the aid of a mathematical process which they call "pseudo-deconvolution". The requirements are a spectrophotometer with digital output, a digital computer, and a digital-analog converter for plotting the corrected spectra. A distortion of the true spectra occurs because the transmission measured at a given wavelength also includes contributions from light of neighboring wavelengths, the extent of this being determined by the dispersion of the prism or lattice and by the slit width. In mathematical terms, the spectrum measured is the result of the "convolution" (folding) of the true absorption spectrum with the slit functions, *i.e.* the degree of transmission of the slit in the neighborhood of the measuring wavelength. Reversal of this convolution is a highly complex mathematical process. It is, however, possible to convolute the measured spectrum further with the slit function (which is assumed to be triangular or Gaussian), by integrating the product of the sample transmission and the slit transmission twice with the wavelength as the integration variable. To a good approximation, the spectrum thus obtained deviates twice as strongly from the true spectrum as the measured one. The true spectrum can thus be reconstructed. The method was tested with simulated spectra (both isolated and overlapping bands with Lorentz profile). The increase in resolution is the same as that obtained by halving the spectral slit width. / Spectrochim. Acta *23* A, 925, 941 (1967) / –Hz.
[Rd 783 IE]

Carbanion formation from esters of orthothiocarbonic acid was observed by *G. A. Wildschut*, *H. J. T. Bos*, *L. Brandsma*, and *J. F. Arens* when the esters were allowed to react with butyllithium in THF at –70 °C. As a result of nucleophilic attack at the sulfur, the metalated triester of orthothioformic acid *(1)* and the corresponding butyl sulfide *(2)* were formed



(1) *(2)*

R = C_6H_5, C_2H_5

Compound *(1)* is smoothly alkylated with alkyl iodide or allyl bromide [CH_3–$C(SC_6H_5)_3$: 88–90 %, m.p. 146–148 °C; CH_2=CH–CH_2–$C(SC_2H_5)$: 76 %, b.p. 77–92 °C/0.45 torr], and is carboxylated with gaseous CO_2 [$(C_6H_5S)_3C$–COOH: 82 %, m.p. 97–100 °C]. If alkylation does not take place, then tetrakis(phenylthio or ethylthio)ethylene *(5)* is formed (R = C_6H_5: 45 %, m.p. 154–156 °C; R = C_2H_5: 68 %, m.p. 153–156 °C); carbenes *(4)* must be an intermediate product in this conversion. They are formed in an equilibrium reaction from *(1)* by the elimination of lithium thiolate *(3)*. Compound *(5)* is only obtained easily if *(3)* is removed from the equilibrium mixture by alkylation.

$$\underset{(1)}{2\ Li{-}C(SR)_3} \rightleftharpoons \underset{(3)}{2\ Li{-}S{-}R} + \underset{(4)}{2{:}C(SR)_2} \rightarrow \underset{(5)}{(RS)_2C{=}C(SR)_2}$$

Compound *(1)* may also be prepared from orthothioformic esters and butyllithium. / Mh. Chem. *98*, 1043 (1967) / –DK. [Rd 755 IE]

The dimer-monomer equilibrium of triethylaluminum in *n*-hexadecane solution was determined calorimetrically by *M. B. Smith* in a specially developed apparatus (quantities: approx. 160 ml *n*-hexadecane, a few ml of $Al(C_2H_5)_3$; ΔT determination with a resistance thermometer to within 10^{-4} °C); the values were determined experimentally from 60 to 150 °C, and by extrapolation up to 0 and 210 °C. The total heat of dilution Q_T can be resolved mathematically into the heat of dissociation Q_D and the heat of mixing Q_M (which decreases linearly with increasing mole fraction of $Al(C_2H_5)_3$). The calculation of the thermodynamic data (computer program for a nonlinear least-squares relationship for Q_T) is based on the following assumptions: (a) only dimers and monomers are present (K_D = monomer²/dimer); (b) K_D is the same in liquid $Al(C_2H_5)_3$ and in *n*-hexadecane solutions of various concentrations (same behavior as for a mixture of two hydrocarbons); (c) the temperature dependence of Q_D is negligible.

$$\Delta H_D^\circ = 16.9_{30} \pm 0.2_{30}\ \text{cal·mole}^{-1}$$

$$\Delta S_D^\circ = 32.1_9 \pm 0.6_3\ \text{cal·deg}^{-1}\text{·mole}^{-1}$$

$$\log K_D = 7.03_{44} = 370_{0.4}/T$$

From this it follows that K_D (0 °C) = 3.072×10^{-7} and K_D(210 °C) = 0.2374. On the other hand, molecular-weight determinations show that $Al(C_4H_9)_3$ and $Al(C_6H_{13})_3$ are already considerably dissociated at 0 °C. / J. physic. Chem. *71*, 364 (1967) / –Jg. [Rd 788 IE]

The existence of the tetrafluoroammonium cation has been definitely proved, according to *K. O. Christe, J. P. Guertin, A. E. Pavlath*, and *W. Sawodny*. The structure $NF_4^\oplus AsF_6^\ominus$ had already been assumed for the adduct $NF_3{\cdot}AsF_5{\cdot}F_2$, prepared in 1966 from an $NF_3/AsF_5/F_2$ mixture by glow discharge, on the basis of thermal stability and X-ray data. The following proofs can now be produced for two highly symmetrical ions: from the NMR spectrum (94 MHz, $CFCl_3$ as external standard; 25 °C, HF solution) the authors obtained δ_{As-F} = 69.5 ppm (Q) and J_{As-F} = 870 Hz (similar values for the structures $Ag^\oplus AsF_6^\ominus$ and $NO^\oplus AsF_6^\ominus$) and also δ_{N-F} = –213.5 ppm (T; half-width max. 10 Hz) and J_{N-F} = 234 Hz. The triplet and the low half-width indicate a symmetrical electric field around the ^{14}N nucleus (I = 1; T_d); $N_2F_3^\oplus$, $N_2F^\oplus$, $NF^\oplus$, $NF_3^\oplus$, *etc.*, give much broader signals. The infrared and Raman spectra, recorded for the crystal or in hydrofluoric acid solution, showed all the bands that would be expected for $AsF_6^\ominus$ [709(F_{1u}), 687(A_{1g}), 581(E_g), 406(E_{1u}), 378(F_{2g}), 147(F_{2u})] and for $NF_4^\oplus$ [1159(F_2), 813–815(A_1), 611(F_2), 488(E)]. A bond order of 0.85 is derived for the N–F bond in $NF_4^\oplus$ from the force constants. / Inorg. Chem. *6*, 533 (1967) / –Jg. [Rd 787 IE]

Volatile silanes can be halogenated in stages with silver chloride or bromide, as *R. P. Hollandsworth, W. M. Ingle*, and *M. A. Ring* have shown. Chloro- and bromogermanes have already been prepared in a similar manner. The silane (1–2.2 mmole) is passed over layers of silver halide (approximately 22.5 g), which are retained by layers of glass wool, in a Pyrex tube at 90–280 °C; the experiment is carried out in a vacuum apparatus. Up to the present, the systems given in the table have been converted according to eq. (a) or (b).

$$\text{Si–H} + 2\ AgCl \longrightarrow \text{SiCl} + HCl + 2\ Ag \qquad (a)$$

$$\text{SiH} + AgBr \longrightarrow \text{SiBr} + {}^1/_2\ H_2 + Ag \qquad (b)$$

System	Yield (%) monochlorinated product	dichlorinated product
$SiH_4/AgCl$	38	7.5
$CH_3SiH_3/AgCl$	60.5	8
$(CH_3)_2SiH_2/AgCl$	37	18.5
$(CH_3)_3SiH/AgCl$	39	–
$SiH_4/AgBr$	31.5	3
$Si_2H_6/AgCl$	30	(5.5)

The method is now being tested for the synthesis of disilanes. / Inorg. Chem. *6*, 844 (1967) / –Jg. [Rd 786 IE]

Isotope-exchange experiments to determine the mechanism of the enzymatic phosphoenolpyruvate (PEP) synthesis are proposed by *R. A. Cooper* and *H. L. Kornberg*. The reaction (1) which is catalyzed by PEP synthase from *Escherichia coli*, takes place in stages (2), (3), and (4).

(1) ATP + pyruvate ⇌ AMP + phosphate + PEP

(2) Enzyme + ATP ⇌ enzyme pyrophosphate + AMP

(3) Enzyme pyrophosphate + H_2O ⇌ enzyme phosphate + phosphate

(4) Enzyme phosphate + pyruvate ⇌ enzyme + PEP.

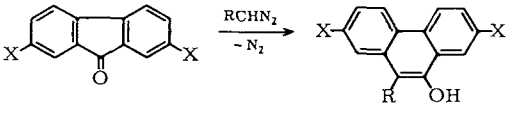
The formulation of reaction (2), (3), and (4) is supported by the following isotope-exchange reactions: (a) ^{14}C–AMP is rapidly incorporated into ATP on incubation with the enzyme, $MgCl_2$, and ATP; ADP has no influence on this reaction, but it is inhibited by fluoride and ethylenediaminetetraacetate (EDTA); (b) ^{32}P-phosphate is incorporated into ATP on incubation of ATP with enzyme, $MgCl_2$, and AMP; pyruvate is not necessary, but AMP must be present; (c) ^{14}C-pyruvate is incorporated into PEP if PEP is incubated with enzyme and $MgCl_2$; phosphate, ATP, and AMP are not necessary. These reactions are inhibited by EDTA but not by fluoride. Reactions (2)–(4) are more rapid than the forward reaction of (1). There is no proof for a direct phosphate transfer from ATP to pyruvate. / Biochim. biophysica Acta *141*, 211 (1967) / –Hö. [Rd 775 IE]

***N*-Acetyl-phenylalanyl-tRNA** is the starter for the polyuridylic acid-controlled synthesis of polyphenylalanine, according to *J. Lucas-Lenard* and *F. Lipmann*. The most important prerequisite for a starter appears to be the blocked amino group, since dipeptidyl-tRNA is also active. *N*-Formylmethionyl-tRNA generally functions as a starter in intact biological systems. In polyphenylalanine synthesizing systems from *Pseudononas fluorescens*, at lower (4 mM) magnesium-ion concentrations two further factors, f_1 and f_2, are involved in the start mechanism; they have been recovered from ribosomes by washing with 1 M ammonium chloride. They bind the *N*-acetyl-phenylalanyl-tRNA to the ribosomes; the cofactor for this reaction is GTP. The two factors are not identical with one of the three enzyme fractions G, T_s, T_u, which are also necessary for polypeptide synthesis. / Proc. nat. Acad. Sci. U.S.A. *57*, 1050 (1967) / –Hö. [Rd 770 IE]

Copper is a catalytically active component of cytochrome c oxidase from ox heart muscle. The copper content of the enzyme was already known, but the non-specific redox behavior of copper made its biological function appear questionable. *P. M. Nair* and *H. S. Mason* showed that removal of the copper from the enzyme caused a loss of enzymic activity, and that the enzyme could be reactivated with Cu(I). The copper was removed by means of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonic acid ("bathocuproinsulfonic acid"), but only under anaerobic conditions in the presence of reduced cytochrome c. On incubation of the deactivated enzyme with equimolecular amounts of Cu(I)-acetonitrile perchlorate ($Cu(CH_3CN)_4ClO_4$), 3 to 4 fold stimulation over the initial activity was obtained. The assumption that the normal enzyme preparations are deficient in copper is supported by the fact that untreated cytochrome c oxidase is also activated by a factor of about 3 on treatment with Cu-acetonitrile. / J. biol. Chemistry *242*, 1406 (1967) / –Hö.

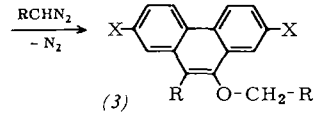
[Rd 776 IE]

Ring expansion of fluorenones to phenanthryl ethers was achieved by *B. Eistert* and *M. A. El-Chahawi* with diazomethane or diazoethane.



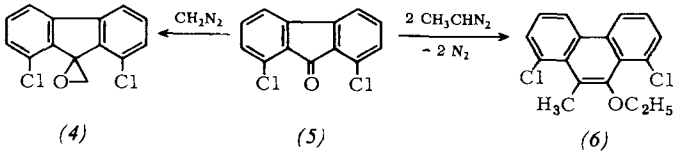
(1) *(2)*

(a): R = X = H
(b): R = H, X = Br



(3)

Fluorenone *(1a)* and dibromofluorenone *(1b)* react to give alkoxyphenanthrenes *(3)* only if pure distilled diazomethane or diazoethane solutions are used, the yields being respectively 90 and 75 %. If diazomethane is produced *in situ* from *N*-nitroso-*N*-methylurethane, as suggested by *R. F. Schultz et al.*, then then main product is the non-alkylated phenanthrol *(2a)* (30 %), with only a little *(3a)* (1.5 %). 1,8-Dichlorofluorenone *(5)* also reacts with diazoethane to give a



(4) *(5)* *(6)*

ring expansion product [*(6)*, m.p. 103–104 °C], but with diazomethane it gives the epoxide *(4)* (m.p. 240 °C). / Mh. Chem. *98*, 941 (1967) / –WG.

[Rd 767 IE]

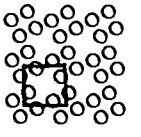
Catalase from human erythrocytes crystallizes in the form of tubes, as shown by micrographs taken by *N. A. Kiselev C. L. Shpitzberg*, and *B. K. Vainshtein.* The tube walls are formed from a monomolecular layer. The diameter of the tubes is 420 Å and the wall thickness is approximately 65 Å. The molecules (molecular weight 250000) are arranged in two parallel strands, each 75–80 Å in width, which form a helix. Thus the pitch of the helix is 150–160 Å; each turn of each strand contains about 23 molecules. The coordination number of the individual molecules is 6. The crystals studied were obtained from 1.5M ammonium sulfate solution at pH 6.5–7. Catalase obtained from ox liver crystallizes in the same form under these conditions, but with slightly different dimensions. / J. Molecular Biol. *25*, 433 (1967) / –Hö.

[Rd 768 IE]

Diagonal electrophoresis techniques, interesting and simple variations of paper electrophoresis, were used by *R. N. Perham* and *G. M. T. Jones* to resolve problems in the analysis of amino acid sequences. In this method, the mixture of substances is subjected to two successive electrophoreses under identical conditions but in directions at right angles to one another; a diagonal of substance spots is obtained. If a component or a group of components is chemically modified between the two electrophoreses, preferably on the electrophoresis paper, the modified substances will not lie on the diagonal after the second electrophoresis. For amino acid sequence analyses, proteins with trifluoroacetylated ε-amino groups in the lysine residues are cleaved with peptidases. After the first electrophoresis of the fragments, the paper is treated with gaseous ammonia, which liberates the amino groups. After the second electrophoresis all the lysine-containing peptides will not lie on the diagonal. / European J. Biochem. *2*, 84 (1967) / –Hö.

[Rd 769 IE]

Ribosome crystals are formed in chick embryo cells at temperatures below the normal physiological levels (5–15 °C). The arrangement of ribosomes in the crystals was studied by *B. Byers*, using an electron microscope. In interphase cells, layers are formed which are one ribosome thick and which may be bent into the form of closed cylinders. In mitotic cells, three-dimensional crystals are formed by the superposition of such layers. The ribosomes (diameter approx. 24 nm) are arranged as follows: the "unit cell" is a square,



the length of whose side is 57.3 nm. The layers may crystallize on a matrix or together with a structure-forming substance, since in cross-sectional pictures of the layers it is always possible to distinguish an optically denser and an optically less dense side to each layer. The particle weight of the ribosomes is approximately 4 million. / J. molecular Biol. *26*, 155 (1967) / –Hö.

[Rd 771 IE]

Chemotaxonomy der Pflanzen. Eine Übersicht über die Verbreitung und die systematische Bedeutung der Pflanzenstoffe. (Chemotaxonomy of Plants. A survey of the distribution and the systematic significance of plant substances). Volume 4, Dicotyledons: Daphniphyllaceae to Lythraceae. Chemical Series. Textbooks and Monographs in the Field of the Exact Sciences. Birkhäuser Verlag, Stuttgart-Basel 1966. 1st Edit., 551 pp., DM 106.–.

Of the six projected volumes of this already very well introduced work, Volume 4 is now available. It deals with the essential substances contained in a total of 71 dicotyledonous plant families, namely (in alphabetical order) Daphniphyllaceae to Lythraceae. Approximately 28000 species are included. The families Euphorbiaceae, Gesneriaceae, Labiatae, and Lauraceae are particularly large; the important family Leguminosae is left for a later volume.

The plan and the presentation of the subject matter follows the customary scheme. With supplements, the literature is covered to about the end of 1965 and includes many difficultly accessible references. Misprints and factual errors are rare, and the printing and presentation are as usual excellent. The scientist interested in the results of phytochemical research will find the volume very rewarding. *Hegnauer*'s conclusions in regard to the systematic inclusion of debatable genera are careful and conservative. Conclusions concerning the families that are discussed often include sentences such as: "For the time being the available data permit only a superficial chemotaxonomic assessment...". The situation is likely to alter as soon as sufficient detailed chemotaxonomic investigations become available. *C. H. Eugster* [NB 650 IE]

Die wissenschaftlichen Grundlagen des Pflanzenschutzes. By *H. Martin*. Based on the 5th Edit. (1964) of: *The Scientific Principles of Crop Protection*, translated and supplemented by *K. J. Schmidt*. Verlag Chemie GmbH., Weinheim/Bergstr. 1967. 1st Edit., xii, 696 pp. and 3 tables, DM 68.–.

The present book is divided into 16 chapters, the first of which introduces the subject matter. Chapters II, III, and IV deal with the resistance of plants to pathogenic agents and pests, the influence of external factors on the susceptibility of plants, and the methods of biological pest control. Chapters V to XVI discuss the chemical and physical agents and methods for the protection of plants, the problems that arise in their use, mechanisms of action, and special questions concerning the treatment of infection centers and vectors. The translation has been supplement by valuable references to recent publications, *e.g.* to recent German works on biological pest control, to the "ultralow volume" technique, which involves the spraying of highly concentrated substances, to new methods for the production of insecticidal aerosols, to the antibiotics Blasticidin-S and Kasugamycin, to the phosphorus insecticides, which are not discussed in the English text, to the mercury-free seed dressing Voronit, and the use of simulated bat cries to scare insects. Tables giving the Latin, German, and English names of important arthropods and fungi, as well as data on their classification, are included as an appendix. The book ends with comprehensive subject and author indexes.

The translation contains a number of shortcomings and printing errors, which should be corrected in a new edition. Thus the fungicide "Nirit" is referred to as "Nitrit", Dinocap sometimes appears as "Dinocab", Prometryn as "Prometrin" and Ametryn as "Ametrin". The statement that the herbicide Linuron was "placed on the market in 1960 by DuPont Nemour Inc." should also be corrected, since Linuron is a product of Farbwerke Hoechst AG. (*Scherer et al.*, German Patents, 1956 and 1958). The alkali metal and ammonium salts of "3,5-dinitro-*o*-cresol" are not "soluble in all proportions in water"; the solubility of the sodium salt at room temperature is only 5 %. DDT is not readily soluble "in most organic solvents". Gamma-HCH contains no "cyclodiene grouping".

The common names recommended by the International and the British Standards Organisations (ISO and BSI) are occasionally confused with trade names of crop protection agents, *e.g.* in the cases of Carbaryl ("the B.S. trade name is Carbaryl"), DNOC, and Dioxathion. In many cases the common names used in English, *e.g.* Azinphos, Fenthion, and Trichlorfon, are replaced in the translation by trade names, while in other cases substances, such as Monuron, Diuron, Neburon, and Linuron, are referred to by the common names but not by trade names. This disorderly use of names makes the book unnecessarily difficult to use. The chemical names should all be formed in accordance with the IUPAC nomenclature rules in the next edition.

The German translation of the article will be warmly received, since the English author has succeeded brilliantly in providing the biologically and agriculturally oriented reader with a clear picture of the physico-chemical and toxicological aspects of crop protection, and at the same time offering chemists and toxicologists working on the synthesis and testing of crop protection agents an insight into the biological problems encountered in crop protection. *H. Maier-Bode* [NB 686 IE]

Methoden der organischen Chemie (Methods of Organic Chemistry) (Houben-Weyl), Vol. VI, Part 3, Oxygen Compounds I, Edited by *Eugen Müller*. Georg Thieme Verlag Stuttgart 1965. 4th Edit., xlvii, 832 pp., 4 figures, 70 tables, DM 212.–.

The present Volume VI, Part 3, Oxygen Compounds I, of Houben-Weyl continues the sequence of monographs on the methods of preparative organic chemistry in the accustomed thorough manner.

The book begins with chapters on the preparation and transformation of ethers, acetals, orthocarbonates and oxonium salts; the literature references for the ethers embrace those up to and including 1962, and those for the remaining three classes of substances to 1963.

These chapters, written by *H. Meerwein*, leave nothing to be desired in respect of clarity of expression, completeness of the synthetic procedures, and the amount of personal experimental experience incorporated.

The following chapters deal with methods of preparing and transforming epoxides, oxetanes, and dihydro- and tetrahydrofuran derivatives, with literature references up to 1963. These chapters too are characterized by a strict systematic arrangement and admirable thoroughness of treatment.

The chapter "Ethers" is subdivided into purely aliphatic, aryl aliphatic, purely aromatic, and unsaturated ethers, so that the variations of comparable procedures can be viewed against the reactivities of the individual classes of substances. It should be emphasized that the methods of sugar alkylation are dealt with in a comprehensive manner; the biochemist engaged in preparative work should derive particular benefit from this aspect. The methods of ether transformation embrace all the oxidation, cleavage, and rearrangement reactions observed in ethers in systematic order. Consideration has been given to the generally neglected steric factors in the addition of alcohols to unsaturated ethers (p. 42).

The chapter on the methods of preparing acetals and ketals lays particular emphasis on the universally applicable procedures with orthoesters. Procedures for preparing spiroketals, which are basic to a number of natural substances (cf. *F. Bohlmann et al.*, Chem. Ber. *94*, 3193 (1961)), may perhaps be missed but they can be found later in a different connection (pp. 552 and 699ff).

Ketene acetals should also be included in a subsequent edition; a single example only is referred to in the chapter "Epoxides" (p. 484).

Under the subject "Conversions of oxonium salts" synthetic methods involving pyrylium salts are mentioned briefly (pp. 352–358 and 363–365). On the other hand, acid- and base-catalyzed ring-opening reactions of epoxides are described twice (p. 42ff. p. 448ff.). Perhaps this is inevitable in a work written by several authors. Among the transformation reactions of epoxides, the preparatively interesting removal of the oxygen atom by triphenylphosphine with the formation of an olefin may deserve a comment. In the treatment of the methods of oxetane preparation by cycloaddition of olefins to ketones (p. 503) there is no mention of the photochemical formation of oxetanes (Paterno-Büchi reaction) from olefins and carbonyl compounds; this method is of preparative interest and in many cases proceeds stereospecifically. In relation to the dihydrofuran-diene adducts (p. 559) in the chapter on the preparation of five-membered cyclic ethers, some remarks concerning the stereochemistry of the adducts, such as have been made in the case of similar compounds on page 641, would be entirely appropriate.

Further, it would seem useful to the reviewer to adopt the IUPAC nomenclature (pp. 559, 641, 643, 647), because finding of the compounds discussed in collected works from the subject index would then be made easier.

These few critical remarks are the only ones to have occurred to the reviewer during a careful reading, in which he was assisted by Dr. *H.-D. Scharf*. In view of the abundance of the material presented and discussed, this is proof of the quality of the work. The volume is a rich mine of chemical knowledge.

F. Korte [NB 640 IE]

Biochemie der Vitamine (Biochemistry of the Vitamins). By *Th. Bersin*. Akademische Verlagsgesellschaft, Frankfurt/Main 1966. 1st Edit., vii, 296 pp., 16 figures, DM 44.–.

The author, who was compelled to undertake this venture by his early work on the subject, attempts to describe the biochemical function and the therapeutic use of vitamins for the benefit of physicians and dieticians. Such a work cannot be more than a literature review, with more or less successful attempts at systematization, and certainly cannot be original. The book is divided into a general part, in which much of the material is distorted though not actually incorrect, and a special part, in which the various vitamins are discussed in an old-established manner. A large quantity of material, divided into biosynthesis, mode of action, therapeutic action, and analogs, is compressed into a relatively small space, but the discussion is frequently not sufficiently critical. In many cases matters cannot be regarded in such an unambiguous and schematic way. It would indeed be delightful if they were as certain as they appear to be from this presentation to the uninitiated reader (*e.g.* in the methionine synthesis and the mode of action of mercaptopurine). No definite function of vitamin B_{12} has been established in higher plants; the vitamins formed by intestinal bacteria are scarcely a source of self-provision.

The unbalanced treatment of the material is a particularly striking weakness. Trivia are given importance by a few words (orbitals, nonpolar, translational motion); Americanisms (absorption instead of resorption) and non-standard units (γγ, mcg) are simply adopted. Strange nomenclature (isoalloxazinebenzopteridine, pyridoxaminium-5′-phosphate) and interpretations (mongolism as mutation) seem dubious. Apart from incorrect references (*Wolley, Jacobs, etc.*) the references to the authors own work (*e.g.* Function of the nucleic acids: Vitalstoffe *8* (1963) 5) and the style are irritating.

On the other hand, the book contains a great deal of carefully collected and useful material. The medical material will seem interesting to the chemist and the chemical material to the physician.

L. Jaenicke [NB 586 IE]

Kurze Anleitung zur Berechnung von π-Elektronensystemen (A Short Introduction to the Calculation of π-Electron Systems). By *J. D. Roberts*. An extended translation of "Notes on Molecular Orbital Calculations" by *F. Wille*. S. Hirzel-Verlag, Stuttgart 1966. 1st Edit., xi, 165 pp., paperback, DM 19.80.

The "lecture notes" type of textbook, with its economic presentation, whose availability up to recent times has been unfortunately restricted predominantly to English-speaking countries, is here available in an exemplary form. The didactically sovereign, easily understandable, and sometimes unorthodox manner, which follows that of the basic *Roberts* lectures, including those given in Munich in 1962, introduces the student to the Hückel molecular orbital theory (HMO) as the simplest quantum-mechanical approximation procedure – "to be able to make MO calculations while swinging in a hammock beside a mountain lake". No extensive mathematical knowledge is assumed, and numerous exercises provide an opportunity of becoming familiar with quantities such as charge and bonding order, free valence, and delocalization energies. Further chapters deal with the application to aromatic, heteroatom-containing, or nonplanar electron systems, and to the prediction of chemical reactivities. In conclusion, the quantities neglected by the HMO theory are discussed critically. There is an appendix consisting of worked examples, two original publications, and a bibliography. The German text is lucid; the number of misprints is tolerable (*e.g. cis*-butadiene (p. 55) is always treated as linear in the HMO scheme without making additional assumptions, "$>$" on p. 93 should be "$<$". The chapter dealing with determinant factorization with the help of group theory has been extended to the general case, although only two-digit symmetry elements are used. A successful introduction to determinant algebra has been added as a further appendix. Numerical solutions of all exercises and an introduction to the use of the now available HMO tables would have been equally desirable. The book, provided with a preface by *R. Huisgen*, can also be recommended to the beginner as a simple introduction to HMO theory and its application to organic compounds.

H. Bock [NB 638 IE]

Techniques in Protein Chemistry. By *J. Leggett Bailey*. Elsevier Publishing Company, Amsterdam-London-New York 1967. 2nd Edit., xiv, 406 pp., 118 figures, 53 tables, Dfl. 55.–.

The very rapidly developing methodology of protein chemistry reached a comprehensive level a few years ago. Standard methods are now available for characterizing and purifying the proteins themselves and their degradation products. In many cases these may have to be combined in different ways or even modified, but when used together they generally succeed in elucidating structure. Some of these procedures may well be replaced by superior techniques, but this book attempts to select several proved and particularly well developed methods. Moreover, it chooses procedures which are applicable to research where purification or sequence analysis is only occasionally employed.

The limitation to reliable manipulative techniques such as paper chromatography, ion-exchange chromatography, and fingerprint procedures for amino acids and peptides, N- and C-terminal sequence determination, column chromatography, strip electrophoresis, dialysis, and molecular sieve separation of proteins, splitting of disulfide bonds and sulfhydryl determination in protein together with certain important basic methods such as protein, nitrogen and tryptophan determination, finds expression in an arrangement hardly changed from the first edition. The final chapter deals with methods of synthesizing simple peptides such as the enzymologist selects as substrates.

New developments in this field account for the substantial increase in size of the second edition. Here again *J. L. Bailey* has succeeded in selecting successful and reliable new devel-

opments and in describing them in a comprehensive manner, while giving a short account of promising, but as yet little tested techniques.

The individual chapters are very detailed, and are well suited for providing information to workers in other fields. Quite deliberately, attention has been directed to the preparation or purely chemical analysis of protein and peptide mixtures that can be accomplished without the need for elaborate instrumentation – with the possible exception of amino-acid analysis. Physicochemical methods have been left in the background. A somewhat wider-based presentation of the radioactive labeling of proteins would perhaps be desirable, for example with enzyme substrates, and also the analysis of the peptides and amino-acids of their labeled derivatives. Where several proved methods are available for achieving a particular aim, as for the determination of N-terminal sequences, all are described with equal thoroughness.

The book has been produced with care, and the printing, the high-quality illustrations, and the arrangement combine to make it very lucid. The abundance of material which it presents recommends it highly to everyone interested in protein methodology. *H. Fasold* [NB 633 IE]

Microbial Transformations of Steroids. By *A. Čapec, O. Hanč*, and *M. Tadra*. Translated from the Czech by *O. Macek, L. Urbanek* and *O. Hanč*. Dr. W. Junk, Publishers, Den Haag 1966. 1st Edit., iv, 253 pp., bound Dfl. 25.00/$ 6.95.

The conversion of steroids by microbial enzymes has been intensively investigated by numerous groups of workers during the past decade, and has led not only to scientifically interesting information but also to practically useful results. Although no detailed classification of papers published in scientific periodicals, reviews, and patents has yet been carried out, the present monograph attempts to rectify this omission. The brief introduction is followed by a discussion of the types of microbiological reactions and of reaction mechanisms. In this, the authors have not relied on speculations. Next comes a brief discussion of the influence exerted by the steroids on microorganisms. The practical hints concerning fermentation are very helpful. A detailed treatment of the analytical methods, identification, and constitution-determination methods is unnecessary, because all these are well known. No fundamentally new aspects arise in bacterially produced steroids. The necessity for determining physical data such as the melting point, optical rotation, and light absorption is taught to every student at the outset of his practical organic chemistry course, and in addition the treatise "Steroid Reactions" by *C. Djerassi* (1963) provides exhaustive information about chemical methods in steroid chemistry.

The sections that classify the microorganisms according to their reactions are very useful, as are the lists of steroid metabolites (together with physical data and the nature of their preparation) and the comprehensive bibliography (unfortunately reaching only to the end of 1963) which includes patent literature. This carefully produced work will render valuable service to both expert and outsider wishing to employ microbiological reactions. *Ch. Tamm* [NB 648 IE]

Growth, Function, and Regulation in Bacterial Cells. By *A. C. R. Dean* and *Sir C. Hinshelwood*. Clarendon Press: Oxford University Press, Oxford 1966. 1st Edit., xii, 439 pages, 120 figures, 29 tables, 2 plates, 84s.

In 1946, *Sir C. Hinshelwood* published a book entitled "The Chemical Kinetics of the Bacterial Cell". The present volume is based on the same material with the contents brought up to date. It would probably have been better to retain the old title, instead of arousing unfounded hopes by a title that does not agree with the contents. The book is by no means an introduction to the problems of the growth, function, and regulation of the bacterial cell. Nowadays, these problems can no longer be discussed without recourse to the chemical and morphological principles of bacteria as a basis.

The great value of this book lies in the detailed treatment of the biophysical aspects of bacteriology, which will become increasingly important with further research. The biophysical side of the various problems of bacteriology is familiar to very few microbiologists, so that this book is also a very welcome addition to the literature on bacteriology. The problems discussed are taken largely from the fields in which the authors work: this on the one hand is a guarantee of authenticity, but on the other leads to a rather unbalanced selection of material.

Both authors give a neat account of the biophysical principles of the intact bacterial cell, hardly touching on the biophysical problems of molecular biology. In their opinion the situation prevailing in intact cells must be elucidated before one can proceed into the molecular-biological domain. The idea that the reverse route may also be possible is evidently familiar only to the younger generation. *H. Zähner* [NB 606 IE]

Carbocyclic Non-Benzenoid Aromatic Compounds. By *D. Lloyd*. Elsevier Publishing Company, Amsterdam-London-New York 1966. 1st Edit., x, 220 pages, 2 figures, Dfl. 35.00.

The present monograph is intended as a concise presentation of the existing knowledge on non-benzenoid carbocyclic aromatic compounds. In the introduction (15 pages), a recapitulation of the historical development of the concept of "aromaticity" is followed by a description of the results of the molecular orbital theory that are of greatest importance to the preparative organic chemist. The next few chapters deal with derivatives of cyclopropene (19 pages), cyclobutadiene (20 pages), cyclopentadiene (43 pages), tropylium salts (19 pages), tropone and tropolones (45 pages), cyclooctatetraene and cyclononatetraene derivatives as well as annulenes (19 pages), and polycyclic compounds (35 pages), in particular the azulenes. The choice of material is generally reasonable, though the space devoted to the various classes of substances is not always in keeping with their importance. For example, the fulvenes are dismissed in 6 pages, whereas 45 pages are given to the tropones and tropolones.

In each section, the author describes in a readily understandable manner the methods of preparation, properties, chemical reactions, and principal spectral data. Each chapter is followed by a list of references, the total number of entries for the book being about 1000 (literature up to 1965). In comparison with other books on the same subject, a particularly pleasing feature is the clear formulation of the reactions, though no preparative details are given and the spectroscopic findings are not discussed. The inclusion of spectra of some characteristic compounds would undoubtedly have been helpful.

No previous theoretical knowledge is required in order to read the book, which can be recommended to chemists who wish to gain a general picture of recent results in the field of carbocyclic non-benzenoid aromatic compounds.

M. Neuenschwander [NB 608 IE]

Methods of Elemento-Organic Chemistry. Edited by *A. N. Nesmeyanov* and *K. A. Kocheshkov*. Vol. 1: The Organic Compounds of Boron, Aluminum, Gallium, Indium, and Thallium. By *A. N. Nesmeyanov* and *R. A. Sokolik*. North Holland Publishing Company, Amsterdam 1967. 1st Edit., xiii, 628 pp., 40 illustrations, 27 tables, Dfl. 87.–.

The first volume of this new series was published in 1964 by Nauka Press in Moscow and has been partly revised for translation into English. The various sections (*e.g.* boron 362 pp.; Al 140 pp.) of the book are mostly arranged according to methods of synthesis; for boron and aluminum, compounds without a metal-carbon bond are included. In a few sections, *e.g.* chapters 10–12 and 15 on boron compounds and in chapter 8 on aluminum compounds, division is

according to the substances described. An article on analytical methods for each element discussed is also included.

The book is intended above all for the chemist engaged in preparative work in organometallic chemistry and it will help him in his search for the best preparative method for a given compound by providing him with a wealth of procedures. However, because of the division by methods the same class of compound is often described in several places, and then the necessary cross-references are lacking so that the required data is not always very easy to find. In spite of the large amount of information given, much work is often required of the reader in selecting what is best suited to his needs.

The value of the individual chapters varies because of the different treatments of the literature – in some cases covered up to 1965, but mostly up to 1962/63. Whereas many sections, *e.g.* the synthesis of organoboranes by means of organometallic reagents, are relatively clear and uniform, others deal with too heterogeneous a material. It is, for instance, unintelligible why "symmetrization reactions" of boron compounds (p. 179ff.) is followed by a section on "exchange reactions" (p. 199ff.). Moreover, other analogous reactions are spread over several chapters.

It is unfortunate that not all the chapters have been carefully revised. The printing of formulas is often technically unsatisfactory. Interchanged headings, even of large subchapters (pp. 70 and 75), are to be found as well as numerous misprints and false references. In a number of cases, the inclusion of more recent knowledge would have greatly improved the selection of experiments described.

In spite of these failings, the book does provide a useful review of this complicated material although critical evaluation is still required of the reader. If this volume were thoroughly revised by the authors and editors it would fulfil a useful purpose among the literature of preparative organometallic chemistry. *R. Köster* [NB 656 IE]

Progress in Reaction Kinetics, Vol. 3. Edited by *G. Porter.* Pergamon Press, Oxford 1965. 1st Edit., vii, 515 pp., several figures, 100 s.

The editor has managed to bring out the third volume surprisingly quickly after the first two [1] of the series and also the cumulative index of the reactions whose kinetics form the subject of these three volumes. Substantially more than 1000 reactions are cataloged in the three groups "Reactions in gases", "Surface reactions", and "Reactions in condensed phases"; the arrangement and subdivision permits rapid successful searching.

The present, third, volume contains 10 contributions: *K. J. Laidler* and *J. C. Polanyi* present the theory of the kinetics of bimolecular reactions for advanced students (54 pp., 169 references). This is followed by a survey of "Reactions of hydrogen atoms in the gas phase" by *B. A. Thrush* (30 pp., 162 references), in which combination and transfer reactions are discussed. *R. Wolfgang* gives an introduction to "The chemistry of hot atoms in the gas phase", *i.e.* an indication of possible reaction paths for atoms containing kinetic energy in excess of the activation energy (70 pp., 162 references). In Chapter 4, *B. G. Gowenlock* discusses "The inhibition of radical chain reactions in the gas phase (25 pp., 133 references), with emphasis on the results of research of the past decade. The chapter by *A. W. Read* on "Vibration relaxation in gases" (30 pp., 141 references), which is fundamentally a progress report on the past five years, concludes the subject of the gas phase.

L. M. Dorfman and *M. S. Matheson* present a chapter on "Pulse radiolysis" (60 pp., 165 references), which is a very important technique for fast reactions, and treat the experimental methods in a welcome, detailed manner. *W. G. Burns* and *R. Barber* are the authors of a chapter on correlations of dose efficiency, linear energy transfer (= differential energy loss along the path of an ionized particle), and product yield during ionizing irradiation of nonaqueous systems, using the diffusion models that have proved themselves for aqueous systems (60 pp., 131 references). *E. J. Land* describes electron spectra and the kinetics of aromatic radicals (30 pp., 132 references). The assignment of the spectra is explained in exemplary fashion; ESR investigations are included in the references.

The last two contributions deal with polyreactions. *R. C. P. Cubbon* and *D. Margerison* discuss the organolithium-induced polyreactions of vinyl monomers (40 pp., 101 references). (Inexplicably, the authors have made a mistake in the interpretation of the kinetic formulas by a German group of workers. The problem stated on p. 427 has been solved.)

"The investigation of radical polymerization in solution" by *G. M. Burnett* concludes the volume. Here the presentation is unusually short (18 pp., 58 references) and the proportion of references that are older than 10 years is very high. Nevertheless, this chapter, like the others, documents the present state of knowledge and indicates possible lines of research. The presentation of the book is faultless. It is self-evident that this volume (like its predecessors) is a must in every chemical library and even more so in the personal library of all chemists concerned with kinetics. *H. Sinn* [NB 631 IE]

Histoire Brève de la Chimie (A Short History of Chemistry) by *L. Velluz.* Librairie Maloine, Paris 1966. 1st Edit., 115 pp., paperback F 14.–.

No one who is interested in the long and eventful journey of mankind to the point of understanding science can be indifferent to the flowering and the extraordinary development of chemistry. Is there a more beautiful masterpiece of logic than the theory of matter, built up patiently on experience, to which modern physics merely had to add details at the start of the twentieth century? On 115 pages *L. Velluz* surveys the development of fundamental ideas and recreates the leading actors of the drama.

The attempt by man to resist decay, and dreams of riches through transmutation of elements led to alchemy, a pseudoscience which clothed its unskilful metallurgical procedures in phantastic formulations. True chemistry did not begin until the end of the seventeenth century, still entirely as an appendix to philosophy. *Stahl* forged the first link between apparent and related facts with his phlogiston theory. These tenets, in turn, prevented *Priestley* about a hundred years later from drawing the correct conclusions from his discovery of oxygen. It was left to *Lavoisier* to discover the general principle of oxidation by developing precise weighing methods. The general awakening of interest in science early in the nineteenth century favored the initial successes of chemistry. This was the age when the educational system in Europe was established under the influence of *Liebig* and *Dumas*, when *Chevreul* recognized the existence of definite organic compounds, and when careful analyses were performed by *Berzelius* to establish the foundation of quantitative chemistry. This promising beginning was followed by the era of "lack of gratitude" of *ca.* 1840, reverberating with polemics and producing a generation of devoted chemists who resolved the conflicts founded in the dualistic views of *Berzelius*. Following the discovery of the laws of substitution by *Laurent*, this turbulent but fruitful period saw the triumphant type theory of *Gerhardt* and, *ca.* 1850, the origin of the chemical symbols, so devotedly defended by *Wurtz*.

The understanding of molecular architecture did not come about until after the discovery of the universal principle of molecular asymmetry by *Pasteur*. One chapter describes the stages in *Pasteur*'s discovery, soon to be completed by the work of *Le Bel*, *vant'Hoff*, *Kekulé*, and others. Modern structural chemistry had been established, and chemistry stood at the threshold of the promised land. *Mendeleev*'s classification of the elements, the discovery of radioactivity by *Pierre* and *Marie Curie*, and the progress in synthetic

[1] For a review of Volume 2 see Angew. Chem. *77*, 435 (1965); Angew. Chem. internat. Edit. *4*, 454 (1965).

chemistry became the basis of soaring chemical research, emphasized by the founding of the first dyestuff factory. Only a few reflections are devoted to the subsequent stormy and restless era. How many surprises does the future hold – perhaps the creation of psychological chemistry enabling man to act on his psyche?

The author has had a difficult task in condensing the historical development into so little space and yet giving the most important events their due attention. Critical selection became essential, and the author has succeeded by interposing anecdotes and by the use of a flowing style to make the actors of the exciting drama appear before our eyes in the atmosphere of their own age.

This small volume will instruct the layman in a friendly manner and will relate many new things or put old ones in perspective to the initiated. Once begun, the book will not be put down before the last page is read.

J. Rigaudy [NB 655 IE]

Solvent Effects on Reaction Rates and Mechanisms. By *E. S. Amis*. Academic Press, New York/London 1966. 1st Edit., xi, 326 pp., numerous figures and tables, $ 10.50.

Although *M. Berthelot* and *L. de St. Gilles* observed and studied the effect of solvents on the rate of chemical reactions as long ago as 1862, and *N. Menshutkin* stated in a fundamental work published in 1887 that "a reaction is inseparable from the medium in which it takes place", no critical compilation of the extensive experimental and theoretical work on the effects of solvents on reaction rates and mechanisms has appeared until the present monograph by *E. S. Amis*.

The first four chapters form theoretical attempts to interpret the effect of solvents on reactions involving different electric charges (reactions between ions, dipolar molecules, dipolar molecules and ions, and also electron exchange reactions between ions). Chapter V is devoted to the effect of external and internal pressure (cohesion) in addition to the comparison between gas-phase and solution reactions, and also the effect of solvent viscosity on the above types of reactions. Insofar as they describe the effect of the solvent on the reaction rate empirically, linear free energy relationships are listed in the following chapter.

The last two chapters deal with the qualitative solvation model proposed by *E. D. Hughes* and *C. K. Ingold* and also with further special solvent effects such as selective solvation, cage effects, primary and secondary salt effects, and hydrogen bonding.

The presentation of the often complex material is interspersed with numerous examples, 26 illustrations, and 30 tables. Theoretical physical aspects are emphasized rather than chemical ones. Considering the scope of the subject, it is perhaps inevitable that some aspects of particular importance to the organic chemist have been left out. No indications are given of the great importance which the dipolar, aprotic solvents have achieved in nucleophilic and electrophilic substitution reactions (*A. J. Parker*), or of the control of the reactivity of ambident anions and cations by the solvent (*N. Kornblum*). The value of the detailed bibliography (about 500 references, in part complete to 1965) is unfortunately marred by numerous misprints (*e.g.* references 16, 18 (p. 29); 33 (p. 57); 48, 56, 59, 65, 74 (pp. 119–120); 4, 6, 11, 15, 36, 41 (pp. 145–146); 8, 43 (pp. 181–182); 24, 25, 80, 108, 110, 113, 135, 136, 153, 157, 166 (pp. 251–255)). Some equations are badly set out typographically or actually wrong (*e.g.* eqs. 2.67; 5.16; 7.16; 7.17; 7.18; 7.124; 7.132; 7.143 and 7.144). No strict differentiation is made between mesomerism and equilibrium arrows.

In all, the book is suitable both as an introduction and for further study by inorganic and organic chemists. Its use is facilitated by good author and subject indexes, and it can serve as a valuable aid to discussing the rates and the mechanisms of chemical reactions in solution.

C. Reichardt [NB 647 IE]

Oxidation in Organic Chemistry. Edited by *K. B. Wiberg*. From the series of monographs "Organic Chemistry", Vol. 5. Part A. Academic Press, New York-London 1966. 1st Edit., xi, 443 pages, $ 14.00.

Those who are familiar with the excellent reviews in "Neuere Methoden der präparativen organischen Chemie" will welcome this English-language collection of critical reviews of the literature on selective methods. Oxidizing agents are still among the most important reagents of organic chemistry, and a general need will be filled by the two volumes (the second is in preparation) devoted to this field by the publishers of "Organic Chemistry", a collection of monographs published since 1964.

The first part of this book includes oxidation with permanganate (*R. Stewart*), with chromic acid and chromyl compounds (*K. B. Wiberg*), with vanadium(v), cobalt(III), and manganese(III) (*W. A. Waters* and *J. S. Littler*), with cerium ions (*W. H. Richardson*), and with lead tetraacetate (*R. Criegee*), as well as the cleavage of glycols (*C. A. Bunton*). All the known experimental results are included, as well as the theoretical principles, the solvents and reaction conditions used, and the inorganic and particularly the organic substrates to be oxidized. In some cases extensive tables of kinetic data, and occasionally even laboratory procedures, are given. The largest sections are naturally those dealing with topics of interest to the preparative organic chemist. The present volume may therefore be described as the most up-to-date and comprehensive work of its kind, and will prove a valuable aid to any chemist. The uniform layout of the six chapters and the detailed subject and author index are excellent.

G. Anner [NB 616 IE]

Encyclopedia of Polymer Science and Technology. Plastics, Resins, Rubbers, Fibers. Edited by *H. F. Mark*, *N. G. Gaylord*, and *N. M. Bikales*. Vol. 2: Amino Resins to Casein. Interscience Publishers, a Division of John Wiley & Sons, New York-London-Sydney, 1965. 1st Edit., xiii, 871 pp., many illustrations and tables, single copies 375s; subscription price 300s.

The second volume of this handbook [*] contains 41 contributions; most of the authors are active in industry in the United States. The diversity of the subject matter is demonstrated by the following details.

"Amino Resins" is the heading of an admirably illustrated article (94 pp., 101 references), which deals not only with the basic reactions of this class of compounds, but also delves deeply into the technical side of the subject. The production of polymers is treated in the sections entitled "Anionic Polymerization" (143 references; important advances made in 1963 and 1964 are unfortunately omitted), "Block and Graft Copolymers" (44 pp., 254 references, preparation, properties, and uses of these copolymers), "Cage Effect" (6 pp. paying special attention to phenomena which appear during polymerization), and "Bulk Polymerization" (24 pp., 82 references). In the last named article the heat of polymerization of vinyl chloride is given as 14.4–16.7 kcal mole^{-1} without any comment of the sort that one would expect to accompany such a wide range of values; furthermore, the table of densities of monomers leaves much to be desired.

The contribution headed "Antibodies and Antigens" is rather brief (only 12 pages) in view of the general importance of this field of study. On the other hand, the wealth of well-arranged material in "Biocides" make this contribution really exemplary. The copious list of commercially available stabilizers in the article "Antioxidants" is also very welcome; a similar list is missed in "Antistatic Agents" (25 pp.). Although "Aqueous Polymerization" (144 references, 37 pp.) gives a good summary of the widely varying types of initiators, information concerning the water solubility of the monomers at various temperatures is rather sparse.

[*] Cf. Angew. Chem. *78*, 156 (1966); Angew. Chem. internat. Edit. *5*, 148 (1966).

Problems of a more technical nature are covered in the sections headed "Annealing" (rather brief, having only 13 pages), "Automotive Applications" (12 pp.), "Bag Molding" (17 pp.), "Belting" (12 pp.), "Biaxial Orientation" (34 pp., several illustrations), "Bituminous Materials" (36 pp., 18 tables), "Bleaching" (46 pp., much information concerning apparatus), "Blowing Agents" (detailed information concerning the applicability of various classes of compound as foaming agents), "Building and Construction Applications" (with several illustrations taken from practice), "Calendering" (19 pp.), and "Casein" (13 pp.).

Special polymers are dealt with in the contributions headed "Bicycloheptene and -heptadiene Polymers" (the tabular summaries are worthy of praise; the literature is covered up to the end of 1964), "Butadiene Derivatives, Polymeric" (12 pp., 87 references), "Butadiene Polymers" (76 pp., 262 references), "Butylene Polymers" (40 pp., 79 references), and "*N*-Carboxyanhydrides". Strangely, the copolymers are not mentioned at all in the section on butadiene derivatives and only very briefly in that on butylene polymers; the table of r-values of the copolymerization of butadiene could well be more complete. In the articles concerned with individual polymers the reviewer missed lists of trade names and would therefore venture to suggest that the following editions should include tables in which the various polymers are listed alphabetically, both under their commercial designations and their systematic names.

Information about auxiliary agents for polymerization and for the polymerizate is given under the headings "Antiozonants" (8 pp.), "Azo Catalysts" (very detailed tables listing characteristic properties of 71 azo compounds), "Antifoaming Agents" (8 pp.), and "Brighteners, Optical" (9 pp.). The definitions of terms such as "A-Stage" and "B-Stage", which refer to the production of thermosetting resins, are given in merely 2 and 4 lines, respectively (without examples). The diffusion of gases through polymer films is treated in "Barriers, Vapor" (13 pp.). Finally, mention should be made of the chapters entitled "Boron Compounds" (16 pp., many pieces of information about the compounds of boron), "Bagasse" (5 pp.), and "Carbon" (18 pp. devoted to a discussion of the most important types of soot).

Apart from the main headings listed above there are of course others; for example, in the present work alone, the contribution "Biocides" is given under a further four headings. This kind of subdivision greatly facilitates use of the book.

O. Fuchs [NB 623a IE]

Encyclopedia of Polymer Science and Technology. Plastics, Resins, Rubbers, Fibers. Edited by *H. F. Mark, N. G. Gaylord,* and *N. M. Bikales.* Volume 3: Casting to Cohesive Energy. Interscience Publishers, a division of John Wiley & Sons, New York-London-Sydney 1965. 1st Edit., xiii, 862 pp., numerous illustrations and tables. Single copies 375 s; subscription price 300 s.

More than half of the third volume (28 contributions from 48 authors) of this work is devoted to cellulose and its derivatives. The treatment of cellulose itself covers 97 pages and includes 436 references; the most important physical and chemical properties are well presented in 56 figures and 18 tables. Some overlapping does, however, occur between this article and those entitled "Cellulose, Biosynthesis" (13 pages, 43 references), "Cellulose, Graft Copolymers" (44 pages, 81 references, including impressive photomicrographs and author's [*Immergut*] unpublished results), "Cellulose Derivatives" (17 pages, in which only the "non-classical" cellulose derivatives such as deoxy-, aminodeoxy-, halogenodeoxy-cellulose, *etc.* and oxidized cellulose and derivatives are treated), "Cellulose, Microcrystalline" (7 pages), and "Cellulose, Analytical Methods" (too short with 5 pages). If such repetition had been avoided, much more space could have been devoted to other sections.

Cellulose foil is dealt with in the chapter entitled "Cellophane" (20 pages, 150 references, production, applications); the firm [*Kalle*] which owns the trade mark *Cellophan*, is not mentioned although the names of three American manufacturers are given. Further subject headings are: "Cellulose Esters, Inorganic" (18 pages on nitrates, half a page on other esters; no table showing the dependence of solubility on the degree of nitration is given). "Cellulose Esters, Organic" subdivided into "Manufacture" (28 pages, 102 references, good tabular summaries), "Plastics" (66 pages, 74 references; although emphasis is placed on technological aspects, properties are summarized in large tables), "Fibers" (56 pages describing production and applications, 58 references; tables extending over many pages give trade names – a feature that is often neglected), and "Miscellaneous Cellulose Esters" (4 pages). "Cellulose Ethers" (91 pages, 181 references) with the main divisions ethyl, methyl, hydroxyalkylmethyl, hydroxyethyl, sodium carboxymethyl, cyanomethyl, and carbamoylethyl-cellulose, as well as other cellulose ethers; most of these contributions do not contain a clear representation of the solubility and plasticizing properties that are so important in practice.

Material concerning the manufacture of polymers and polymerization kinetics is provided in the sections "Cationic Polymerization" (25 pages, 66 references; although the mechanism is treated thoroughly only a selection of catalysts is given), "Catalysis" (short description of methods for the production of macromolecules, 9 pages), "Ceiling Temperature" (too short with one page, only four examples, literature not covered beyond 1958), "Chain Reaction Polymerization" (26 pages, 112 references; in this section and in the one entitled "Catalysis" Ziegler catalysts are treated briefly but a full treatment will not appear until the last volume), "Chain Transfer" (30 pages, 126 references; determination of transfer constants with results, special technical applications), and "Chemically Resistant Polymers" (30 pages, 57 references including many from the years 1963 and 1964, particular attention being given to polymers suitable for use in rocket technology).

Applications of a technical nature are dealt with in the sections entitled Casting" (20 pages, contains superfluous illustrations), "Coating Methods" (69 pages, comprehensive descriptions of methods involved, 89 illustrations), and "Cellular Materials" (51 pages, 152 references, processes, statistical data, properties). The individual types of polychloroprenes are described in "2-Chlorobutadiene Polymers" (36 pages, 79 references, production, applications, *etc.*).

Analytical methods are given in the following sections: "Characterization of Polymers" (21 pages, 77 references, some characteristic structural features such as branching, sequence length distribution in block copolymers, problems of determining chemical non-uniformity, head to head structures, foreign groups, and networks are merely touched upon, if mentioned at all), "Chemical Analysis" (34 pages, 197 references, physical methods such as IR and NMR spectrometry and differential thermal analysis are given in addition to chemical methods), and "Chromatography" (32 pages, 76 references, methods, examples). "Castor Oil" (6 pages) and "Chitin" (11 pages) are treated as individual compounds. A section headed "Cohesive-Energy Density" (30 pages, 75 references covering the literature up to 1964, tables of solubility parameters for low and high molecular-weight compounds, special cases of compounds containing strongly polar groups) concludes the volume under review.

To summarize it may be said that this volume, like its predecessors, contains a wealth of data from the field of polymer science, which can otherwise be found only by searching the specialized literature. In view of the rapid development of the science and technology of macromolecular materials the encyclopedia represents a valuable source of information for workers in this field.

O. Fuchs [NB 623b IE]

Guaianolides and Germacranolides. By *F. Šorm* and *L. Dolejš*. Monograph in the series "Chemistry of Natural Products", edited by *E. Lederer*. Holden-Day, Inc. (Publishers), San Francisco 1966. 1st Edit., 153 pages, $ 10.75.

This book is an excellent review of the principal results obtained over the past eight years in the field of these two groups of substances of the sesquiterpene series. The reader is first acquainted with the basic structures guaiane and dimethylisopropylcyclodecane (germacrane) and with the physiological effects of these bitter plant constituents. The next chapter gives a short historical account of guaianolides, followed by a description of the individual groups of substances. The description of the lactones from the artabsine group of substances is followed by that of the ketolactones from the matricarin group. Lactones with abnormal skeletons are then described, and mention is also made of guaianolides whose structures are not yet certain.

The second chapter deals with the germacranolides, the detailed investigation of which is due to the authors of this monograph. Like the guaianolides, these occur only in plants of the *Compositae* family, and have recently attracted special interest because some of them have a carcinostatic action. The physical properties of all the guaianolides and germacranolides known at present are collected in an appendix, and special mention should be made of the inclusion of 25 IR spectra. A book dealing with a narrow specialized field obviously cannot appeal to a large public; however, the present work will prove an excellent reference work and review to the chemist who is interested in this topic. Steps should be taken in subsequent editions to correct a few minor printing errors (an oxygen atom is missing from the acetal group in formula 71, and the CH_3 groups on C-5 are missing from the formulas of ambrosin and damsin on p. 110) as well as the incorrect arrangement of the IR spectra of the guaianolides under the germacranolides and *vice versa*. The presentation of the book, the clear print, and the clear formulas are exemplary. On the whole, this book is recommended as an addition to the natural-product chemist's library.

E. Klein [NB 603 IE]

Electroanalytical Chemistry, Vol. 1. By *A. J. Bard*, Marcel Dekker, Inc., New York 1966. 1st Edit., x, 426 pp., 42 figures, $ 15.75.

The aim of the editor of the new series is to introduce electroanalytical methods in the widest possible sense. The review articles are intended to provide information about established techniques as well as about more recent developments.

The first contribution, by *D. E. Smith*, is entitled "AC Polarography and Related Techniques" (155 pp.). Alternating-current polarography has been studied since the middle of the nineteen-forties, but has lately received particular impetus from developments in second-harmonic polarography, phase-sensitive amplification, and RF polarography. In the theoretical section, *Smith* deals systematically with diffusion-dependent waves, quasi-reversible reactions, systems with coupled chemical reactions of first, second, and higher order, and multi-step charge transfer and adsorption – some detailed derivations are included.The section on instrumentation is much shorter, and is directed to the use of operational amplifiers. Fundamental knowledge of electrode kinetics and AC circuits is assumed. The analyst expecting a compilation of methods of determination or even simply ideas for practical analysis is going to be very disappointed. On the other hand, the article is of great value to all those who wish to participate in the introduction of alternating-current methods in the analytical laboratory.

The arrangement of the second article on "Applications of Chrono-potentiometry to Problems in Analytical Chemistry" (40 pp.) by *G. Davies* likewise relies on the nature of the rate-determining step. A very careful description of instrumentation and the decisive electrode pretreatment follows. Examples are given of application in adsorption, and in chemical and electrode kinetics, as well as a tabular compilation of analytical determinations together with source references.

In the contribution "Photoelectrochemistry and Electroluminescence" (44 pp.), *T. Kuwana* deals only with photoeffects at electrodes immersed in solution. The photopotentials in organic systems (including photopolarography), on oxide surfaces and semiconductors, the irradiation of metal electrodes in nonabsorbing solutions, and the luminescence on electrodes are described. The article can be recommended as an introduction to a field that is still in a state of flux.

The article "The Electrical Double Layer, Part I, Elements of Double Layer Theory" (169 pp.) has been written by *D. M. Mohilner*. Both in electrode kinetics and in electroanalysis, particularly in trace analysis, failure to allow for double-layer effects can lead to serious errors in the evaluation of experimental results. The present, very clearly written, first part develops the thermodynamic theory of electrocapillarity, explains the fundamental postulates concerning the structure of the double layer, and in this way establishes the basis for the treatment of kinetics planned for the second part.

F. v. Sturm [NB 651 IE]

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Methods and Results of Optical Investigations on Semiconductor Interfaces

BY K. H. BECKMANN [*]

Measurement of the state of polarization of reflected light (ellipsometry) permits the determination of the thickness and refractive index of thin layers formed on a surface. The IR absorption spectra of such thin layers, which can be measured by means of internal reflection spectroscopy (IRS), provide information about their chemical composition. These methods have been used to study adsorption processes and the formation of reaction layers at semiconductor interfaces, and may also be used for measurements of free charge carriers in the space-charge region and in surface states. Results of such investigations are given in this article.

1. Introduction

The expansion of semiconductor research in recent years has been accompanied by intensified investigation of the surfaces of these substances. The growing use of solid-state components in electronics presented a need for the recognition and elimination of troublesome surface effects, while at the same time semiconductors offer the advantage that more informative measuring methods can be used in fundamental research on interfaces. (For the charge and potential distributions at semiconductor-electrolyte interfaces, see [1].)

The present article deals with methods of investigation and the results that they provide. In the methods in question, information about the electric and chemical state of these surfaces is obtained from changes in optical quantities, such as radiation intensity and state of polarization, on interaction of light with the semiconductor surface. As far as possible, changes produced by light, particularly in the electric state of the semiconductor surface (*e.g.* formation of charge-carrier pairs, surface photoeffect), will not be taken into account in this article. The wavelength and intensity of the light used for the measurements must therefore be so chosen that its effect on the electric and chemical processes under investigation is minimal.

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[1] *R. Memming* and *G. Schwandt*, Angew. Chem. *79*, 833 (1967); Angew. Chem. internat. Edit. *6*, 851 (1967).

2. Methods

The optical methods to be discussed here permit the determination of the refractive index n and the absorption constant k of a reflecting medium. If the reflecting interface is covered with a thin film of a third material, the thickness d and the optical constants n and k of this layer can be measured; However, only two of these quantities can be determined from any one measurement. In certain circumstances n and k provide information about the chemical composition of the layer, while d is important in connection with reaction kinetics. However, more detailed information about the chemical constitution can be obtained by measurement of the IR absorption which is made possible even for very thin films by a special technique.

2.1. Methods using Polarized Light

A method developed by *P. Drude* [2] before the turn of the century permits the detection of a very thin film ($\leq$ 1 Å) on the surface of a solid if the layer and the substrate differ in their optical constants. It is also possible by this method to follow the growth of a layer up to thicknesses of several tens of thousands of Ångströms. If the film absorbs light of the wavelength used, this process can be used only so long as the penetration depth of the light is at least of the same order of magnitude as the thickness of the film.

[2] *P. Drude*, Ann. Physik Chem. *36*, 865 (1889).

The reflection of polarized light at the interface between two media having different optical constants is described by the Fresnel equations. The light vector E is split into the components E_p, which is polarized parallel to the plane of incidence, and E_n, which is polarized normal to the plane of incidence. The change in these vectors on reflection is given by

$$E_p^{(r)} = r_p \cdot E_p^{(i)} \qquad E_n^{(r)} = r_n \cdot E_n^{(i)} \tag{1}$$

where $E^{(r)}$ is the vector of the reflected light and $E^{(i)}$ that of the incident light. r_p and r_n are the Fresnel amplitude reflection coefficients. If the light is incident from medium "0" (see Fig. 1a) and the refractive index of the adjacent medium is n_1, then

$$r_n = \frac{n_0 \cos\varphi_0 - n_1 \cos\varphi_1}{n_0 \cos\varphi_0 + n_1 \cos\varphi_1} \qquad r_p = \frac{n_1 \cos\varphi_0 - n_0 \cos\varphi_1}{n_1 \cos\varphi_0 + n_0 \cos\varphi_1} \tag{2}$$

where φ_0 is the angle of incidence and φ_1 the angle of refraction in medium 1. Since the refractive indices of nonabsorbing media are real and those of absorbing media are complex, r_n and r_p may also be either real or complex. A complex r means that phase differences that are not equal to zero or π exist between $E^{(i)}$ and $E^{(r)}$.

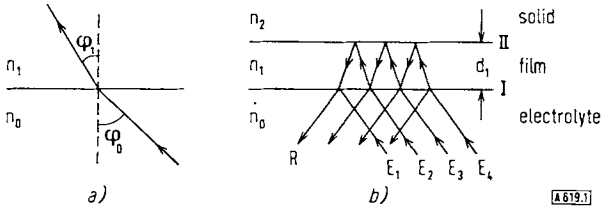

Fig. 1. (a) Refraction of light at an interface: n = refractive index; φ_0, φ_1 = angles of incidence and of refraction, respectively.

(b) Reflection of light at a surface covered with a film; d_1 = thickness of layer; E = incident beam; R = reflected beam.

If two media 0 and 2 are separated by a layer whose thickness is small in relation to the length of coherence of the light, and which absorbs the incident radiation only weakly or not at all, multiple reflections are possible in this thin film. As is indicated in Figure 1b, not only does the component of the incident ray E_1 reflected at the interface I contribute to the reflected ray R, but the incident rays E_2, E_3, *etc.* also contribute to R, since after traversing the thin film several times, they leave the layer with an amplitude determined by the reflection losses. This is substantially true of all the points of the interface I on which the beam falls.

If the thickness of the layer is uniform in the irradiated region, then in addition to the beam reflected at surface I, there will be contributions at every point due to other beams that have traversed the thin film two, four, or more times, and because of coherence, these beams superimpose there in magnitude and phase. The result is that the reflected light also has a uniform, definite state of polarization. Calculation of this superposition leads to the following expression for the amplitude reflection coefficient $\boldsymbol{R}$ of a thin film [3]:

$$\boldsymbol{R} = \frac{r_I + r_{II} \cdot \exp\left\{-\frac{4\pi i}{\lambda} n_1 d_1 \cos\varphi_1\right\}}{1 + r_I \cdot r_{II} \cdot \exp\left\{-\frac{4\pi i}{\lambda} n_1 d_1 \cos\varphi_1\right\}} = R \cdot e^{i\delta} \tag{3}$$

In this equation, r_I and r_{II} are the Fresnel coefficients of the interfaces I and II respectively; n_1 is the refractive index and d_1 the thickness of the film, φ_1 is the angle of refraction in the layer, λ is the wavelength, in vacuum, of the radiation used, R is the magnitude and δ is the argument of $\boldsymbol{R}$, and $i = \sqrt{-1}$. Insertion of r_n and r_p for r_I and r_{II} in accordance with equation (2) gives $\boldsymbol{R}_n$ and $\boldsymbol{R}_p$.

Equation (3) shows that $\boldsymbol{R}$ will generally be a complex number, even when all three of the media in question are non-absorbing and so have real optical constants. This means that when linearly polarized light falls on the coated interface, the reflected light is generally elliptically polarized.

For simplicity, linearly polarized light whose plane of vibration is inclined at 45 ° to the plane of incidence is used in reflection experiments of this type. In this case

$$E_n^{(i)} = E_p^{(i)}$$

After reflection, the amplitudes are

$$\boldsymbol{E}_n^{(r)} = \boldsymbol{R}_n \cdot E_n^{(i)} \qquad \boldsymbol{E}_p^{(r)} = \boldsymbol{R}_p \cdot E_n^{(i)} \tag{4}$$

Since $\boldsymbol{R}_n$ and $\boldsymbol{R}_p$ are different complex numbers, there is a phase difference between $\boldsymbol{E}_n^{(r)}$ and $\boldsymbol{E}_p^{(r)}$, and the two components differ in magnitude after reflection.

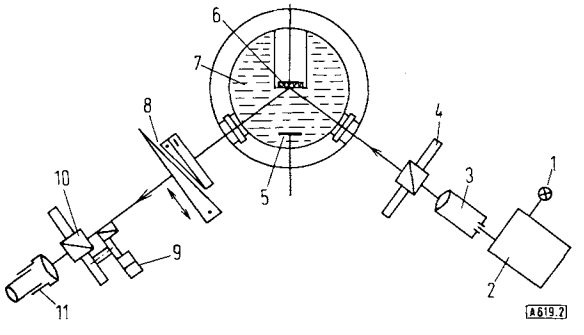

Fig. 2. Ellipsometer for the measurement of the growth of films on electrodes; 1. light source, 2. monochromator, 3. collimator, 4. polarizer, 5. counterelectrode, 6. sample, 7. electrolyte, 8. compensator, 9. half-shade device, 10. analyzer, 11. telescope.

These changes in the state of polarization of the reflected light can be measured with the apparatus shown in Figure 2, by means of which the growth of a layer on solid electrodes can be followed. A monochromator supplies monochromatic light which leaves the collimator as a parallel beam and is then linearly polarized. This polarized light then passes through the quartz window into the measuring cell, where it proceeds through the electrolyte to fall on the surface under examination, is reflected at this surface, and leaves the cell again through a second window. A platinum counterelectrode is

[3] *H. Mayer*: Physik dünner Schichten. Part I, Wissenschaftliche Verlagsgesellschaft mbH., Stuttgart 1950, p. 145ff.

situated opposite the sample for electrochemical polarization, and a calomel reference electrode also dips into the cell for measurement of the potential.

After leaving the cell, the reflected light passes through a Soleil-Babinet compensator, by means of which it is possible to obtain any desired phase difference between the components of the light vector polarized normal to and parallel to the plane of incidence. The compensator is adjusted in such a way as to convert the elliptically polarized light into linearly polarized light, and the magnitude of the phase difference is determined in this way. The adjustment is made on the basis of observations with a telescope, an analyzer, and a Tronstad [4] elliptic half-shade device, the half shade providing an accurate criterion of whether the light is elliptically or linearly polarized.

If we form the ratio of equations (4), taking into account (3), we find that since $E_n^{(i)} = E_p^{(i)}$,

$$\frac{E_p^{(r)}}{E_n^{(r)}} = \frac{R_p}{R_n} = \frac{R_p \cdot e^{i\delta_p}}{R_n \cdot e^{i\delta_n}} = \tan\psi \cdot e^{i\Delta} \qquad (5)$$

The quantity Δ is the phase difference between the components of the electric vector, and ψ is the angle between the plane of the restored linear polarization and the normal to the plane of incidence. This angle is found by measurement of the azimuth of the linearly polarized light leaving the compensator by means of a Lippich half shade.

The set-up described here may be modified. Thus instead of visual observation, a photoelectric cell may be used as an indicator. The optical compensator may be replaced by a $\lambda/4$ plate [5]. (For other methods for the determination of the state of polarization of reflected light see [6, 7].) Various kinds of information can be obtained from such measurements depending on the nature of the problem. We are interested in the case in which the optical constants of the substrate (medium 2 in Fig. 1b) and of the medium 0, from which the light is incident, are known, and the optical constants of the thin film (medium 1) and its thickness are to be determined.

It can be seen from equations (5), (3), and (2) that the quantities ψ and Δ depend in a complicated manner on the optical constants of the media 0, 1, and 2. The only practically possible method of evaluation, even for nonabsorbing layers, is therefore to calculate the values of ψ and Δ for various constants n_0, n_1, d_1, and n_2 by means of a computer. The calculated values of ψ and Δ are seen to be unique functions of the refractive index n_1 of the film and its thickness d_1 for practically all values of these quantities [8]. Ambiguity can arise only with very large values of n_1, but such high refractive indices are generally found only in the neighborhood of strong absorption lines. Further difficulties arise in measurement and evaluation in these regions in any case, since it would then be necessary to determine three unknowns (d_1, n_1, and the absorption constant k_1) from the two measured quantities Δ and ψ.

For very thin films ($d_1 < 100$ Å), it is possible to use approximate solutions in which Δ and ψ vary linearly with the thickness d_1 of the layer [9] and the proportionality factor depends on the refractive indices of the media involved.

The ellipsometric measurements discussed here allow the determination of even very small film thicknesses. According to *Archer* and *Gobeli* [9], the maximum sensitivity is 0.07 Å, which is less than the thickness of a monolayer. It should be possible to have layers one monolayer thick and with an incomplete coverage of the surface of the substrate, but not a layer whose thickness is much less than that of a monolayer. However, a layer that contains (evenly distributed) only a fraction Θ of the number of particles required for a monolayer behaves optically in the same way as a layer of thickness $\Theta \cdot d_0$, where d_0 is the thickness of the monolayer [10,11]. This theoretical deduction was confirmed by *Bootsma* and *Meyer* for the adsorption of noble gases on germanium. They determined the surface coverage volumetrically and the thickness of the adsorption layers ellipsometrically [12].

During the adsorption of polar organic molecules on metal surfaces, the layer thickness was determined ellipsometrically and with isotopes [13]. The results of the two methods agreed down to effective layer thicknesses considerably less than the thickness of a monolayer.

Owing to the periodic variations of Δ and ψ with d_1, the accuracy is different in different ranges of film thickness; however, it is always better than 1 %. The smallest layer thickness that could be measured with our apparatus by visual observation was 1 Å. An area of 0.2–1 cm² is illuminated for the measurement.

2.2. Measurement of the IR Absorption by Internal Reflection Spectroscopy (IRS)

Detailed information about the chemical composition of thin films can be obtained by measurement of the IR absorption. The great sensitivity of this process permits spectroscopic measurements with a single transmission of the beam through the layer, even for thicknesses of several 100 Å (depending on the strength of the absorption). Since all semiconducting substances, unless they are too highly doped, are transparent to IR radiation, the layers to be studied can be left on the semiconductors on which they have grown. However, a single transmission is not sufficiently sensitive for very thin layers.

Spectroscopic measurements can be carried out even on layers as thin as a few Å by a method given by *Harrick* [14]. A specially shaped semiconductor covered

[4] *L. Tronstad*, J. sci. Instruments *2*, 144 (1934).

[5] *R. J. Archer*, Physic. Rev. *110*, 354 (1958).

[6] *O. Schönrock* in *H. Geiger* and *K. Scheel*: Handbuch der Physik. Vol. 19, Springer, Berlin 1928, p. 705ff.

[7] *A. B. Winterbottom* in *E. Passaglia*, *R. R. Stromberg*, and *J. Kruger*: Ellipsometry in the Measurement of Surfaces and Thin Films. Nat. Bureau Standards Miscell. Publ. *256*, 97 (1964).

[8] *R. J. Archer*, J. opt. Soc. Amer. *52*, 970 (1962).

[9] *R. J. Archer* and *G. W. Gobeli*, J. Physics Chem. Solids *26*, 343 (1965).

[10] *C. S. Strachan*, Proc. Cambridge philos. Soc. *29*, 116 (1933).

[11] *D. V. Sivukhin*, Sov. Physics JETP (English translation of Ž. exper. teoret. Fiz.) *3*, 259 (1956).

[12] *G. A. Bootsma* and *F. Meyer*, unpublished.

[13] *J. R. Miller* and *J. E. Berger*, J. physic. Chem. *70*, 3070 (1966).

[14] *N. J. Harrick*, J. physic. Chem. *64*, 1110 (1960). For a detailed treatment see *N. J. Harrick*: Internal Reflection Spectroscopy. Interscience, New York, 1967.

by the thin film on two opposite sides is used. Monochromatic infrared radiation falls from the semiconductor onto one of the coated surfaces (see Fig. 3) in such a way that total reflection takes place at this

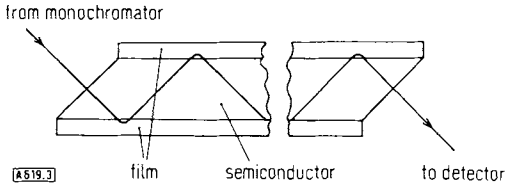

Fig. 3. Principle of the measurement of the IR absorption of thin films by internal reflection spectroscopy (IRS).

interface. This is nearly always possible, since semiconducting materials generally have very high refractive indices. The radiation penetrates a short distance (of the order of the wavelength) into the rarer medium (the film), and can thus interact with the molecules of the layer. According to the law of conservation of energy, the energy that is not absorbed in the layer must return to the semiconductor, and the process is repeated at the opposite face, as shown in Figure 3. In this way the absorption process is repeated several times in succession, with the result that the absorption signal is intensified. The number of reflections, and hence the number of absorption processes, depends on the length and thickness of the semiconductor on which the layer is situated. Figure 4 shows a comparison of the absorption spectrum obtained by the normal transmission method for a germanium oxide film containing hydride with the spectrum obtained by internal reflection spectroscopy with 50 reflections. (The semiconductor consisted of intrinsic germanium.)

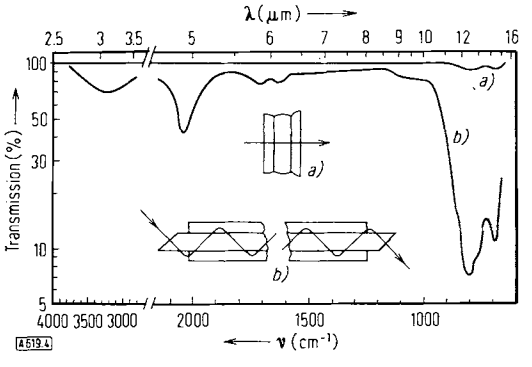

Fig. 4. IR spectrum of a film of germanium oxide containing hydride (on intrinsic germanium).
(a) transmission,
(b) with internal reflection (50 reflections).

To record absorption spectra, chopped light is usually passed through the sample. With objects that absorb only weakly, this means that relatively large signals are received by the detector, whereas the variations in these signals due to absorption are very small. The sensitivity can be considerably increased in the case of an absorption process whose intensity can be altered by means of external factors (*e.g.* electric fields). Unchopped light is passed through the object, and the alternating light component obtained by modulation of the absorption is measured at maximum amplification (effect modulation).

A correspondingly large increase in sensitivity can be achieved by difference methods for objects whose absorption cannot be influenced by external parameters. This involves the measurement of the difference between the signals produced after the splitting of the beam into two; one of the resulting beams is unattenuated and is allowed to fall on one detector while the other beam, which is attenuated by absorption, falls onto a second detector. These voltages, which are very small for weak absorptions, can then be amplified.

3. Results

3.1. Adsorption Processes on Semiconductor Surfaces

Archer and *Gobeli*[9,15] used ellipsometric methods to study the adsorption of oxygen on silicon. The samples were prepared by cleavage of single crystals of silicon in a high vacuum (5×10^{-10} torr). At this pressure, the reflection behavior of the cleavage face did not change during the first 10–15 min after cleavage. It was only on addition of oxygen that it became possible to record the changes in phase difference shown in Figure 5, which were interpreted as resulting from the formation of a monomolecular adsorption layer. The detection sensitivity was 0.07 Å.

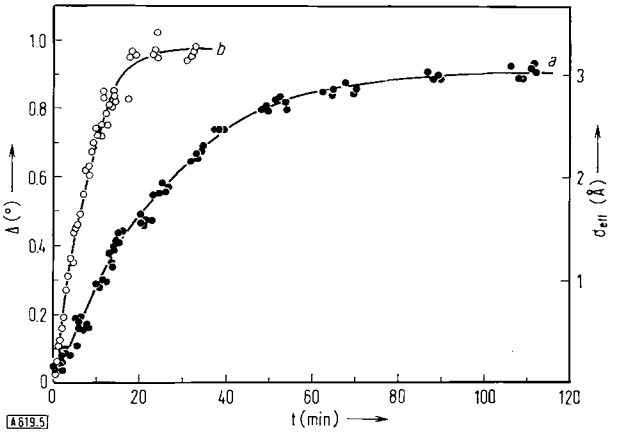

Fig. 5. Ellipsometric measurement of the adsorption of oxygen on silicon surfaces (obtained by cleavage of single crystals) at room temperature (after [9]).
(a) $P_{O_2} = 3.6\times10^{-7}$ torr
(b) $P_{O_2} = 1.8\times10^{-6}$ torr.

Since the measured quantity ψ remains practically constant for such small changes in the thickness, only one unknown can be determined. The phase difference Δ varies in proportion to the degree of coverage. The fact that a constant phase difference is reached after a long time is interpreted by the authors as indicating that the formation of the monolayer is complete, and that the adsorption then becomes considerably slower. The sticking coefficients were determined from the resulting data by comparison with the number of molecules impinging on the semiconductor surface. The values obtained

[15] *R. J. Archer* [7], p. 255.

are an order of magnitude lower than those found by other methods; the authors attribute this difference to the fact that they used cleavage faces of high surface perfection. Further growth to form a triple layer is also approximately proportional to the logarithm of time.

Archer[15] also reported on the adsorption of vapors on silicon surfaces that were covered with a 15–20 Å layer of silicon oxides and hydrides formed as a result of etching (with various HF/HNO_3 mixtures). The surface of this layer could be made hydrophilic by immersion in HF/HNO_3, so that the adsorption of water vapor was intensified. (For measurement of the adsorption of organic molecules on silicon, see also [16].)

Becker and *Gobeli*[17] used internal reflection spectroscopy to study the IR absorption of hydrogen adsorbed on the surface of silicon crystals. The surfaces of these samples were cleaned by bombardment with argon ions at 5×10^{-4} torr and heating to 1000 to 1200 °K in an ultrahigh vacuum. A pressure of 10^{-6} torr of hydrogen was established, and atomic hydrogen, which was produced by means of a glowing tungsten filament, was chemisorbed on the surface of the silicon. With the aid of a difference method, the authors were able to detect the resulting Si–H bond by its IR absorption. After about 45 min, the thickness of the adsorption layer became constant despite the continued action of atomic hydrogen, and the coverage did not decrease even in a high vacuum. The authors assume that this coverage must be at most monatomic, since it could be removed by a relatively short bombardment with argon ions. Bombardment of the silicon surface with hydrogen ions in a gas discharge led to the formation of thicker silicon hydride layers.

3.2. Investigations on the Formation of Reaction Layers on Semiconductor Surfaces

Archer[18] used ellipsometric measurements to follow the growth of oxide layers on germanium and silicon in air at room temperature after specified etching and rinsing of the polished surfaces. After etching in mixtures of acetic, hydrofluoric, and nitric acids, layers 12 Å thick were found on silicon and layers 16 Å thick on germanium. After 30 hours, the thickness of these layers had increased to about 30 Å. The growth of the layers followed the Elovich equation, according to which the layer thickness is proportional to the logarithm of time. The measured refractive indices agreed well with those of the oxides of these semiconducting substances.

Andreeva and *Shishakov*[19] studied the absorption of air and the subsequent oxidation of the surfaces of vapor-deposited germanium films. They allowed air to act on the surface for periods of 20–30 min, alternating with six-hour periods during which the sample container was evacuated. The 10–30 Å layer that was formed in air partly disappeared on evacuation; an additional layer was formed under the further action of air, and this could again be partly removed by evacuation. On evacuation for 6 hours, films that had taken 34 days to grow to 80 Å were reduced in thickness to 46 Å. These phenomena are explained by the vaporization or decomposition of the oxide formed. The oxidation of vapor-deposited germanium films was much slower in dry oxygen than in moist air. Freshly evaporated germanium films adsorbed water only very slowly. While the growth of the layer formed in air on polished single crystals of germanium and silicon was found to be proportional to $t^{1/2}$, film thicknesses of between 30 and 80 Å (Si) or even 135 Å (Ge) could be detected on etched surfaces of both materials immediately after etching, but further growth of these layers was only very slight, and some actually became thinner.

Stricha and *Kiltschizkaja*[20] determined ellipsometrically the reflection parameters for uncoated germanium and silicon surfaces which had been formed by cleavage at 10^{-9} torr. These quantities were then used to evaluate reflection measurements on germanium and silicon after etching in various solutions. For example, silicon has a 60 Å film after etching in HF solution, a 35 Å film after mechanical polishing, and a 50 Å film after cleavage in air. With germanium they found a 25 Å film after etching in H_2O_2, and a 35 Å film after cleavage in air (the time taken for layer formation is not given).

Archer[21] used polarization measurements to follow the growth of layers on silicon during corrosion. The corroding electrolyte consisted of 20 M aqueous hydrofluoric acid containing nitric acid, sodium nitrite, or nitric oxide in concentrations of 10^{-1} to 10^{-3} M. The growth of the layer was determined as a function of the concentration of the additives and as a function of the type and magnitude of the conductivity of the semiconductor sample. Simultaneous measurement of the refractive index (see also [8]) showed that it evidently depended on the type and value of the conductivity. Whereas the refractive index of the layer was generally 2.7 in the cases of n-type and p-type material, the value for p-type Si having specific resistances of 0.1 to 0.001 ohm·cm was about 4.1. Moreover, the formation of the film was five times as fast within this resistance range as for samples having other resistance values.

Chemical studies[22] had shown that similar films, which also have a high chemical reactivity, can be produced on silicon by anodic polarization in hydrofluoric acid. On the basis of the chemical behavior of these layers, it was thought that they consist either of very reactive elemental silicon or of silicon hydrides. Owing to the high refractive index of 4.1, *Archer* concluded that layers of elemental Si are formed on

[16] *B. H. Claussen*, J. electrochem. Soc. *111*, 646 (1964).

[17] *G.E.Becker* and *G.W.Gobeli*, J.chem.Physics *38*, 2942 (1963).

[18] *R. J. Archer*, J. electrochem. Soc. *104*, 619 (1957).

[19] *V.V.Andreeva* and *N.A.Shishakov*, Russ. J. physic. Chem. (English transl. of Ž. fiz. Chim.) *35*, 663 (1961).

[20] *W. J. Stricha* and *S. S. Kiltschizkaja*, Instruments exper. Techn. (English transl. of Pribory Techn. Eksperimenta) No. 3, 177 (1964).

[21] *R. J. Archer*, J. Physics Chem. Solids *14*, 104 (1960).

[22] *D. R.Turner*, J. electrochem. Soc. *105*, 402 (1958).

p-type material having specific resistances of 10^{-1} to 10^{-3} ohm·cm, while layers of silicon hydrides are formed when the material has a specific resistance outside this range. However, IR studies [23] showed that their approximate composition ranges between $SiOH_2$ and $SiO_{1.5}H$, *i.e.* that they contain an appreciable amount of oxygen. No relationship was found between the chemical composition of the layer and the resistance of the semiconductor. A similarly high oxygen content was also found by proton-activation analysis [24], and the relationship found by *Archer* [21] between the rate of growth of the film and the conductivity of the silicon used was confirmed.

We investigated the properties of reaction layers of similar composition produced on p-type silicon by anodic polarization in strong aqueous solutions of hydrofluoric acid [23]. Curve a in Figure 6 shows the transmission spectrum of the layer produced on a silicon disk in a deuterium-enriched solution. The absorption with maxima at 2135, 2115, and 2090 cm^{-1} is assigned to the stretching vibrations of SiH_x groups, and the absorption with maxima at 1560, 1530, and 1520 cm^{-1} to the stretching vibrations of SiD_x groups. The magnitude of the frequency shift confirms this assignment. The broad band at 1070 cm^{-1} shows that some Si–O bonds are also present. After the layer had been exposed to the action of 30 % H_2O_2 for 16 hours, we found a large number of OH groups (absorption at about 3400 cm^{-1}, curve b). The very large decrease in transmission at this point indicates an increase in the number of SiOH groups.

This absorption could also be due to H_2O incorporated in the layer. However, this possibility can be ruled out in view of the absence of the corresponding deformation vibration at 1600 cm^{-1}. Moreover, the intensity of the band at about 1100 cm^{-1} has increased greatly. This absorption is due to the stretching vibrations of the SiO_x groups and/or the stretching vibration

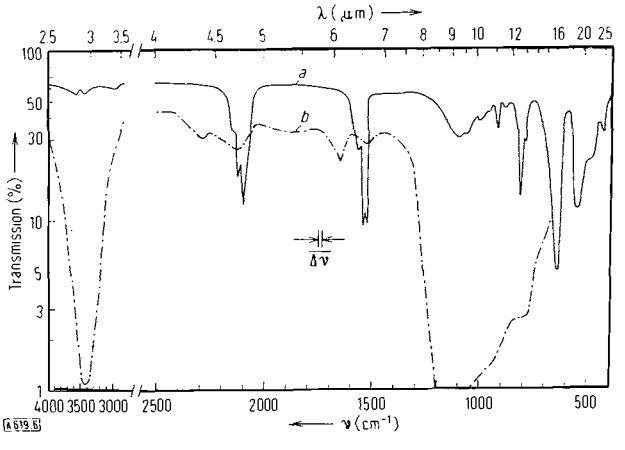

Fig. 6. Transmission spectrum of a reaction layer produced anodically on p-type silicon (from [23]). Electrolyte: 10 N aqueous hydrofluoric acid, deuterium-enriched.

(a) Immediately after film formation.

(b) After treatment for 16 hours with 30 % H_2O_2.

[23] *K. H. Beckmann*, Surface Sci. *3*, 314 (1965).

[24] *J. C. Ritter, M. N. Robinson, B. J. Faraday*, and *J. I. Hoover*, J. Physics Chem. Solids *26*, 721 (1965).

ν(Si–OH) of the SiOH groups. ν(Si–OH) is the vibration in which the OH group vibrates toward the Si atom.

Figure 7 shows the changes in the transmission spectrum of a thinner film after additional treatments. Whereas freshly formed layers (curve a) react explosively with 65 % HNO_3, a layer that has been preoxidized in H_2O_2 (curve b) can be further oxidized by nitric acid (curve c). The number of SiOH groups increases; the intensity of the SiH_x stretching vibrations remains practically unchanged (see below), but the bands are partly displaced toward higher wave numbers. The increase in absorption at 1070 cm^{-1}, in conjunction with the intensification of the band at 870 cm^{-1}, points to the formation of chains having the chemical composition Si_2O_6. The SiOH and SiH groups suffer substantial decomposition during heat treatment at 1000 °C, and the absorption at 810 cm^{-1} (curve d) suggests that the layer then consists of SiO_2 with a disordered arrangement of the SiO_4 tetrahedra such as occurs in amorphous quartz.

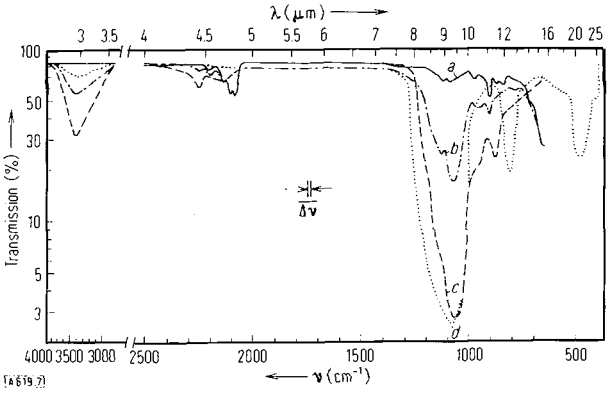

Fig. 7. Influence of oxidation processes on the transmission spectrum of an anodically produced reaction layer on p-type silicon (after [23]). Electrolyte: 10 N aqueous hydrofluoric acid.

(a) Immediately after layer formation.

(b) After treatment for 16 h with 30 % H_2O_2.

(c) After additional treatment for 10 s with 65 % HNO_3.

(d) After subsequent annealing in air at 1000 °C for 5 min.

Quantitative evaluation of these spectra showed that the freshly prepared layers have approximately the composition $SiH_{1.5}$, *i.e.* that they consist of polymerized silicon hydrides. Oxidation with H_2O_2, subsequent oxidation with HNO_3, and oxidation in air have practically no effect on the integrated absorption strength due to the SiH_x stretching vibrations (Fig. 8); as the original band at 2100 cm^{-1} decreases in intensity a new band appears at 2275 cm^{-1}. In conjunction with the simultaneous increase in the number of SiO oscillators, this means that the $-(SiH_2)-(SiH_2)-$ chains are gradually converted into $-(SiH_2)-O-(SiH_2)-$ chains. The displacement of the $(SiH)_x$ stretching vibration is due to the change in the SiH force constant as a result of the attachment of oxygen to the silicon. The absorption bands below 900 cm^{-1}, which are particularly noticeable in curve a of Figure 6, could not be assigned. They could be due to the presence of SiF bonds, but this assumption has not been proved.

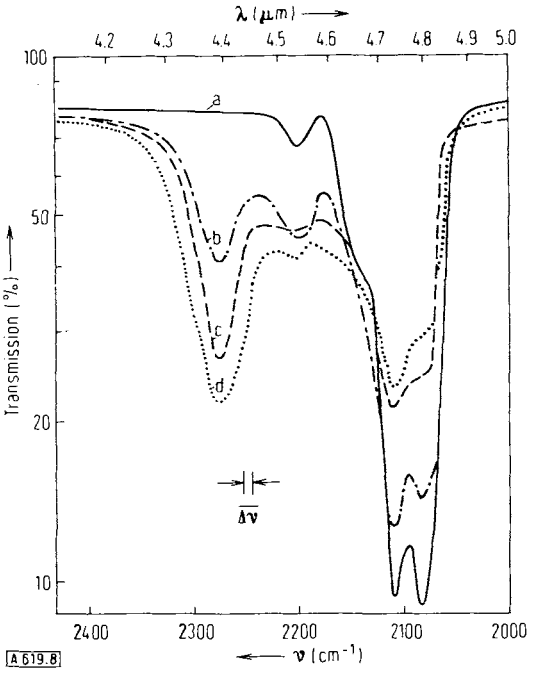

Fig. 8. Displacement of the frequency of the stretching vibrations $\nu(SiH_x)$ of reaction layers on silicon as a result of the incorporation of oxygen into silicon chains (after [23]).
(a) Fresh layer.
(b) After storage for 40 days in air.
(c) After storage for 200 days in air.
(d) After storage for 300 days in air.

The question of how reaction layers of this nature can be formed on anodic polarization has not yet been answered. Though the individual steps in the anodic dissolution of silicon in hydrofluoric acid have been studied[25], the formation of silicon hydrides cannot yet be explained.

Reaction layers having comparable chemical compositions can also be formed on germanium in etching solutions containing nitric acid or hydrogen peroxide as well as hydrofluoric acid[26]. IR analysis of the layers was carried out by internal reflection spectroscopy, since they are very thin. An HF/HNO_3 mixture (40 % HF/65 % HNO_3, 7:3 v/v) gave essentially GeO_2, which could be readily determined from

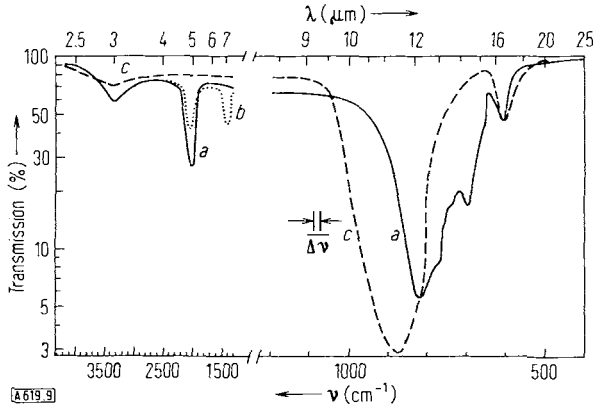

Fig. 9. (a) IRS-transmission spectrum of a layer formed on intrinsic germanium in an etching solution consisting of 40 % HF and 30 % H_2O_2 (10:1 v/v).
(b) Partial spectrum of the layer formed in the same solution enriched in deuterium.
(c) Transmission spectrum of the layer of (a) after annealing in air at 500 °C for 8 min (after [26]).

[25] *R. Memming* and *G. Schwandt*, Surface Sci. *4*, 109 (1966).
[26] *K. H. Beckmann*, Surface Sci. *5*, 187 (1966).

the absorption. The strongest absorption for layers formed in HF/H_2O_2 (40 % HF/30 % H_2O_2, 10:1 v/v) occurred at 825 cm^{-1} (see Fig. 9). The wave number of this vibration was too far from the characteristic frequencies of the GeO_2 modifications to allow assignment to one of these modifications without further investigation. It was only after formation of such a layer in an ^{18}O-enriched solution ($[^{16}O]/[^{18}O] = 8.5$) that this absorption could be assigned to a GeO stretching vibration on the basis of the transmission spectrum shown in Figure 10.

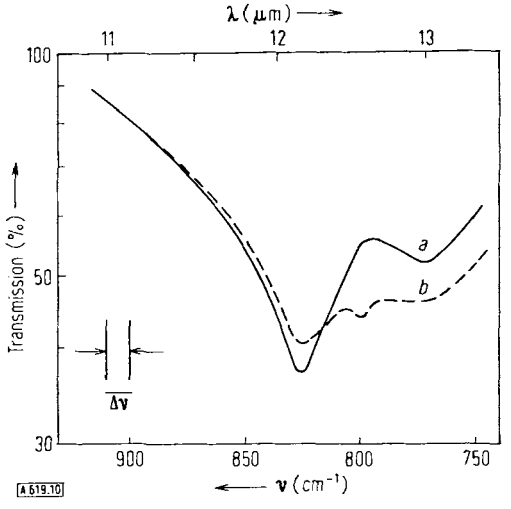

Fig. 10. Absorption band of the GeO_x stretching vibration of a reaction layer formed on germanium by etching as described in Fig. 9 (after [26]).
(a) Layer contains only ^{16}O.
(b) Layer also contains ^{18}O ($[^{16}O]/[^{18}O] = 8.5$).

Since the added ^{18}O is probably present in the layer in the form of ^{16}O–Ge–^{18}O groups, we found that curve a (only with ^{16}O) was replaced by curve b with an additional absorption at 800 cm^{-1} due to vibration of the ^{16}O–Ge–^{18}O group corresponding to that occurring at 825 cm^{-1} in the case of ^{16}O–Ge–^{16}O. This displacement by 25 cm^{-1} corresponds to the calculated isotope effect, and this confirms the assignment of the absorption at 825 cm^{-1} to the GeO stretching vibration.

Moreover, the short-wavelength part of the spectrum of curve a in Figure 9 shows that some OH groups (3300 cm^{-1}) and a larger number of GeH bonds (2000 cm^{-1}) are present. The latter assignment is confirmed by the appearance of the GeD stretching vibration after deuteration (curve b). Heating for 8 min at 500 °C leads to the disappearance of these hydride bonds, and the GeO stretching vibration is displaced to 860 cm^{-1}, which is also its known position in the soluble modifications of GeO_2. Quantitative estimation of the absorption intensities from curve a gave the approximate composition $GeOH_2$ for the original reaction layer.

While these surface films formed on germanium in HF/H_2O_2 have a certain similarity to the corrosion layers formed on silicon in HF/HNO_3, and while similar layers can be produced on silicon by anodic polarization in HF solution, anodic formation of such films on germanium was found to be impossible. In the film-forming range, silicon goes into solution in a bivalent state[25], whereas germanium always gives a tetravalent state on anodic dissolution in hydrofluoric acid solutions of various concentrations[27].

[27] *G. Schwandt*, unpublished.

Ellipsometric studies on the formation of a layer on germanium anodes in alkaline electrolytes showed the potential-dependent film growth illustrated in Figure 11 [28]. This current density-potential curve is explained by the fact that OH^- ions from the electrolyte are required for the anodic dissolution of germanium, but owing to the relatively high concentration of the conducting salt, these ions are replenished only by diffusion to the semiconductor surface. The concentration gradient of the OH^- ions in front of the semiconductor surface reaches a maximum at a potential of about −400 mV; if the potential is raised further, the diffusion current remains constant, and the anodic dissolution consequently cannot be increased. Water reacts directly with germanium only above +100 mV, so that a steep increase in current begins at this point.

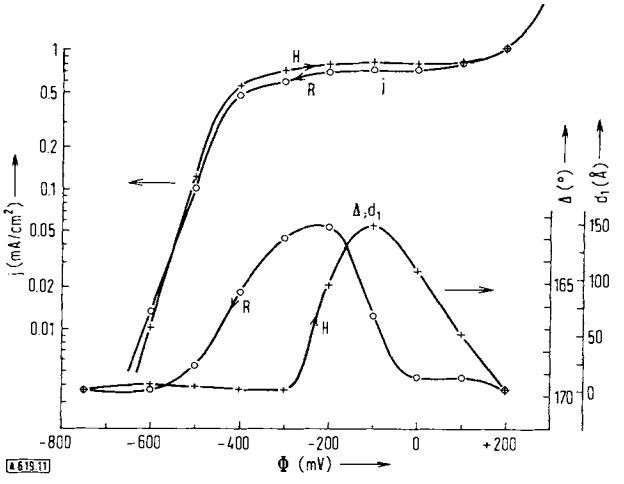

Fig. 11. Characteristic of a p-type germanium electrode (ρ = 10 Ω cm) in alkaline electrolyte with conducting salt (upper curves) and ellipsometrically measured film growth (lower curves) as a function of the potential Φ (after[28]).Electrolyte:3×10⁻² M KOH,0.6 M KBr,1.1×10⁻² M GeO_2, potential against saturated calomel electrode, angle of incidence 50°, wavelength of the light λ = 565 nm. H = forward run, R = reverse run.

The potential-dependent film growth shown in Figure 11 was observed in the region of this limiting diffusion current. Figure 12 shows the increase in the thickness of the layer at a constant potential as a function of time. In this case Δ is plotted against ψ (cf. eq. (5)] with time as the parameter. Corresponding relationships with the film thickness were calculated by computer for various refractive indices of the layer and plotted in Figure 12. For film thicknesses greater than 700 Å, the experimental curve follows the calculated curve for $n_1 = 1.5$ with an accuracy of $\delta n_1 = \pm 0.01$. The thickness of the layer increases almost linearly with time, and it is therefore concluded that the layer is fairly porous.

Figure 13 shows the Δ (ψ) curve for a layer formed in an electrolyte in which the alkali metal is cesium. The experimental curve, unlike that in Figure 12, is unsymmetrical and is not closed. Curves calculated for absorbing layers are therefore shown in Figure 13; the experimental curve agrees more closely with these.

[28] *K. H. Beckmann*, Ber. Bunsenges. physik. Chem. *70*, 842 (1966).

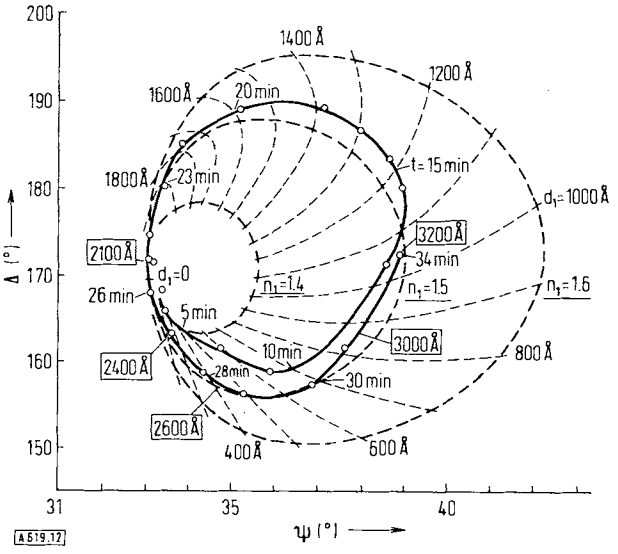

Fig. 12. Comparison of the quantities Δ and ψ measured in the forward run H at a constant potential of −100 mV (full curve) with values calculated for various thicknesses (d_1) and refractive indices (n_1) of the layer (after [28]). Electrolyte and other data as in Fig. 11. The lines of equal thickness are valid only for the first tracing of the experimental curve.

The refractive index of the layer is found from this plot to be $n_1 \approx 1.43 - i\,0.15$. It can therefore be seen that the reaction products formed on anodic dissolution of germanium depend partly on the alkali metal ion present in the electrolyte. The alkali metal ion is very probably incorporated into the layer. This assumption was confirmed by IR studies, since the IR spectrum corresponded to that of the acidic germanates. The layer thus had a composition such as $NaHGeO_3$ or $CsHGeO_3$; however, the exact formula cannot be given.

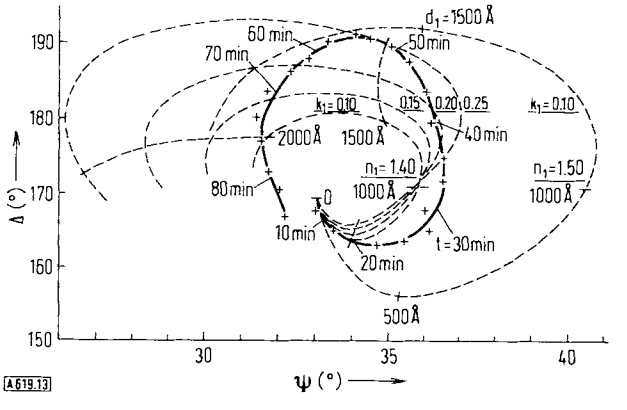

Fig. 13. Comparison of the quantities Δ and ψ measured in the forward run at a constant potential of −200 mV (——) with the values calculated for various thicknesses (d_1) and refractive indices (n_1, k_1) of the layer (after [28]). Sample and optical data as in Fig. 11. Electrolyte: 3×10⁻² M CsOH, 1 M CsBr, 1.1×10⁻² M GeO_2.

Thermally produced oxides are very important in industry as passivating substances on the surfaces of semiconductors, particularly silicon. Many optical investigations have been carried out to establish the structure and chemical composition of these films. *Sládková* [29] studied the growth of thermally produced SiO_2 layers on silicon as a function of the temperature.

[29] *J. Sládková*, Czechoslov. J. Physics *13B*, 452 (1963).

Below 950 °C, the thickness of the layer increased linearly with time, while between 950 and 1000 °C it increased parabolically in accordance with $d_1 \propto \sqrt{t}$. This means that the layers formed at higher temperatures are more dense, so that the rate of diffusion of the oxygen in the silicon dioxide layer is rate-determining.

The same growth pattern was found by *Claussen* and *Flower*[30] for thermal oxidation at 1200 °C in dry and in moist oxygen as well as in moist argon, the proportionality constant varying with the composition of the gas. The oxidation of the surface of Si is slowest in dry oxygen and in argon saturated with water at 28 °C, and fastest in oxygen saturated with H_2O. The same growth law was found by *Edagawa et al.*[31] from IR measurements; the activation energies for the oxidation in various atmospheres were determined from the temperature dependence.

Revesz and *Zaininger*[32] determined the compactness of SiO_2 films on silicon relative to amorphous quartz from the ellipsometrically measured refractive indices of the films by comparison of the refraction $(n^2 - 1)/(n^2 + 2)$ with that of the quartz. It was found that SiO_2 layers formed anodically in methylacetamide reach a density of only 77 % of that of amorphous quartz. *Pliskin* and *Lehman*[33] also found that the refractive index of SiO_2 layers increases with increasing density, and also with increasing concentration of oxygen vacancies. Increasing concentration of oxygen vacancies is also accompanied by a displacement of the SiO stretching vibration toward lower wave numbers. The authors also used similar optical methods as well as etching processes to study silicon dioxide layers formed by thermal oxidation, vapor deposition, pyrolysis of tetraethoxysilane $Si(C_2H_5O)_4$, catalysis of the reaction of oxygen with silicon by lead oxide, sputtering, and anodic polarization in the electrolyte. When the films obtained at lower temperatures were subsequently "densified" in a moist atmosphere at about 980 °C, their optical properties became practically the same as those of the thermally produced oxide.

IR measurements on silicon nitride (Si_3N_4) layers produced on silicon surfaces by sputtering or pyrolytic deposition from a mixture of SiH_4 and NH_3 have also been reported[34,35]. The frequency of the Si–N stretching vibration varies slightly according to the method of production of the layer.

Very few optical investigations have been carried out on interfaces of compound semiconductors. *Saxena*[36] used ellipsometry to study film-free indium antimonide surfaces in order to determine the refractive index of this semiconductor. Values of 3.5 to 4.1 were obtained, depending on the surface treatment. *Zaininger* and *Revesz*[37] found that the oxide layers formed on thermal oxidation of GaAs surfaces are possibly inhomogeneous and their composition is so complex that evaluation of the measured quantities after stepwise etching gives values of the optical constants that vary with the thickness of the film. The authors concluded from this and from the results of other investigations that arsenic is deposited at the interface between the semiconductor and the layer during oxidation.

3.3. Optical Studies on the Space-Charge Region and on Surface States

The electric and electrochemical behavior of semiconductor interfaces depends strongly on the properties of the space-charge region immediately under the semiconductor surface[1]. By application of a voltage between the semiconductor surface and a counterelectrode, it is possible to vary the potential drop across this space-charge region and hence the energy of the electrons in this region (band bending), and since their density follows the Fermi distribution, the number of electrons and holes present also changes. The counterelectrode may consist of a metal plate situated at a very short distance away from the semiconductor electrode, with which it forms a condenser. In certain circumstances the semiconductor may be immersed in an electrolyte, and the voltage required for bending of the energy bands may be applied between the semiconductor and a platinum counterelectrode.

The free electrons or holes in the semiconductor absorb infrared radiation in a characteristic manner. In the range in which we are interested, with radiation energies $h\nu$ smaller than the distance between bands $E_g = E_c - E_v$ (see Fig. 14), this absorption leads to an increase in the energy of the absorbing carriers, which either remain in their band or pass into another conduction or valence band. However, this absorption is so weak that measurable signals are obtained only at very high carrier densities.

Even in internal reflection spectroscopy measurements with 100 reflections, the number of additional free carriers present in the space-charge region is still too small to be measured. However, a measurable signal is obtained if the measurements are carried out with unchopped light and effect modulation. The band bending can be modulated between U_{R1} and U_{R2} (see Fig. 14) by application of an alternating field between the sample and the counterelectrode. The densities of the electrons and holes then change in accordance with the Fermi distribution given in Figure 14c, which is plotted on the same energy scale. The quantity f is the ratio of the number of electrons present in the band in question at this energy to the

[30] *B. H. Claussen* and *M. Flower*, J. electrochem. Soc. *110*, 983 (1963).

[31] *H. Edagawa, Y. Morita*, and *S. Maekawa*, Jap. J. appl. Physics *2*, 765 (1963).

[32] *A. Revesz* and *K. H. Zaininger*, J. Physique *25*, 66 (1964).

[33] *W. A. Pliskin* and *H. S. Lehman*, J. electrochem. Soc. *112*, 1013 (1965).

[34] *S. M. Hu*, J. electrochem. Soc. *113*, 693 (1966).

[35] *V. Y. Doo, D. R. Nichols*, and *G. A. Silvey*, J. electrochem. Soc. *113*, 1279 (1966).

[36] *A. N. Saxena*, Appl. Physics Letters *7*, 113 (1965).

[37] *K. H. Zaininger* and *A. G. Revesz*, J. Physique *25*, 208 (1964).

number of possible sites. The quantity $(1 - f)$ is the corresponding number for the holes in the valence band. It can be seen from Figure 14 that for band bending by U_{R1} at the surface (Fig. 14a), the valence band contains more holes and the conduction band fewer electrons than in the case of U_{R2} (Fig. 14b). The infrared beam, which passes through the space-charge region immediately before and after each total reflection, is therefore weakened to various extents by absorption in the two modulation half-waves, depending on the carrier densities. It is only this small change that is electronically amplified and recorded after the beam reaches the detector.

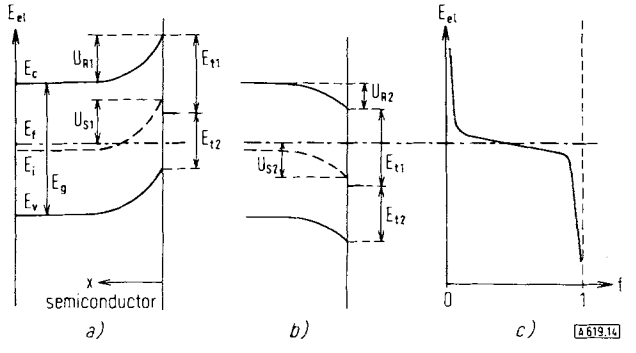

Fig. 14. (a), (b) Variation of the electronic energy (band model) near the semiconductor surface for two different band bendings.

(c) Fermi distribution on the same energy scale.

E_C: bottom of the conduction band; E_V: top of the valence band; E_F: Fermi level; E_i: middle of the forbidden zone; U_R: band bending at the surface; E_t: energy of the surface state; E_{el}: energy of the electrons; x: perpendicular distance from the surface; E_g: band gap; U_S: surface potential.

In addition to this absorption by free carriers, another process is also possible. There may be surface states situated in the forbidden zone between the two bands. This means that there are energy states within the band gap at the surface that can be occupied by electrons. These states or centers are due to attached foreign atoms or even simply to the breakdown of the properties of the periodic lattice at the surface. The occupation of these centers also follows the Fermi distribution; centers below the Fermi level E_F (see Fig. 14) are almost totally occupied by electrons, while those above the Fermi level are mostly empty. The change in the energy of the electrons in both bands as a result of the application of an electric field between the semiconductor and the counterelectrode (change of band bending) is the same as the change in the energy of the electrons in surface states. This means that the center is always situated at a distance E_{t1} from the conduction band and at a distance E_{t2} from the valence band, irrespective of the magnitude and direction of U_R. Thus if the magnitude of U_R is such that the energy of the center is above E_F (see Fig. 14a), the center is substantially unoccupied, and it may be occupied by an electron from the valence band by absorption of a light quantum $h\nu_2 = E_{t2}$ by this electron. Conversely, if the center lies below E_F (Fig. 14b), the occupied center may be emptied by absorption of a quantum $h\nu_1 = E_{t1}$, the electron being raised into the conduction band. If the band bending caused by the direct current is such that the energy of the surface state coincides with the Fermi level, there is a constant change in the occupancy of this state, even at small amplitudes of the applied alternating voltage, and hence in the optical absorption due to the charge carriers occupying or leaving this surface state. Since E_{t1} and E_{t2} (see Fig. 14) are generally different, changes in absorption will be observed at two wavelengths if the probabilities of the above transitions are sufficiently high, and these changes will then also differ in phase.

Harrick [38] carried out measurements of this type between 1.1 and 5.4 μm on n-type silicon surfaces that had been thermally oxidized in an atmosphere of wet oxygen. The sample was always kept at a positive potential with respect to the counterelectrode by means of a DC voltage (bending up of the band), and an alternating voltage was superimposed on this direct voltage. With large positive DC voltages, the magnitude of the observed absorption change increased approximately with λ^2. This spectral behavior demonstrates the absorption by free holes in silicon. Since the absorption by free holes is stronger than that by free electrons, no absorption due to the change in the density of the free electrons with the applied AC voltage could be observed at low bias voltages ($U_R \approx 0$). At wavelengths shorter than 4 μm, absorption changes appeared whose magnitude and sign are strongly dependent on the applied DC voltage. These changes were assigned to transitions of the charge carriers into or from the surface states. A broad distribution of surface states was deduced from the spectral behavior of the magnitude and phase of these changes, and in the range in which measurements were possible, the density of these states was found to decrease from the center of the band to zero at the upper edge of the valence band. The physical or chemical nature of these centers is not yet known.

Figure 15 shows the absorption spectra of free holes (curve a) and of free electrons (curve b), the density of which was modulated by variation of the band bending over the space-charge region in intrinsic germanium. In this measurement the semiconductor was immersed in an electrolyte; the bending of the band could be changed by means of the applied alternating field. Since the absorption cross section of the free holes is very much greater than that of the free electrons at these wavelengths, the band bending at the surface had to be changed to a greater extent for curve b in order to obtain roughly equal modulation. The resulting change in the number of charge carriers per cm² of surface, as calculated from the change ΔI in the incident intensity I_0 and the known absorption cross sections of holes and electrons, are $\Delta P \approx 4\times10^{11}$ cm^{-2} and $\Delta N \approx 4\times10^{12}$ cm^{-2}. The variation of the carrier densities as a result of this change in band bending can be calculated with the aid of the Fermi distribution and the Poisson equation. The values obtained agree very closely with the experimental results.

[38] *N. J. Harrick*, Physic. Rev. *125*, 1165 (1962).

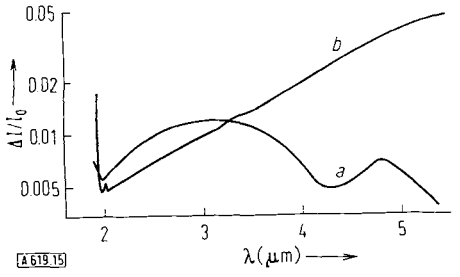

Fig. 15. Relative change in transmission on modulation of the hole density (a) for upward bending of the bands ($U_R \approx -100$ meV) and of the electron density (b) for downward bending of the bands ($U_R \approx 250$ meV) in intrinsic germanium. The approximate changes in the carrier densities are:
(a) $\Delta P \approx 4 \times 10^{11}$ cm^{-2}
(b) $\Delta N \approx 4 \times 10^{12}$ cm^{-2}.

The fast increase in $\Delta I/I_0$ below 2 μm is due to another effect. At these wavelengths the absorption of the radiation increases very rapidly in the case of germanium, since the incident energies ($h\nu \approx E_g = E_c - E_v$, see Fig. 14) are sufficient to raise electrons from the valence band into the conduction band. If strong electric fields are present, as is the case at the surface, they favor the transition, *i.e.* they effectively decrease the band gap (Franz-Keldysh effect), so that the absorption increases even at greater wavelengths (see *e.g.* [39]).

Samoggia et al. [40] observed transitions from surface states into the conduction band in n-type germanium (see Fig. 16). The bending of the bands U_{S0} (surface potential) is given by the distance of the middle of the forbidden zone on the surface from the position of the Fermi level in units of kT (see Fig. 14).

Curve A was recorded with upward bending of the bands. The intensity change ($\Delta I/I_0$) due to the superimposed AC voltage corresponds to the absorption spectrum of the free holes. Curve B, which was obtained with less pronounced upward bending of the bands, shows smaller changes in the hole density as a function of the AC voltage, as well as an additional absorption shifted in phase by 180° in a narrow energy range around 0.44 eV. The absorption signal of the free holes in this case is due to the fact that the upward bending of the bands is stronger, and the hole density on the surface is therefore greater, in the positive than in the negative half-wave of the superimposed alternating voltage. The fact that the signal β is opposite in phase means that this absorption takes place in the negative half-wave. The restriction of this additional signal to a narrow energy range indicates that a discrete state is involved in the transition. Corresponding to the observations concerning Figure 14, it follows from the opposite phase that this signal is due to a transition from the occupied state into the conduction band. The transition reaches its maximum rate at a surface potential $U_{S0} = +1.8$. Thus at this band bending, the center coincides in its energy with the Fermi level. The center is therefore situated 0.045 eV above mid gap. The broad selective absorption band denoted by α can be assigned to a continuum of surface states distributed about an energy of 3.5 kT above mid gap. If the band is bent further downward we finally obtain the absorption spectrum of the free electrons (curve g). Another absorption band opposite in phase to β should now occur as a result of transitions from the valence band into the same state. However, the authors believe that the quantum-mechanical transition probabilities are too low for this band.

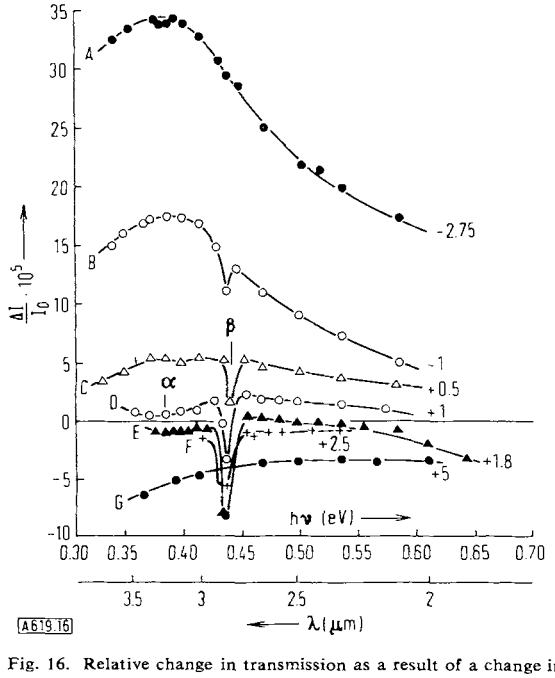

Fig. 16. Relative change in transmission as a result of a change in the density of the free charge carriers in the space-charge region and in the occupancy of the surface states (after [40]). The band bending in units of kT is given at the right hand end of each curve.

It has been shown by the examples that the optical measuring methods are suitable for use in the study of film-forming processes down to monolayers. However, the chemical compositions found for the reaction layers by optical investigations in the chemical and electrochemical studies sometimes do not agree with the models proposed for the dissolution of these substances. The reason for this discrepancy is probably that the layers in question are formed only in a secondary reaction of the dissolved semiconductor atoms. The layers therefore do not provide any insight into the actual dissolution process.

Definite results concerning the formation of surface compounds in electrochemical reactions should be provided by studies with effect modulation. The term "surface compounds" here refers to the compounds formed between the surface semiconductor atoms, whose bonds to the solid may already be weakened, and atoms from the surrounding medium. If the density of these surface molecules changes sufficiently rapidly, *i.e.* with a time constant smaller than 0.1 s, with the potential, these changes with effect modulation should permit the observation of absorption bands in the IR spectrum at the characteristic frequencies of these molecules.

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German version: Angew. Chem. *80*, 213 (1968)
Translated by Express Translation Service, London

[39] *A. Frova* and *P. Handler*, Physic. Rev. *137*, A 1857 (1965).
[40] *G. Samoggia, A. Nucciotti*, and *G. Chiarotti*, Physic. Rev. *144*, 749 (1966).

New Methods of Preparative Organic Chemistry VI[**]

Reactions with *N*-Carbonylsulfamoyl Chloride

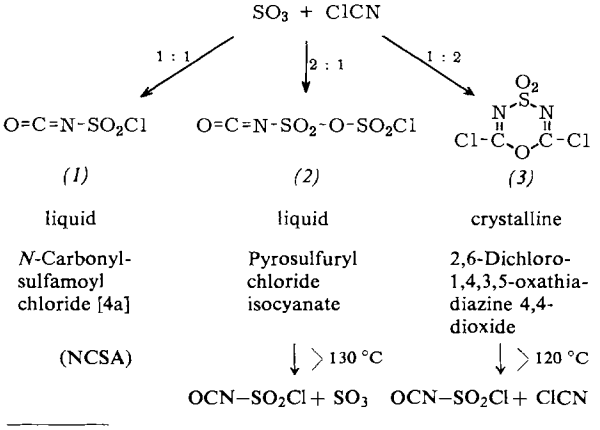
BY R. GRAF [*]

N-Carbonylsulfamoyl chloride (NCSA) is an intermediate that can be obtained from cyanogen chloride and sulfur trioxide, and which reacts with many compounds, via electrophilic substitution, much more readily than other isocyanates. Reactions with compounds containing hydroxyl, amino, or carboxyl groups lead to N-chlorosulfonyl-urethanes, -ureas, and -amides, respectively. This group of products also includes the parent substance sulfamoyl chloride (amidosulfonyl chloride). The reaction of N-carbonylsulfamoyl chloride with olefins provides an easy route, not only to derivatives of β-amino acids and unsaturated carboxylic acids, but also to many β-lactams. New, very reactive sulfonylisocyanates of several types can be obtained by further reactions of primary products obtained from N-carbonylsulfamoyl chloride and by the reaction of N-carbonylsulfamoyl chloride with olefins in the presence of free-radical formers. When allowed to react with a number of compounds, NCSA undergoes loss of carbon dioxide to form products containing the grouping =N–SO₂Cl.

1. General

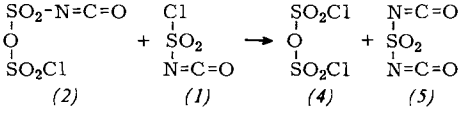
1.1. Preparation[1-4]

The reaction of sulfur trioxide with cyanogen chloride at a temperature not exceeding 0 °C leads to the formation of compounds *(1)*, *(2)*, and *(3)* by combination of the components in the ratios 1:1, 2:1, and 1:2.



Whereas NCSA is thermally stable up to 300 °C, *(2)* and *(3)* decompose slightly above 100 °C to give *(1)* and sulfur trioxide or *(1)* and cyanogen chloride respectively; the sulfur trioxide and cyanogen chloride react to form *(1)*. This explains why by far the most abundant product obtained on reaction of sulfur trioxide with cyanogen chloride above 130 °C is *N*-carbonylsulfamoyl chloride.

A roughly equimolar mixture of pyrosulfuryl chloride *(4)* and sulfonyl diisocyanate *(5)* is formed as a by-product (1–2%, based on the reacted cyanogen chloride); this remains behind as a high-boiling residue on fractionation of the crude *(1)* under reduced pressure, and is probably formed from *(1)* and *(2)*.



The boiling points of *(4)* and *(5)* are too close to each other to permit a complete separation by distillation. Reaction with cyanogen chloride at high temperatures converts this mixture into the more readily separable components chlorine, sulfur dioxide, NCSA *(1)*, and sulfonyl diisocyanate *(5)* [5].

Technical *N*-carbonylsulfamoyl chloride sometimes contains traces of sulfonyl diisocyanate and pyrosulfuryl chloride, but these are generally not objectionable. On the other hand, even a very small quantity of sulfur trioxide has extremely undesirable effects, particularly in the reaction with olefins. NCSA containing sulfur trioxide rapidly darkens the walls of polyethylene vessels. Cyanogen chloride in small quantities (at most a few tenths of one per cent) is advantageous in the NCSA, since this ensures the absence of free sulfur trioxide.

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[**] The articles in this series have been published in five volumes by Verlag Chemie, Weinheim/Bergstrasse. They are also obtainable in an English edition. The present article will appear in Volume VI of the series, with additional experimental procedures.

[1] *R. Graf*, German. Pat. 928896, Farbwerke Hoechst AG (1952); Chem. Zbl. *1955*, 11687.

[2] *R. Graf*, Chem. Ber. *89*, 1071 (1956).

[3] *R. Graf*, Org. Syntheses *46*, 23 (1966).

[4] *R. Graf*, German Pat. 944009, Farbwerke Hoechst AG (1953); Chem. Zbl. *1958*, 2246.

[4a] Instead of the name "*N*-carbonylsulfamoyl" chloride one often finds in the literature the designation "chlorosulfonyl isocyanate", as well as the abbreviation "NCSA".

[5] *R. Graf*, German Pat. 1084714, Farbwerke Hoechst AG (1959); Chem. Zbl. *1961*, 4519.

Physical Properties: *N*-Carbonylsulfamoyl chloride is a colorless liquid (m.p. −44 to −43 °C; b.p. 107–108 °C/760 torr, 38 °C/50 torr; $d_4^{20} = 1.626$; $n_D^{27} = 1.4435$), which fumes slightly in air, has a choking smell, and undergoes thermal decomposition only above about 300 °C.

Storage: Glass stoppers of bottles used for storage of NCSA stick fast after a short time, even when coated with silicone grease. Glass bottles with rubber stoppers covered with polythene film are suitable for storage for short periods. Polyethylene bottles with screw caps are best for longer storage times (a few weeks). NCSA can be kept indefinitely in sealed glass ampuls.

Handling: NCSA reacts explosively with water to form sulfamic acid, hydrogen chloride, and carbon dioxide. Otherwise the same precautions must be taken as for chlorosulfuric acid, oleum, or thionyl chloride. In cases of contact with the skin, the area should at once be washed thoroughly with water. No specific toxic effect other than the caustic action has so far been observed.

Solvents and Diluents: The choice of inert solvents is limited by the high reactivity of NCSA. Suitable solvents include saturated aliphatic hydrocarbons (more or less limited solubility below 0 °C), aromatic hydrocarbons such as benzene and toluene, chlorinated hydrocarbons such as CH_2Cl_2, $CHCl_3$, CCl_4 and chlorobenzene, diethyl ether, diisopropyl ether, and acetonitrile. Liquid sulfur dioxide is particularly favorable, since it increases the reactivity of NCSA still further. Substances such as acetone or ethyl acetate can be used to a limited extent, but only at low temperatures. Tetrahydrofuran is unsuitable, as are members of all the classes of compounds mentioned below, which react with *N*-carbonylsulfamoyl chloride.

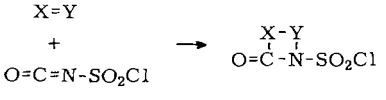
1.2. General Chemical Behavior

N-Carbonylsulfamoyl chloride is the most reactive isocyanate known. This appears to be due to the particularly high degree of electropositive polarization as a result of the direct attachment of the isocyanate group to the strongly electron-attracting SO_2Cl group. The isocyanate group generally reacts more rapidly than the sulfonyl group. The three main types of reactions of NCSA are illustrated below.

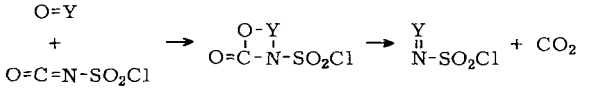
I. Compounds, X–H, containing reactive hydrogen add to NCSA, the H adding to the nitrogen and the residue X to the carbonyl group:

$$O{=}C{=}N{-}SO_2Cl + XH \rightarrow X{-}CO{-}NH{-}SO_2Cl$$

II. Compounds containing a double bond, X=Y, can add to NCSA to form a four-membered ring:



If X is oxygen, carbon dioxide is readily eliminated:



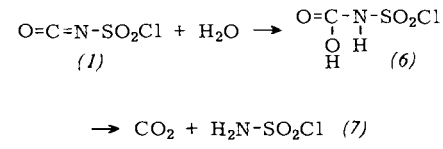
III. Under special conditions, or with compounds X–Y that cannot react with an O=C=N group, the sulfonyl chloride group reacts:

$$O{=}C{=}N{-}SO_2Cl + X{-}Y \rightarrow O{=}C{=}N{-}SO_2X + YCl$$

2. Special Reactions of NCSA

2.1. Water (Reaction Type I)

When concentrated (aqueous) hydrochloric acid is added dropwise to a solution of liquid sulfur dioxide containing NCSA, the NCSA reacts with 1 mole of water to form *N*-chlorosulfonylcarbamic acid *(6)*, which readily decomposes into sulfamoyl chloride *(7)* [6,7] and carbon dioxide.



This method can also be carried out on a large scale, and gives a colorless, extremely pure product. *R. Appel* and *G. Berger* used anhydrous formic acid as the water donor [8].

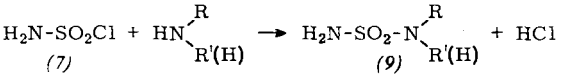
Sulfamoyl chloride (amidosulfonyl chloride) *(7)* decomposes with elimination of hydrogen chloride on prolonged heating at 80–100 °C, and can be distilled only in very small quantities under high vacuum. Compound *(7)*, which can be readily recrystallized from methylene chloride by intense cooling, reacts extremely vigorously with water to form amidosulfuric acid and hydrogen chloride.

Sulfamoyl chloride *(7)* offers a variety of possibilities as an intermediate:

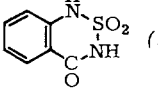
2.1.1. It reacts with sodium alkoxides or alcohols in the presence of tertiary amines to form esters *(8)* of sulfamic acid [9]:

$$\underset{(7)}{H_2N{-}SO_2Cl} + ROH \rightarrow \underset{(8)}{H_2N{-}SO_3{-}OR} + HCl$$

2.1.2. Reaction with primary or secondary aromatic amines leads to derivatives *(9)* of sulfamide [7,10]:



E. Cohen and *B. Klarberg* [11] described the reaction with methyl anthranilate to form 3,4-dihydro-1*H*-2,1,3-benzothiadiazin-4-one 2,2-dioxide *(10)*.



(10)

They also studied the cleavage of *o*-nitrophenylsulfamide *(11)* and the transfer reaction with aniline

[6] *R. Graf*, German Pat. 937645, Farbwerke Hoechst AG (1952); Chem. Zbl. *1956*, 9008.

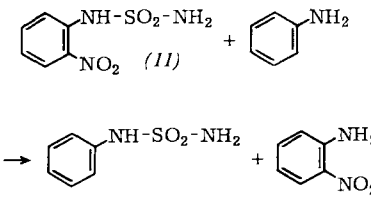
[7] *R. Graf*, Chem. Ber. *92*, 509 (1959).

[8] *R. Appel* and *G. Berger*, Chem. Ber. *91*, 1339 (1958).

[9] *R. Appel* and *W. Senkpiel*, Angew. Chem. *70*, 504 (1958).

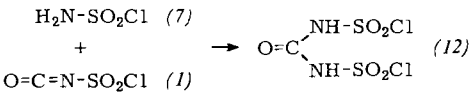
[10] *R. Graf*, German Pat. 947554, Farbwerke Hoechst AG (1953); Chem. Zbl. *1957*, 5416.

[11] *E. Cohen* and *B. Klarberg*, J. Amer. chem. Soc. *84*, 1994 (1962).



Derivatives of the compound NH_2-SO_2-NR-SO_2-NH_2 are readily obtained by reaction of *(7)* with aliphatic amines. *R. Appel* and *G. Berger* obtained bissulfamoylhydrazine NH_2–SO_2–NH–NH–SO_2–NH_2 by reaction of *(7)* with anhydrous hydrazine in acetonitrile [8].

2.1.3. NCSA slowly adds on amidosulfonyl chloride with formation of urea-*N,N'*-bissulfonyl chloride *(12)* [12].



2.1.4. Reaction with aromatic hydrocarbons and $AlCl_3$ gives amides of aromatic sulfonic acids *(13)* [13]:

$$RH + ClSO_2–NH \xrightarrow[AlCl_3]{} R–SO_2–NH_2 + HCl$$

2.1.5. Amidosulfonyl chloride reacts with potassium fluoride in boiling acetonitrile to form amidosulfonyl fluoride [14], which, unlike amidosulfonyl chloride, can be distilled without decomposition and is not hydrolyzed rapidly by water below about 60 °C. Amidosulfonyl fluoride can also be obtained from *N*-carbonylsulfamoyl fluoride (cf. Section 2.15) by reaction with an equimolar quantity of water (cf. formation of amidosulfonyl chloride) [15].

2.2. Alcohols, Phenols, Thiols (Reaction Type I)

Alcohols, phenols, or thiols react with NCSA to form (thio)esters of *N*-chlorosulfonylcarbamic acid *(14a)* or *(14b)* [16, 17]

$$\underset{(1)}{R–XH + O=C=N–SO_2Cl} \rightarrow \underset{\begin{matrix}(14a),\ X = O\\(14b),\ X = S\end{matrix}}{RX–CO–NH–SO_2Cl}$$

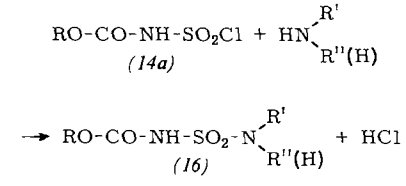
which are in turn capable of undergoing many further reactions. Owing to the violence of the reaction, diluents are used with lower alcohols, and to avoid side reactions only the equivalent quantity of the alcohol is used. The *N*-chlorosulfonylurethanes *(14a)* crystallize well and are stable on storage, whereas the esters of *N*-chlorosulfonylthiocarbamic acid decompose more or less rapidly on storage.

2.2.1. Hydrolysis of *(14a)* leads *via* the free *N*-sulfonic acids, with elimination of hydrogen chloride and sulfuric acid, to the ester *(15)* of carbamic acid. This reaction greatly simplifies the preparation of urethanes from alcohols and phenols.

$$\underset{(14a)}{RO–CO–NH–SO_2Cl} + 2\,H_2O \rightarrow \underset{(15)}{RO–CO–NH_2} + H_2SO_4 + HCl$$

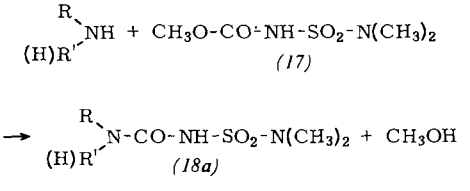
When the hydrolysis is carried out in alkaline solution, it leads to the mono- or bisalkali metal salts [*] of the urethane-*N*-sulfonic acids. The bisalkali metal salts are more stable on storage, dissolve more readily, and give a more strongly alkaline reaction than the monoalkali metal salts. On the other hand, the monoalkali metal salts of arylurethane-*N*-sulfonic acids, which are derived from phenols, decompose rapidly even in weakly alkaline solution into the phenol, sulfamic acid, and carbon dioxide [17].

2.2.2. Amines containing reactive hydrogen give stable acyl-substituted sulfamides *(16)* [17, 18].



It is possible in this way to link any alcohol or phenol to any amine *via* the $-CO-NH-SO_2-$ group; for example, the herbicide dodecyl *N*-(phenylsulfamoyl)-thiocarbamate can be obtained by reaction of NCSA with dodecyl mercaptan and aniline, *via* *S*-dodecyl *N*-chlorosulfonylthiocarbamate [19]. This and similar compounds containing the grouping $-CO-NH-SO_2-$, which will be repeatedly encountered in the following sections, act as monobasic acids and form stable alkali metal salts.

2.2.2.1. Methyl *N*-dimethylsulfamoylcarbamate *(17)* reacts with primary and secondary aliphatic and aromatic amines with liberation of heat and elimination of methanol to give substituted sulfamides *(18a)* [12]:



Compounds of this type are also formed as described in Section 2.3.2. if the reaction of the more nucleophilic aliphatic amines with NCSA in accordance with Section 2.3 cannot be stopped at the stage of the sulfonyl chloride R–NH–CO–NH–SO_2Cl.

[12] *R. Graf*, unpublished results.

[13] *R. Graf*, German Pat. 1002331, Farbwerke Hoechst AG (1955); Chem. Zbl. *1957*, 10336.

[14] *R. Appel* and *W. Senkpiel*, Angew. Chem. *70*, 572 (1958); German Pat. 1098494 (1958).

[15] *H. Jonas* and *D. Voigt*, Angew. Chem. *70*, 572 (1958).

[16] *R. Graf*, German Pat. 931467, Farbwerke Hoechst AG (1952); Chem. Zbl. *1955*, 11094.

[17] *R. Graf*, Chem. Ber. *96*, 56 (1963).

[*] The bis-salts are $RO–CO–\overset{\ominus}{N}–SO_3^{\ominus}\ 2\,M^{\oplus}$ (the mono-salts are $RO–CO–NH–SO_3^{\ominus}\ M^{\oplus}$) (cf. Chem. Ber. *96*, 57 (1963)).

[18] *R. Graf*. German Pat. 940292, Farbwerke Hoechst AG (1952); Chem. Zbl. *1956*, 12973.

[19] *E. H. Sheers*, US-Pat. 3113857, American Cyanamid Corp. (1961).

2.2.3. When the sulfonyl chlorides *(14a)* derived from phenols are heated above 80 °C (preferably in the presence of an excess of NCSA), HCl is eliminated to form sulfonyl isocyanates *(19)*, which contain the group $-O-SO_2-N=C=O$ attached to an aromatic residue [20]:

$$\underset{(14a)}{ArO-CO-NH-SO_2Cl} \rightarrow \underset{(19)}{ArO-SO_2-N=C=O} + HCl$$

The same products are obtained directly when aromatic compounds containing one or more phenolic groups are heated above 80 °C with at least one mole of NCSA per equivalent of OH.

$$\underset{(1)}{Ar-OH + Cl-SO_2-N=C=O} \rightarrow \underset{(19)}{ArO-SO_2-N=C=O} + HCl$$

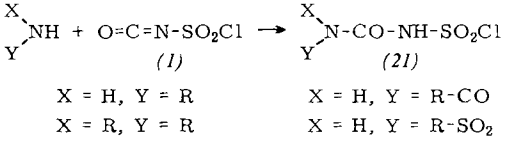
Trichloroethanol has also been converted in good yield into $CCl_3-CH_2-O-SO_2-N=C=O$ by this method.

2.2.4. Reaction with alcohols (even in the absence of HCl acceptors) or phenols (in the presence of HCl acceptors) yields esters *(20)* of urethane-*N*-sulfonic acids [17]:

$$\underset{(14a)}{RO-CO-NH-SO_2Cl} + R'OH \rightarrow \underset{(20)}{RO-CO-NH-SO_2-OR'} + HCl$$

2.3. Amines (and Amides) (Reaction Type I)

Primary and secondary aromatic amines, amides of carboxylic and sulfonic acids, imides, or lactams add to NCSA with formation of *N*-chlorosulfonylureas *(21)* [16]:



To minimize further reaction in accordance with 2.3.2, *(1)* is dissolved in a diluent and a solution of the equivalent quantity of amine is added with cooling and vigorous stirring. This precaution is unnecessary with amides and, for example, with the less nucleophilic nitroanilines. The more strongly nucleophilic aliphatic amines, and to some extent even *e.g.* anisidine, react further in accordance with 2.3.2, despite this precaution, and a more or less large quantity of the compounds $R-NH-CO-SO_2NHR$ is formed as well as the sulfonyl chloride. Ammonia gives the ammonium salt of ureasulfonimide [21].

2.3.1. Hydrolysis of *(21)* leads *via* the unstable *N*-sulfonic acids to substituted ureas *(22)* [12]:

$$\underset{(21)}{X-NH-CO-NH-SO_2Cl} + H_2O \rightarrow \underset{(22)}{X-NH-CO-NH_2} + H_2SO_4 + HCl$$

X = R, R–CO, $R-SO_2$

Hydrolysis in alkaline media leads to the mono- or to the more readily soluble bisalkali metal salts of the *N*-sulfonic acids (cf. Section 2.2.1).

2.3.2. Further reaction of *(21)* with amines yields substituted sulfamides *(18)* [18], which are generally very stable and form neutral salts.

$$\underset{(21)}{X-NH-CO-NH-SO_2Cl} + HN\begin{matrix}R'\\R''(H)\end{matrix} \rightarrow \underset{(18)}{X-NH-CO-NH-SO_2-N\begin{matrix}R'\\R''(H)\end{matrix}} + HCl$$

X = R, R–CO, $R-SO_2$

2.3.3. Reaction with alcohols, even in the absence of hydrogen chloride acceptors, yields esters *(23)* of substituted urea-*N*-sulfonic acids [12]:

$$\underset{(21)}{X-NH-CO-NH-SO_2Cl} + R'OH \rightarrow \underset{(23)}{X-NH-CO-NH-SO_2-OR'} + HCl$$

X = R, R–CO, $R-SO_2$

2.4. Carboxylic Acids (Reaction Type I)

NCSA reacts with carboxylic acids to form *N*-chlorosulfonylamides *(24)* of carboxylic acids, with elimination of carbon dioxide [22]:

$$\underset{(1)}{R-COOH + O=C=N-SO_2Cl} \rightarrow \underset{(24)}{R-CO-NH-SO_2Cl} + CO_2$$

This reaction proceeds readily with saturated and unsaturated fatty acids, aliphatic dicarboxylic acids, or benzoic acid, but is retarded or prevented by electron-attracting substituents (Cl, NO_2). The primary product of the reaction of formic acid with NCSA decomposes into sulfamic acid, carbon monoxide, and carbon dioxide.

The thermal stability and storage stability of the *N*-chlorosulfonylamides *(24)* are generally lower than those of the compounds obtained as described in Sections 2.2 and 2.3, and this must be borne in mind in their preparation and further treatment.

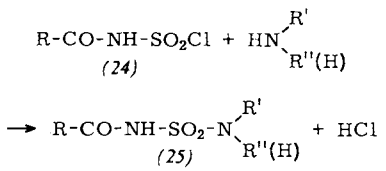
2.4.1. Hydrolysis of *(24)* leads *via* the unstable *N*-sulfonic acids to amides, and provides a very simple method for the conversion even of unstable unsaturated carboxylic acids into their amides [12]:

$$\underset{(24)}{R-CO-NH-SO_2Cl} + 2\,H_2O \rightarrow R-CONH_2 + H_2SO_4 + HCl$$

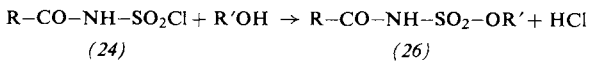
Hydrolysis in alkaline media gives stable alkali metal salts of amide-*N*-sulfonic acids. In this series of compounds, the bisalkali metal salts are again more readily soluble and more stable on storage than the mono salts.

[20] *G. Lohaus*, DAS 1230017, Farbwerke Hoechst AG (1965).
[21] *R. Appel* and *W. Senkpiel*, Chem. Ber. *91*, 1195 (1958).
[22] *R. Graf*, German Pat. 931225, Farbwerke Hoechst AG (1952); Chem. Zbl. *1956*, 3995.

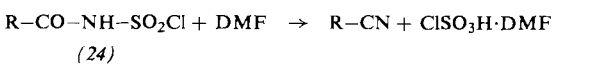
2.4.2. Acylated sulfamides *(25)* can be obtained by reaction with amines [23]:



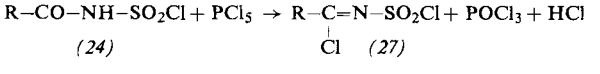
2.4.3. Reaction with alcohols, even in the absence of hydrogen chloride acceptors, gives esters *(26)* of acylated sulfamic acids [12]:



2.4.4. The extremely smooth elimination of chlorosulfuric acid with dimethylformamide (DMF) is a simple and generally applicable method for the preparation of nitriles [24]:

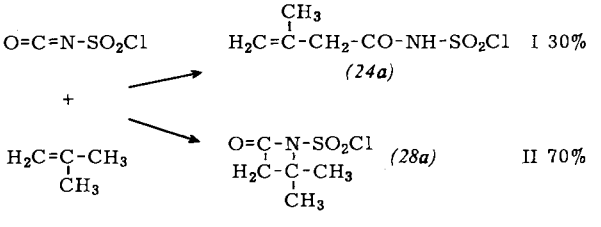


2.4.5. Reaction with PCl_5 leads to *N*-chlorosulfonylcarbimidyl chlorides *(27)* [12]:



2.5. Olefins (Reaction Types I and II)

The cryptoionic reaction with olefins is undoubtedly one of the most interesting reactions of *N*-carbonylsulfamoyl chloride. The products are an unsaturated *N*-chlorosulfonylamide, *e.g. (24a)*, and a β-lactam-*N*-sulfonyl chloride, *e.g. (28a)*, as is shown below for the reaction with isobutylene [25–28].

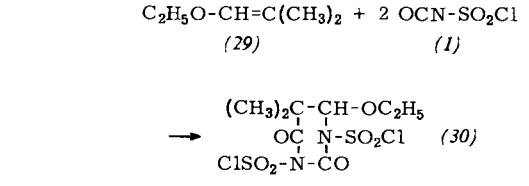


The ratio of the conversions by routes I and II is determined by the constitution of the olefin. This ratio cannot generally be altered by changing either the solvent or the reaction temperature. Route II generally predominates, but in some cases the only product is the open-chain amide *(24)* (cf. Section 2.6).

In accordance with the Markownickoff rule, the nitrogen in NCSA, which carries a partial negative charge, adds on to the carbon atom carrying the smallest number of hydrogens in the olefin.

The *N*-chlorosulfonylamides formed from olefins and NCSA are derived (so far as is known at present) from β,γ-unsaturated carboxylic acids. In the reaction of *n*-1-hexene with NCSA, it has been shown that the *N*-chlorosulfonylamide formed in addition to 4-*n*-butyl-2-oxoazetidine-*N*-sulfonyl chloride is derived from an *n*-heptenoic acid [12]. The mother liquor remaining after hydrolysis of the reaction mixture of *n*-1-hexene and NCSA followed by extraction of the β-lactam gave an unsaturated carboxylic acid on acidification with concentrated hydrochloric acid and steam distillation. Hydrogenation of this unsaturated acid (PtO_2) *via* the chloride ($SOCl_2$) gave an amide, whose melting point, mixed melting point, and IR spectrum showed that it was identical with heptanamide. Thus in the formation of the *N*-chlorosulfonylamide, the CO group of NCSA again attacks the terminal C atom of the olefinic double bond.

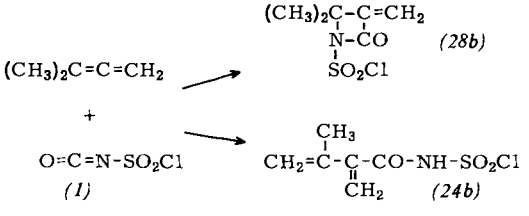
Enol ethers do not react in the same way as simple olefins. 3,4-Dihydro-2*H*-pyran reacts smoothly with NCSA in ether to form *N*-chlorosulfonyl-5,6-dihydro-4*H*-pyran-3-carboxamide [29]. However, while ethyl vinyl ether and NCSA also give the unsaturated amide $C_2H_5O-CH=CH-CO-NH-SO_2Cl$ [29], ethyl isobutenyl ether *(29)*, even when present in excess, reacts



directly with two moles of NCSA to form the dihydrouracil derivative *(30)*, which can be oxidized by chromic acid to dimethylbarbituric acid after removal of the sulfonyl chloride groups [30].

Certain diolefins, such as dipentene (*dl*-limonene) [27] and 1,4-dimethylenecyclohexane [31] give bis-β-lactams.

E. J. Moroconi and *J. F. Kelly* [32] recently described the reaction of allenes with NCSA. In addition to unsaturated *N*-chlorosulfonylamides *(24)*, this reaction gives *N*-chlorosulfonyl-β-lactams having an exocyclic methylene group, *e.g. (28b)*. The allenes *(31a)–(31c)*



[23] *R. Graf*, German Pat. 940529, Farbwerke Hoechst AG (1952); Chem. Zbl. *1956*, 13257.

[24] *G. Lohaus* and *R. Graf*, German Pat. 1218448, Farbwerke Hoechst AG (1963); *G. Lohaus*, Chem. Ber. *100*, 2719 (1967).

[25] *R. Graf*, German Pat. 941847, Farbwerke Hoechst AG (1953); Chem. Zbl. *1957*, 1297.

[26] *R. Graf*, German Pat. 1119277, Farbwerke Hoechst AG (1958); Chem. Zbl. *1964*, 27-2304.

[27] *R. Graf*, Liebigs Ann. Chem. *661*, 111 (1963).

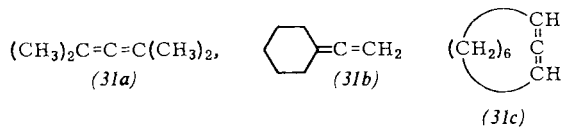
[28] *R. Graf*, Org. Syntheses *46*, 51 (1966).

[29] *F. Effenberger* and *R. Gleiter*, Chem. Ber. *97*, 1576 (1964).

[30] *K. Matterstock*, Farbwerke Hoechst AG, unpublished results.

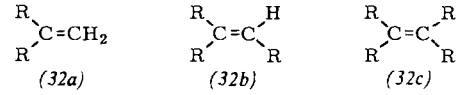
[31] *H. Biener*, Farbwerke Hoechst AG, unpublished results.

[32] *E. J. Moroconi* and *J. F. Kelly*, J. Amer. chem. Soc. *88*, 3657 (1966).



(31a) (31b) (31c)

react in a similar way. Olefins having the constitution *(32a)–(32c)*, in which at least one of the double-bonded C atoms is attached to two alkyl groups, react



(32a) (32b) (32c)

rapidly, *i.e.* the reaction is strongly exothermic at room temperature and is practically complete within a period of a few seconds to a few minutes.

α-Olefins [33] $RCH=CH_2$ and olefins having a non-terminal double bond RCH=CHR [34] react much more slowly with NCSA [27].

The unsaturated hydrocarbons styrene [27], bicyclo-[2.2.1]hept-2-ene [27], and 1,2-dihydronaphthalene [35], which formally belong to the latter group of olefins, are more like the first group in their reaction behavior.

Electron-attracting substituents on the hydrocarbon residue lower the reaction rate, as is shown by the behavior of 4-chlorostyrene, esters of methallylcarboxylic acid, and methallyl alkyl and methallyl aryl ethers [27]. Methallyl chloride reacts even more slowly [31].

The large difference in the rates of reaction of NCSA with olefins with and without branching on the double bond can be utilized for the separation of olefins of these types [27,36,37].

N-Chlorosulfonyl-β-lactams *(28)* are generally relatively stable, though their stabilities, like their rates of formation, can differ very widely in their order of magnitude. On prolonged storage or on heating, for example, they generally undergo primary rearrangement into unsaturated *N*-chlorosulfonylamides *(24)*. The unsaturated *N*-chlorosulfonylamides tend to decompose further. Thus when 4,4-dimethyl-2-oxoazetidine-*N*-sulfonyl chloride *(28a)*, which is obtained from isobutylene, is heated at 100 °C, it decomposes within a few minutes with liberation of heat and formation of tarry products. The thermal rearrangement of *N*-fluorosulfonyl-β-lactams is easier to follow kinetically, since the sulfonyl fluorides are much more stable and do not tend to enter into ill-defined decomposition reactions [27].

It should be emphasized at this point that the *N*-chlorosulfonyllactams *(28)* and the open-chain *N*-chlorosulfonylamides *(24)* are formed independently and simultaneously from isobutylene and homologous olefins, *i.e.* the *N*-chlorosulfonylamide found in the reaction products is not formed *e.g.* by further reaction of the initially formed *N*-chlorosulfonyllactam [27]. This has been clearly shown by IR spectrographic observation of reacting mixtures [38]. The ratio in which the two products are formed remains constant from the beginning to the end of the reaction.

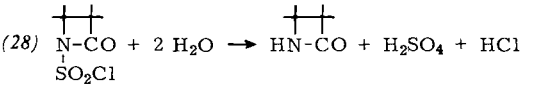
An exception to this rule is found in the case of α-methylstyrene, which gives only the unsaturated *N*-chlorosulfonylamide on normal working-up of the reaction mixture. When the reaction is followed IR-spectrographically, it is found that a β-lactam is in fact formed, but rearranges rapidly into the amide [38].

In general, the monosubstituted *N*-chlorosulfonyl-β-lactams having lower alkyl residues in position 4 have the lowest thermal stabilities; the stability increases with increasing substitution on C-3 and C-4. One of the most stable *N*-chlorosulfonyl-β-lactams is 3-*tert*-butyl-4,4-dimethyl-2-oxoazetidine-*N*-sulfonyl chloride, which is obtained from 2,4,4-trimethyl-2-pentene and which showed no change on storage for 15 years or on being heated at 100 °C. 3,3-Dimethyl-4-phenyl-2-oxoazetidine-*N*-sulfonyl chloride showed no depression of its equilibrium melting point after repeated melting and resolidification, whereas 4-phenyl-2-oxoazetidine-*N*-sulfonyl chloride undergoes partial rearrangement into *N*-chlorosulfonylcinnamamide on melting; this leads to a rapid depression of the equilibrium melting point [27].

The unsaturated *N*-chlorosulfonylamides *(24)*, which can react in accordance with Sections 2.4.1.–2.4.4., differ from the corresponding *N*-chlorosulfonyl-β-lactams *(28)* in their much higher rates of hydrolysis; this difference often facilitates the separation of these compounds [27].

The *N*-chlorosulfonyl-β-lactams enter into an extremely wide variety of reactions, the most important of which appears to be their conversion into the free β-lactams.

2.5.1. The rates of hydrolysis of the *N*-chlorosulfonyl-β-lactams varies with the substituents over a very wide range. In some cases (substitution by one or two small aliphatic residues), hydrolysis to the free lactam takes place with simultaneous neutralization of the acid liberated without further measures [39]:



(28) $+ 2\,H_2O \rightarrow$ $+ H_2SO_4 + HCl$

However, even in the *N*-chlorosulfonyllactams that are more stable to water, the SO_2Cl group can be readily removed *via* unstable *N*-sulfinic acids by the action of reducing agents such as zinc dust or iron powder in aqueous-alcoholic suspension, or, more elegantly, with simultaneous neutralization of the liberated acid in the presence of a small quantity of an iodide, which catalyzes the hydrolysis of the *N*-sulfonyl chloride by a redox reaction [27,40].

When the molten mixture of *N*-chlorosulfonyllactam *(28a)* and unsaturated *N*-chlorosulfonylamide *(24a)* obtained by

[33] *H. Biener*, Belg. Pat. 662257, Farbwerke Hoechst AG (1964).

[34] *H. Biener*, Belg. Pat. 662258, Farbwerke Hoechst AG (1964).

[35] *E. J. Moroconi* and *P. H. Mazzocchi*, J. org. Chemistry *31*, 1372 (1966).

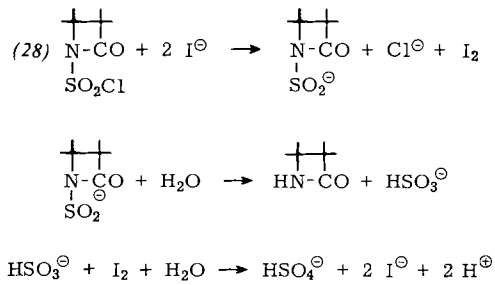
[36] *R. Graf*, German Pat. 1112063, Farbwerke Hoechst AG (1959); Chem. Zbl. *1962*, 6206.

[37] *R. Graf*, German Pat. 1130434, Farbwerke Hoechst AG (1959).

[38] *K. Clauss*, Farbwerke Hoechst AG, unpublished results.

[39] *R. Graf*, German Pat. 1116228, Farbwerke Hoechst AG, (1958); Chem. Zbl. *1964*, 16-2261.

[40] *R. Graf*, German Pat. 1086234, Farbwerke Hoechst AG (1958); Chem. Zbl. *1961*, 6684.



continuous reaction of NCSA and isobutylene in the absence of solvents is hydrolyzed at pH = 5–7, approximately half of the *(24a)* is converted into 3-methyl-3-butenonitrile $CH_2=C(CH_3)-CH_2CN$ by the action of the free lactam formed from *(28a)* (cf. Section 2.4.4). The remainder of the compound *(24a)* is found in the hydrolysis mixture in the form of the salt $CH_2=C(CH_3)-CH_2-CONH-SO_3Na$. When the mother liquor remaining after extraction of the lactam is heated close to its boiling point for a short time after addition of concentrated sodium hydroxide solution, large quantities of the less soluble salt $(CH_3)_2C=CH-CONH-SO_3Na$, which is formed by rearrangement, crystallize out as large shiny platelets on cooling.

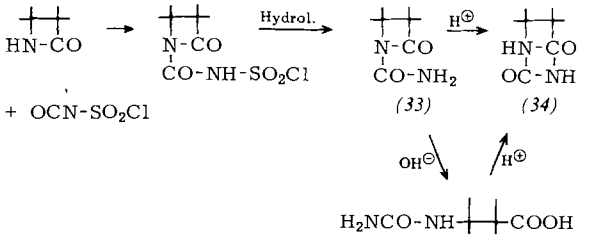
The crude 4,4-dimethyl-2-azetidinone obtained by extraction of the hydrolysis mixture with chloroform contains small quantities of 3-hydroxy-3-methylbutanonitrile $(CH_3)_2C(OH)-CH_2CN$ as well as the unsaturated amide and nitrile. This hydroxy nitrile cannot be separated from the lactam by fractional distillation, and is as stable as the lactam toward permanganate. It appears in the gas chromatogram as a sharp peak before the lactam, and remains in the mother liquor on recrystallization of the permanganate-treated and vacuum-fractionated lactam *e.g.* from diisopropyl ether at −40 °C. After the ready cleavage of any remaining β-lactam with sulfuric acid, the hydroxy nitrile can be isolated from concentrated residual mother liquors by extraction with chloroform. It was identified as the urethane $NC-CH_2-C(CH_3)_2-O-CONH_2$ [colorless needles, m.p. 90–91 °C (from dilute aqueous methanol), obtained by reaction with NCSA followed by hydrolysis in accordance with Section 2.2.1] by comparison (mixed melting point) with the compound [12] obtained in the same way from an authentic sample of the hydroxy nitrile [41].

The special advantage of this synthesis of β-lactams from olefins and *N*-carbonylsulfamoyl chloride, which can also be carried out on the industrial scale, is that it gives β-lactams having unsubstituted NH groups, many of which can be very readily polymerized in the presence of alkaline catalysts and under very mild conditions into high molecular-weight, fiber-forming products; these are characterized by a remarkable stability to oxygen even at high temperatures [42].

The liberation of heat on cleavage of a β-lactam with concentrated hydrochloric acid served as a reliable test for the presence of a β-lactam (in addition to the IR spectrum, which contains CO bands at 5.6–5.7 μm). The failure of this reaction to take place with the lactam obtained from camphene gave the first indication that this was not a β-lactam; the product was in fact found to be a γ-lactam [43].

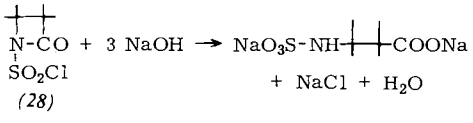
The ready availability of the β-lactams led to the investigations of a series of ring-cleavage and substitution reactions of this class of compounds. Of these reactions, only that with NCSA will be reported here.

2.5.1.1. As internal amides with a free NH group, β-lactams react with NCSA in accordance with the reaction given in Section 2.3. The *N*-carbamoyl-β-lactams *(33)* obtained by hydrolysis of the reaction products can be converted into dihydrouracils *(34)* [12]:



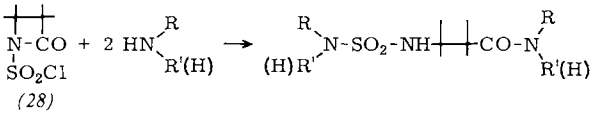
The easy and almost quantitative conversion into the extremely stable, readily crystallizing, sparingly soluble dihydrouracils, which have relatively high and sharp melting points, can be used for the characterization of liquid β-lactams. The intermediate *N*-carbamoyl-β-lactam need not be isolated.

2.5.2. *N*-Chlorosulfonyl-β-lactams *(28)* are cleaved between the nitrogen and the CO group by strongly nucleophilic reagents.



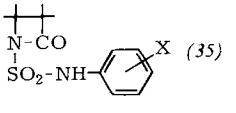
To carry out this reaction, the *N*-chlorosulfonyllactams are added to excess caustic alkali solution [27,44]. When heated in acidic solution, the salts lose sulfuric acid and form salts of β-amino acids.

2.5.3. The reaction of *(28)* with excess aliphatic or aromatic amine results in the introduction of two amine residues into the molecule [27,45].



The products are insoluble in sodium carbonate solution and are only very slowly cleaved by boiling hydrochloric acid.

With aromatic amines having strongly electron-attracting substituents X (*o*-nitroaniline, chloronitroaniline) in the presence of tertiary bases, the β-lactam ring remains intact and only one mole of the amine reacts to give compounds of the type *(35)* [12].



[41] *A. Kjaer* and *R. B. Jensen*, Acta chem. scand. *12*, 1756 (1958); Chem. Zbl. *1959*, 13802.

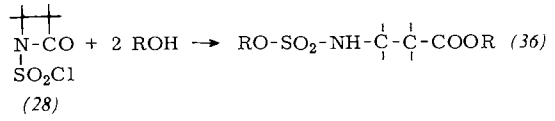
[42] *R. Graf*, *G. Lohaus*, *K. Börner*, *E. Schmidt*, and *H. Bestian*, Angew. Chem. *74*, 523 (1962); Angew. Chem. internat. Edit. *1*, 481 (1962).

[43] *R. Graf* and *H. Biener*, Angew. Chem. *75*, 857 (1963); Angew. Chem. internat. Edit. *2*, 546 (1963).

[44] *R. Graf*, German Pat. 955509, Farbwerke Hoechst AG (1954); Chem. Zbl. *1957*, 6224.

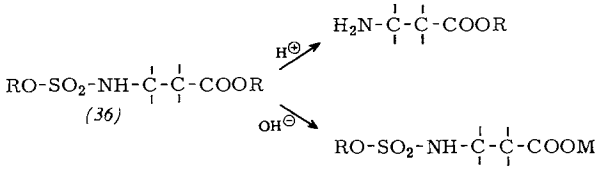
[45] *R. Graf*, German Pat. 1004189, Farbwerke Hoechst AG (1954); Chem. Zbl. *1957*, 9805.

2.5.4. Reaction with alcohols or phenols in the presence of alkoxides (phenoxides) or tertiary amines gives bis-esters *(36)* [27,46]:



(28)

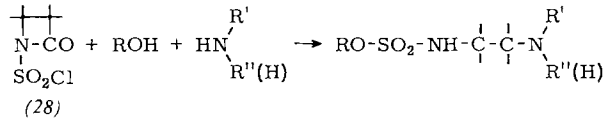
2.5.4.1. The bis-esters *(36)* give different products on hydrolysis by acids and by bases [27]:



(36)

It is possible in this way to obtain esters of β-amino acids directly after working up from *N*-chlorosulfonyl-β-lactams (addition to alcoholic alkoxide solution, introduction of hydrogen chloride, and heating for about 1 hour).

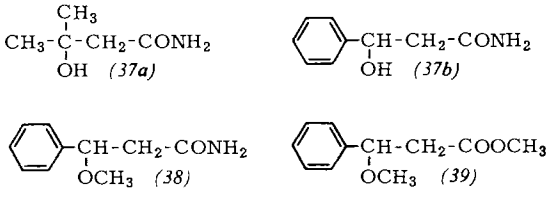
2.5.5. On reaction with an amine in alcohol (phenol), the alcohol residue becomes attached to the SO_2 group and the amine residue to the CO [27].



(28)

On hydrolysis of the products in acidic media, the sulfonate group is split off, and amides of β-amino acids are formed.

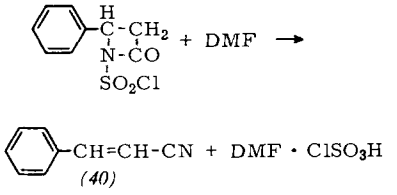
2.5.6. When *N*-chlorosulfonyl-β-lactams are hydrolyzed without neutralization of the liberated acid, amides of β-hydroxy acids are sometimes formed in good yields, whereas alcohols give amides or, under more vigorous conditions, esters of β-alkoxycarboxylic acids, *e.g. (37)*, *(38)*, and *(39)* [47].



(37a) *(37b)* *(38)* *(39)*

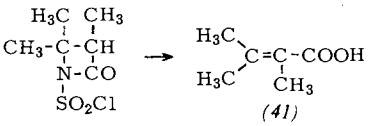
In other cases the hydrolysis of chlorosulfonyllactams is more complicated; the reaction may yield an unsaturated nitrile, together with cleavage back into the olefin, unsaturated acids or amides, or even a lactone (from 2,3,3-trimethyl-2-butene) [27].

2.5.7. Reaction with dimethylformamide gives nitriles of unsaturated acids [48], *e.g. (40)*.



(40)

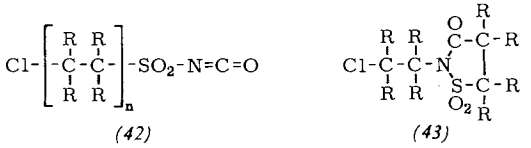
2.5.8. Dissolution in concentrated sulfuric acid followed by pouring into water sometimes leads to high yields of unsaturated acids (*e.g.* cinnamic acid, β,β-dimethylacrylic acid, α,β,β-trimethylacrylic acid *(41)*) [12].



(41)

When the reaction mixture is poured into water, the residue $>N-SO_2Cl$ appears as sulfamic acid. Saturated and unsaturated *N*-chlorosulfonylamides *(24)* can also be converted into carboxylic acids in this way.

2.5.9. *D. Günther* and *F. Soldan* [49] found that the reaction of NCSA with olefins proceeds differently under the action of UV radiation or in the presence of free-radical formers. On the one hand, the olefin adds on with formation of alkyl-substituted 2-chloroethylsulfonyl isocyanates and their lower telomers *(42)*, and on the other, NCSA reacts with two moles of olefin to form alkyl-substituted *N*-2-chloroethyl-3-oxothiazolidine 1,1-dioxides *(43)*.



(42) *(43)*

Olefins of all types, including ethylene, react in this way. This has made available a large number of new sulfonyl isocyanates with a wide range of possible further reactions.

2.6. Other Examples

Many compounds of the type RH enter into electrophilic substitutions with *N*-carbonylsulfamoyl chloride or fluoride to give *N*-chloro- or *N*-fluoro-sulfonylamides R–CO–NH–SO_2Cl(F), which can react further as described in Sections 2.4.1.–2.4.5. Some examples of the possible groups R are listed in Table 1.

The reaction generally proceeds at 20–40 °C, though in the case of anthracene a temperature of about 80 °C is necessary for fast reaction (in toluene).

[46] *R. Graf*, German Pat. 950912, Farbwerke Hoechst AG (1954); Chem. Zbl. *1957*, 4531.

[47] *R. Graf*, German Pat. 1036250, Farbwerke Hoechst AG (1956); Chem. Zbl. *1959*, 6956.

[48] *K. Matterstock* and *G. Lohaus*, DAS 1253704, Farbwerke Hoechst AG (1964).

[49] *D. Günther* and *F. Soldan*, German Pat. 1211165, Farbwerke Hoechst AG (1964).

Table 1. Examples of the reaction

$RH + OCN{-}SO_2Cl(F) \rightarrow R{-}CO{-}NH{-}SO_2Cl(F)$

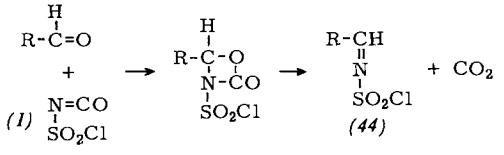
R	Ref.
9-Anthryl	[27]
2-Thienyl	[27]
2-Furyl	[27]
2-Indenyl	[27]
2,2-Diphenylvinyl	[27]
1-Methyl-2,2-diphenylvinyl	[27]
2-Methylene-2-phenyl-ethyl	[27]
2,4,6-Trimethylphenyl	[50]
4-Alkoxy-1-naphthyl	[51]
2-Alkoxy-1-naphthyl	[51]
4-Methoxyphenyl	[51]
2,4-Bis(methoxy)phenyl	[51]
1-Methyl-2-phenyl-3-pyrrolyl	[52]
4-Pyrrolidinophenyl	[52]
2-Hydroxy-4,4-dimethyl-6-oxocyclohexyl	[27]
4,5,6-Trialkyl-4-oxo-4*H*-pyran-3-yl	[52]
1,5-Dimethyl-3-oxo-2-phenyl-pyrazolin-4-yl	[53]
Bis(acetyl)methyl	[30]
Acetyl-ethoxycarbonylmethyl	[30]
2-(*N*-Acyl-*N*-alkylamino)vinyl, *e.g.* 2-(2-Oxopyrrolidino)vinyl	[54]

When the *N*-chlorosulfonylamides are dissolved in concentrated sulfuric acid and the solution poured into water, the free carboxylic acids are formed, as in the case of *N*-chlorosulfonyllactams (cf. Section 2.5.8).

Benzene and toluene can be made to react with NCSA in the presence of $AlCl_3$ at 20–30 °C; hydrolysis of the primary product leads to benzamide or toluamide[55].

2.7. Aldehydes

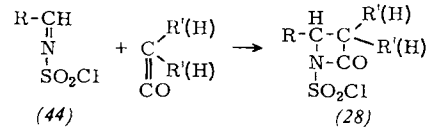
After the addition of NCSA to the carbonyl group (Reaction Type II), carbon dioxide is eliminated and azomethine-*N*-sulfonyl chlorides *(44)* are formed [27,56].



(1) *(44)*

The primary formation of unstable adducts of NCSA and aldehydes has been experimentally verified in some cases by the observation of crystalline products, which decomposed with liberation of CO_2. Azomethine-*N*-sulfonyl chlorides in which R = aryl crystallize particularly readily. They are rapidly cleaved by water to give the starting aldehydes, amidosulfuric acid, and hydrogen chloride.

2.7.1. The azomethine-*N*-sulfonyl chlorides very readily add on ketene or substituted ketenes, such as dimethylketene, to form *N*-chlorosulfonyl-β-lactams *(28)* [27,57].

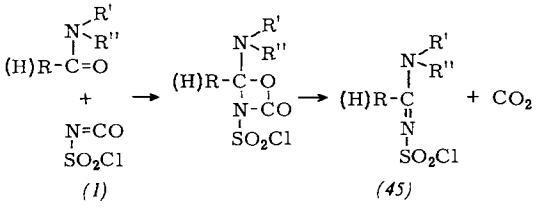


(44) *(28)*

Hydrolysis of these *N*-chlorosulfonyl-β-lactams in accordance with the reaction given in Section 2.5.1. led to a series of new lactams, only some of which could be obtained from the olefin.

2.8. *N,N*-Dialkylamides

N,N-dialkylamides of carboxylic acids, as well as the constitutionally similar *N*-alkyllactams, piperidides of carboxylic acids, *etc.*, add on NCSA in a Type II reaction to give unstable adducts, which readily lose carbon dioxide to form N^2-chlorosulfonylamidines *(45)* [58].

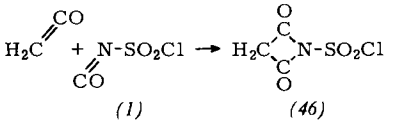


(1) *(45)*

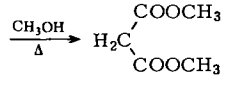
The products can react as described in Sections 2.2.1.–2.2.3. Hydrolysis gives the free amidines [59] *via* the free amidine-*N*-sulfonic acids, which, in some cases, are isolable.

2.9. Ketene

Ketene reacts with NCSA in ether at low temperatures in a Type II reaction to give *N*-chlorosulfonyl-2,4-azetidinedione *(46)*, which can be readily converted into malonic acid derivatives [60,61].



(1) *(46)*



[50] *G. Lohaus*, Farbwerke Hoechst AG, unpublished results.

[51] *M. Seefelder*, DAS 1210792, Badische Anilin- & Sodafabrik (1963).

[52] *M. Seefelder*, Chem. Ber. *94*, 3243 (1963).

[53] *H. Biener*, German Pat. 1226106, Farbwerke Hoechst AG (1963).

[54] *K. Matterstock* and *H. Jensen*, German Pat. 1160432, Farbwerke Hoechst AG (1960); Chem. Zbl. *1964*, 51-2424.

[55] *R. Graf*, German Pat. 1010958, Farbwerke Hoechst AG (1955); Chem. Zbl. *1958*, 2569.

[56] *R. Graf*, German Pat. 1109667, Farbwerke Hoechst AG (1960); Chem. Zbl. *1962*, 7327.

[57] *R. Graf*, German Pat. 1134993, Farbwerke Hoechst AG (1960); Chem. Zbl. *1963*, 14862.

[58] *R. Graf, D. Günther, H. Jensen*, and *K. Matterstock*, German Pat. 1144718, Farbwerke Hoechst AG (1960); Chem. Zbl. *1963*, 20282.

[59] *K. Matterstock* and *H. Jensen*, German Pat. 1168896, Farbwerke Hoechst AG (1962).

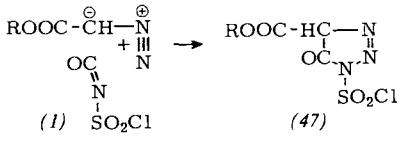
[60] *E. Mundlos* and *R. Graf*, German Pat. 1098515, Farbwerke Hoechst AG (1958); Chem. Zbl. *1964*, 16-2260.

[61] *E. Mundlos* and *R. Graf*, Liebigs Ann. Chem. *677*, 108 (1964).

(46) cannot be isolated since it readily decomposes.

2.10. Diazoacetic Ester

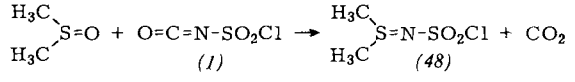
Reaction with diazoacetic ester leads to the ester of 1-chlorosulfonyl-5-oxo-Δ^2-triazoline-4-carboxylic acid *(47)* [31].



(1) *(47)*

2.11. Dimethyl Sulfoxide

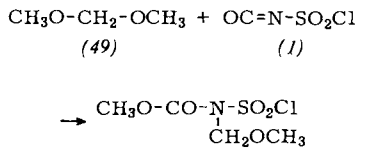
Dimethyl sulfoxide reacts with NCSA with loss of CO_2 and formation of *N*-chlorosulfonyldimethylsulfimide *(48)* (Reaction Type II) [62].



(1) *(48)*

2.12. Bismethoxymethane (Methylal)

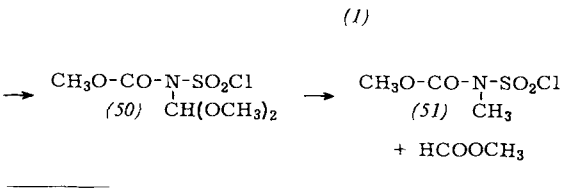
Bismethoxymethane (methylal) *(49)* adds smoothly and exothermally to NCSA in a Type I reaction (the residue $-CH_2OCH_3$ taking the place of H in this case) [12].



(49) *(1)*

2.13. Ortho Esters

NCSA adds to ortho esters, and particularly readily to trimethyl orthoformate, with elimination of formate and formation of esters of *N*-alkyl-*N*-chlorosulfonylcarbamic acid [*e.g. (51)*]. The intermediate *(50)* has not yet been isolated [63,64]



(1) *(50)* *(51)*

[62] *R. Appel* and *H. Rittersbacher*, Chem. Ber. *97*, 852 (1964).

[63] *H. Biener*, German Pat. 1186044, Farbwerke Hoechst AG (1963).

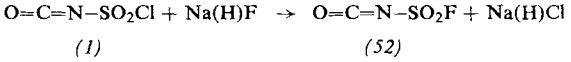
[64] *H. Biener*, Liebigs Ann. Chem. *686*, 102 (1965).

2.14. Pyridine

The addition product of NCSA with pyridine [65], like the SO_3-pyridine adduct, reacts with alkali to give the sodium salt of glutacondialdehyde, which can be detected as the dianil derivative. The NCSA-pyridine adduct reacts only slowly with ice water with loss of CO_2, and certain reactions of NCSA that normally proceed only in anhydrous media can be carried out (though in poor yields) with this adduct in aqueous suspension: an example of such a reaction is the reaction with aniline as described in Section 2.3.2. [12].

2.15. Sodium Fluoride, Hydrogen Fluoride

NCSA reacts with NaF or HF in a Type III reaction to give *N*-carbonylsulfamoyl fluoride *(52)* (CSF) [15, 66,67]. Of all the isocyanates, CSF is closest in its behavior to NCSA. It can in principle be used in the

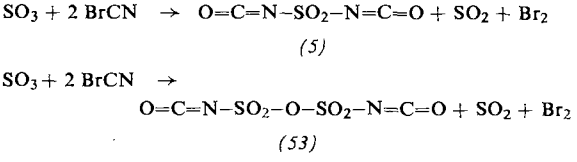


(1) *(52)*

same way as NCSA, but generally reacts a little more slowly [27]. The *N*-sulfonyl fluorides obtained in reactions with *(52)* are generally much more stable to hydrolysis and to heat than the *N*-sulfonyl chlorides [68].

2.16. Pyrolysis of NCSA to Sulfonyl Diisocyanate

The reaction of cyanogen bromide with sulfur trioxide leads *via* thermally unstable sulfonyl bromides, with elimination of bromine and sulfur dioxide, to sulfonyl diisocyanate *(5)* or disulfuric acid diisocyanate *(53)*, depending on the conditions. These two reactions may be represented by the overall equations [69]:



(5)

(53)

NCSA can be converted, in the gas phase at about 400 °C, or more readily and more smoothly in the presence of catalysts containing $FeCl_3$ [70], into sul-

[65] *R. Graf*, German Pat. 1000807, Farbwerke Hoechst AG (1955); Chem. Zbl. *1957*, 8365.

[66] *D. Voigt*, German Pat. 1043293, Farbenfabriken Bayer AG (1957); Chem. Zbl. *1959*, 11730.

[67] *H. Hahn*, German Pat. 1083791, Farbwerke Hoechst AG (1958); Chem. Zbl. *1961*, 12999.

[68] *H. Jonas* and *D. Voigt*, German Pat. 1095806, Farbenfabriken Bayer AG (1958).

[69] *R. Graf*, German Pat. 940351, Farbwerke Hoechst AG (1954); Chem. Zbl. *1956*, 13555.

[70] *K. Matterstock* and *R. Graf*, German Pat. 1152093, Farbwerke Hoechst AG (1961); Chem. Zbl. *1964*, 14-1957.

fonyl diisocyanate, chlorine, and sulfur dioxide in excellent yields:

$$\underset{(1)}{2\ O{=}C{=}N{-}SO_2Cl} \rightarrow \underset{(5)}{SO_2(-N{=}C{=}O)_2} + Cl_2 + SO_2$$

At about 400 °C in the presence of catalysts containing $FeCl_3$, sulfonyl diisocyanate is formed directly from SO_3 and cyanogen chloride [71]:

$$2\ SO_3 + 2\ ClCN \rightarrow SO_2(-N{=}C{=}O)_2 + SO_2 + Cl_2$$

Sulfonyl diisocyanate is also formed on prolonged boiling of NCSA with silver cyanate [72].

Sulfonyl diisocyanate appears to be rather less reactive than NCSA, but reacts with the above-mentioned classes of compounds, including olefins, to give products similar to those obtained with NCSA. Many of these reactions can be controlled to give predominant reaction of both isocyanate groups or of only one isocyanate group [30].

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German version: Angew. Chem. *80*, 179 1968
Translated by Express Translation Service, London.

[71] *K. Matterstock* and *R. Graf*, German Pat. 1171887, Farbwerke Hoechst AG (1961).

[72] *R. Appel* and *W. Senkpiel*, Angew. Chem. *70*, 271 (1958); Chem. Ber. *91*, 1200 (1958).

The Degradation of Poly(ethylene terephthalate)[**]

BY L. H. BUXBAUM [*]

The penetration of new markets by polyester fibers has emphasized the need for increased stability of the polyester toward a variety of degradative reactions. Extensive studies of the nature of the thermal, hydrolytic, oxidative, and radiation-induced degradation reactions have been reported. The interpretation of kinetic investigations and the identification of the reaction products have been facilitated by using suitable esters as model compounds in place of the polymeric species.

1. Introduction

Poly(ethylene terephthalate) has the reputation of being a polymer of great resistance to environments which might be expected to limit its useful life as a fiber, film, or other end product. However, even the small amount of decomposition occurring under normal manufacturing and processing conditions is important to the manufacture of a uniform product. Polyester fibers and films, although of excellent durability, can be affected by hydrolysis, aminolysis, and various kinds of radiation.

To avoid a gradual deterioration of the physical properties of the product, such degradation reactions must be inhibited or retarded. In turn, successful stabilization must be based on an understanding of the precise mechanism by which each type of degradation occurs. Much research in this direction has been conducted by the polyester producers and by textile research institutes.

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The Goodyear Tire and Rubber Co.,
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1.1. Preparation of Poly(ethylene terephthalate)

Poly(ethylene terephthalate) is prepared in two stages from dimethyl terephthalate and ethylene glycol. In the first stage a precondensate is formed which chiefly consists of the diglycol ester together with a certain amount of oligomers (up to the tetramers).

This trans-esterification, which is catalyzed by small amounts of metal salts (Zn, Mn, Cd, Pb, Ca, Mg, *etc.*), is carried out at 200 °C, the methanol formed being continually removed by distillation. The complete removal of the methanol is most important since it can drastically interfere with the formation of sufficiently long chains; as a monofunctional alcohol it forms stable end groups and thus prematurely stops chain growth.

In the second stage, polycondensation of the precondensate is carried out at *ca.* 280 °C in high vacuum (< 1 torr) and with addition of a heavy metal salt (usually Sb), the glycol formed being continually removed.

Concentration of catalyst and temperature control are very significant factors in determining the stability of the resulting polyesters. Additionally, of course, stabilizers (usually P-compounds) can also be added.

1.2. Properties of Poly(ethylene terephthalate)

Poly(ethylene terephthalate) exhibits a number of interesting physical, and chemical, properties, only the most important of which shall be briefly mentioned here. On account of the hydrophobic nature of this polymer (absorption of water at 20 °C and at a relative humidity of 25 % is less than 0.5 %) its mechanical properties are almost uninfluenced by water (*i.e.*

it has a high wet strength, and there is no "flat spotting" of the polyester tire cord). Poly(ethylene terephthalate) is very resistant to attack by most organic solutions and reagents, especially acids, and also to biological degradation. It is much more stable toward the effect of light and atmospheric conditions than most of the other polymers.

Poly(ethylene terephthalate) fibers are distinguished by their excellent resilience and by their dimensional stability. Up to a temperature of *ca.* 150 °C the properties of the fiber deteriorate very little. Other properties which are responsible for the popularity of poly(ethylene terephthalate) fiber in the textile industry are its good permanent-set property and high melting point (260 °C).

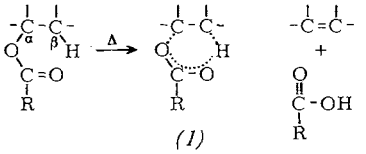
The excellent electrical properties of poly(ethylene terephthalate), such as high specific resistance, high dielectric strength, together with its thermal stability and small moisture absorption, make it a very good insulating material.

2. Thermal Degradation

The nature of thermal degradation of polyesters is not entirely clear. The primary fission of the ester linkage in the polymer is probably not a homolytic reaction, since thermal degradation cannot be inhibited by free radical trapping agents. The close agreement between the behavior of poly(ethylene terephthalate) (PET) and model ester compounds (see Section 2.2) suggests that the mechanism for polymer degradation is probably similar to that for simple ester pyrolysis.

2.1. Thermal Degradation of Carboxylic Esters in General

The mechanism by which esters containing at least one β-hydrogen atom decompose pyrolytically to give olefins and acids is generally considered to involve a cyclic transition state *(1)* [1].



(1)

In *(1)*, the C–H bond and the alkoxy C–O bond are partly broken, while the olefinic C=C bond and the O–H bond are partially formed. Previous work [2] has shown that the C–O bond breakage is heterolytic and that the alpha-carbon atom develops some carbonium-ion character in the transition state. It appears that for a given ester at a fixed temperature, the rate of decomposition is determined more by the stability of the breaking alkoxy C–O bond than by the breaking C–H bond or the forming C=C bond [3].

Maccoll [4] proposed that the reaction is a pseudo bimolecular electrophilic substitution, (E_2), involving nucleophilic attack of the carbonyl oxygen atom on the β-hydrogen atom.

This field has been widely but unsystematically studied. A good survey of the earlier literature up to about 1928 has been presented by *Hurd* [5]. *Ritchie* [6] has summarized nine of the breakdown routes which occur most frequently.

2.2. Thermal Degradation of Model Compounds

Difficulties in studying the polyester itself suggested the use of simplified model systems representing specific segments of the intact PET chain, segments with terminal hydroxyethyl groups and representing the known incorporation of occasional ether linkages. Ethylene dibenzoate *(2)*, 2-hydroxyethyl benzoate *(3)* and diethylene glycol dibenzoate *(4)* have been chosen most often for such studies. The degradation of *(2)*

$C_6H_5–CO–O–CH_2–CH_2–O–CO–C_6H_5$

(2)

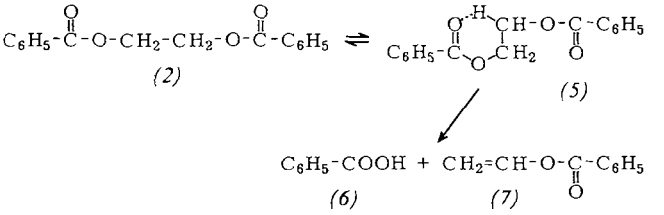
$C_6H_5–CO–O–CH_2–CH_2OH$

(3)

$C_6H_5–CO–O–CH_2–CH_2–O–CH_2–CH_2–O–CO–C_6H_5$

(4)

between 250 °C and 350 °C has been well studied [2, 7, 9], and is thought to proceed *via* a cyclic transition state. Benzoic acid *(6)* and vinyl benzoate *(7)* are formed.



(2) *(5)* *(6)* *(7)*

Ritchie [6] also reported benzophenone as a reaction product, although there is no confirmation of this product by other workers. It is possible that this difference in product formation may have resulted from the use of different temperatures in the pyrolysis.

3-Oxapentylene dibenzoate *(4)* decomposes by a similar route to give benzoic acid and 2-vinyloxyethyl benzoate *(8)*.

$C_6H_5–CO–OCH_2–CH_2–OCH=CH_2$

(8)

[1] *C. H. DePuy* and *R. W. Kong*, Chem. Reviews *60*, 431 (1960), and references therein.

[2] *R. Taylor, G. G. Smith*, and *W. H. Wetzel*, J. Amer. chem. Soc. *84*, 4817 (1962).

[3] *G. G. Smith, F. D. Bagley*, and *R. Taylor*, J. Amer. chem. Soc. *83*, 3647 (1961).

[4] *A. Maccoll*, J. chem. Soc. (London) *1958*, 3398.

[5] *C. D. Hurd*: The Pyrolysis of Carbon Compounds. Chemical Catalog Co., New York 1929.

[6] *P. D. Ritchie*, Soc. chem. Ind. (London) Monograph No. *13*, 107 (1961).

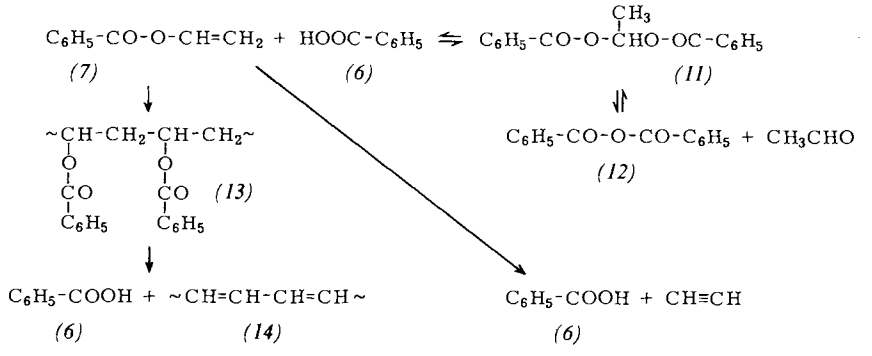
[7] *E. P. Goodings*, Soc. chem. Ind. (London) Monograph No. *13*, 211 (1961).

[8] *H. V. R. Iengar* and *P. D. Ritchie*, J. chem. Soc. (London) *1957*, 2556; *1956*, 3563.

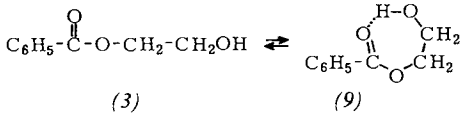
[9] *G. Challa*, Makromolekulare Chem. *38*, 138 (1960).

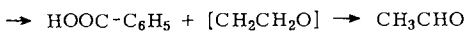
Despite the importance of 2-hydroxyethyl esters in the formation of PET, few studies with model compounds such as 2-hydroxyethyl benzoate *(3)* have been performed. *Iengar* and *Ritchie*[8] studied the pyrolysis of *(3)* at temperatures between 375 °C and 500 °C and proposed a complex degradation mechanism. Our results, which were obtained at 280 °C, suggest a different mechanism involving a seven-membered ring

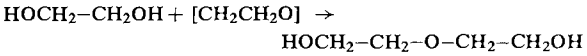
The vinyl compounds formed during these reactions react further to give a complex mixture of end products. The pyrolysis of vinyl benzoate *(7)* has been studied extensively and it has been shown, that, as expected, this vinyl compound reacts very rapidly at 280 °C. After 30 min at this temperature *(7)* yielded a black mass in which benzoic acid *(6)*, benzoic anhydride *(12)* and a diene *(14)* could be detected.

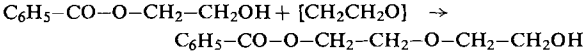


(9) as transition state and the formation of an active species *(10)*[14]. This mechanism explains the low activation energy found for this reaction (28 kcal/mole) and the formation of ether linkages. (The dehydration reaction is not significant at 280 °C, as could be shown with ethylene glycol[9].)









A transesterification reaction takes place also, and at 280 °C the equilibrium 2 *(3)* ⇌ *(2)* + ethylene glycol is established in *ca.* 10 min.

Figure 1 shows the thermal degradation of *(2)*, *(3)*, and *(4)*.

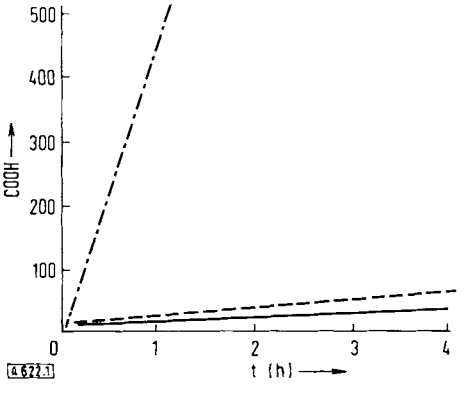
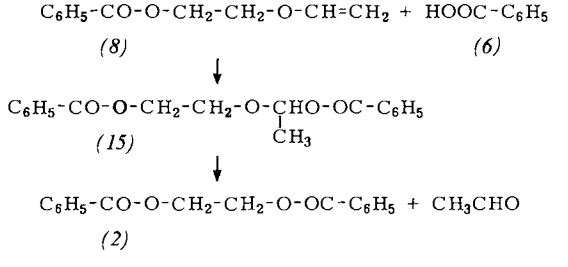


Fig. 1. Thermal degradation of ethylene dibenzoate *(2)* ——, 3-oxapentyl enedibenzoate *(4)* – –, and 2-hydroxyethyl benzoate *(3)* – · – · – at 280 °C under nitrogen.

The following facts can be given as proof that the intermediates *(11)* and *(13)* are formed in the reaction: Ethylidene dibenzoate *(11)* could be isolated from the reaction mixture containing compounds *(6)* and *(7)* by gas chromatography and was identified by IR- and NMR-spectroscopy. Starting from compound *(11)* an equilibrium is once again set up at 280 °C between *(7)* and *(6)* as well as with *(12)* and acetaldehyde. Polyvinyl benzoate *(13)* (prepared from vinyl benzoate and a radical chain initiator) similarly gives compounds *(6)* and *(14)* at 280 °C; the presence of *(14)* was confirmed by IR- and UV-spectroscopy.

Recently *Zimmermann* and *Leibnitz*[10] investigated the influence of catalysts on a number of the individual reactions. The primary chain splitting reaction of ethylene dibenzoate *(2)* to benzoic acid *(6)* and vinyl benzoate *(7)*, as well as the reaction of *(7)* with alcohols and the polymerization of *(7)*, are accelerated *e.g.* by zinc acetate. It was found that the catalysts zinc acetate and lead acetate have no influence on the thermal degradation of polyvinyl benzoate *(13)* to *(6)* and *(14)* or on the formation of acetaldehyde and *(12)* from *(7)* and *(6)*.

2-Vinyloxyethyl benzoate *(8)*, the first degradation product of 3-oxapentylene dibenzoate *(4)*, decomposes further to benzoic acid *(6)*, acetaldehyde, and acetylene at temperatures above 350 °C[8]. At 280 °C, however, another reaction is of importance: in the presence of benzoic acid the diester *(2)* is formed, the "acylal" *(15)*, which is known to form in the reactions of other vinylethers[11], probably occurring as intermediate. At 280 °C at least 50% of the carboxyl groups formed in the degradation of *(4)* react with the vinyl ether *(8)* to give *(2)* and acetaldehyde[14].



[10] *H. Zimmermann* and *E. Leibnitz*, Faserforsch. u. Textiltechn. *16*, 282 (1965).

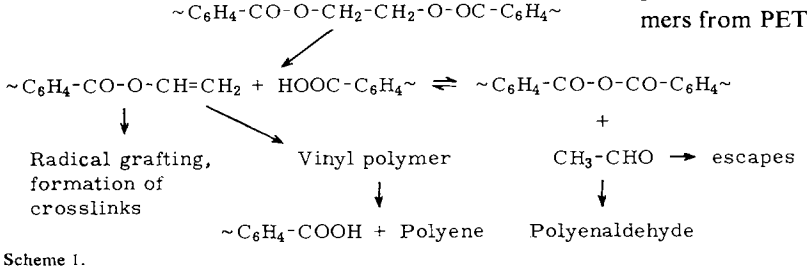
[11] *M. F. Shostakovskii*, Ž. Obšč. Chim .*18*, 1989 (1948); Chem. Abstr. *43*, 3785 h (1949).

In general, caution is necessary in correlating the results obtained from studies with model compounds with the reactions of the polymer itself. However, it has been found that in this case model compound reactions do not differ much from the reactions taking place during the thermal degradation of PET, especially at temperatures between 200 °C and 300 °C.

2.3. Thermal Degradation of Poly(ethylene terephthalate)

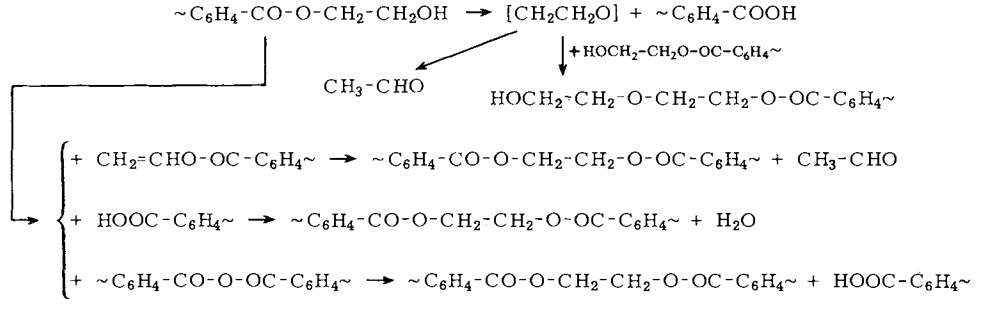
Various research teams have studied the thermal degradation of polyester during the last few years [6,7, 10–13]. From their results and from extensive studies with model compounds we know that PET breaks down by a molecular mechanism with random chain scission at the ester links. Although a radical mechanism has been proposed [12], no evidence for such a mechanism could be established.

Pohl [13] proposed that the principal point of weakness in the polyester chain is the β-methylene group. The main reactions in the thermal degradation of PET are summarized in the following scheme:



Scheme 1.

If 2-hydroxyethyl end groups are present in the polymer the following reactions take place also:



Scheme 2.

Thus, as long as free hydroxyl end groups exist in a PET melt, every broken polymer link will be reformed. When most of the hydroxyl end groups have been consumed, the molecular weight will begin to fall.

2.3.1. Products of Thermal Degradation

When PET is maintained in a molten state under nitrogen at about 280 °C, it decomposes slowly to gaseous and to solid, low molecular weight products; the functional groups react with one another, and the polymer becomes colored.

2.3.1.1. Gaseous Products

A gaseous mixture with the following composition (concentration in mole-%) is formed at temperatures between 280 °C and 306 °C [7]: CO = 8.0; CO_2 = 8.5; H_2O = 0.8; CH_3CHO = 79.5; C_2H_4 = 2.0; 2-methyldioxolane = 0.4; CH_4 = 0.4; C_6H_6 = 0.4. Although this composition varies appreciably with temperature acetaldehyde is always the major product.

2.3.1.2. Non-gaseous Products, Oligomers

During melt spinning of PET a white "dust" is formed and covers various parts of the spinning apparatus [15a]. A similar sublimate can be produced in the laboratory by bubbling nitrogen through molten polyester. This sublimate consists primarily of terephthalic acid and acidic oligomers [7, 14].

Cyclic oligomers (mainly the trimer) are also formed during the thermal degradation of PET. A kind of equilibrium between the cyclic oligomers and the polymer seems to exist. After extracting these oligomers from PET and heating the extracted polymer for about one hour at 280 °C, the same amount of cyclic oligomer is again formed [16]. It is not known how these oligomers are formed in the polymer, although a transesterification involving end groups can be assumed.

Goodings [7] isolated a number of compounds, mainly derivatives of substituted benzoic acids and biphenyldi- and monocarboxylic acids, from extensively pyrolyzed PET. However, these materials were found in very low concentration (0.005–0.09 wt.%).

[12] *I. Marshall* and *A. Todd*, Trans. Faraday Soc. *49*, 67 (1953).
[13] *H. A. Pohl*, J. Amer. chem. Soc. *73*, 5660 (1951).
[14] Unpublished observations by the Polyester Research & Development Division, Goodyear Tire & Rubber Co., Akron, Ohio (USA).
[15] *H. Zimmermann*, Faserforsch. u. Textiltechn. *17*, 228 (1964).
[15a] *A. Mifune, S. Ishida, A. Kobayashi*, and *S. Sakajiri*, Kogyo Kagaku Zassi *65*, 992 (1962).
[16] *I. Goodman* and *B. F. Nesbitt*, Polymer (London) *1*, 384 (1960); J. Polymer Sci. *19*, 423 (1960).

2.3.1.3. Reactions of Functional Groups

PET has an average molecular weight of 25000 (intrinsic viscosity $[\eta] = 0.68$ dl g^{-1}). The concentration of carboxyl groups depends on the catalyst and is of the order 10–50 equiv/10^6 g of polymer. The concentration of hydroxyl end groups is about 60 equiv/10^6 g. During thermal degradation, the concentration of hydroxyl groups tends to fall and the carboxyl group content of the polymer increases. Anhydride groups can be formed; they begin to accumulate when most of the hydroxyl end groups have been consumed [7]. The anhydride groups are formed by the reaction of vinyl end groups with carboxyl groups and by dehydration of two carboxyl groups. *Goodings* [7] reported that PET which had been degraded at 306 °C for 65 hours under nitrogen gave an IR-spectrum indicating that anhydride and carboxyl groups were present in the ratio 1:2.6.

2.3.1.4. Discoloration

Discoloration is a serious problem in the production of PET since the consumer of white polyester goods demands a brilliant white color. As PET degrades, its color changes first to yellow, then to brown, and finally to black. Since the chromophoric substances involved are very difficult to isolate, contradictory results have been reported about their nature and composition. At least part of the chromophore seems to be chemically bonded to the polymer. The chromophore is believed to be a highly unsaturated aliphatic molecule with a molecular weight of about 300–1000 [7, 14]. Two routes leading to color formation in PET are discussed in the literature. *Goodings* [7] assumes the formation of polyenaldehydes from acetaldehyde. *Zimmermann* [10, 15], on the other hand, has shown that unsaturated, color forming molecules are formed from polyvinyl esters. Our own studies show that both reactions contribute to color formation; the precise polymerization conditions will determine which reaction sequence predominates.

2.3.2. Kinetics

Investigations on the kinetics of simple esters [3–5] show that their decomposition reactions are homogeneous, follow first order kinetics in both the vapor and the liquid phase, and are unaffected by radical scavengers. The activation energy found for ester pyrolysis was about 40 kcal/mole; on a theoretical basis pure chain scission of the ester link would require an activation energy of almost 60 kcal/mole. The lower value observed indicates a mechanism probably involving a cyclic transition state *(I)*.

The rate of thermal degradation of PET can be measured in terms of: a) the products formed, b) the rate of change of molecular weight of the polymer (as measured by the melt viscosity or the intrinsic viscosity), or c) the rate of change in concentration of end groups. Table 1 shows reaction rate constants and activation energies found by different authors using one or more of the methods mentioned above. It is interesting that all the rate constants have the same order of magnitude.

The effect of molecular weight (or intrinsic viscosity) on the thermal degradation of PET per unit time, and at various temperatures, is shown in Figure 2.

Table 1. Reaction rate constant and activation energy of the thermal degradation of PET.

k and E_a calculated from	$k(h^{-1} \cdot 10^3)$ at 282 °C	E_a (kcal/mol)
$[\eta]$ [a]	1.3 2.3 1.4	62.3
M.V. [b]	1.7 (290 °C)	32.0 48
Total gas	—	38
—COOH	3.5	41.7
—OH	2.4	
—CHO	0.2	
Total end groups	1.2	58.7
References	[7] [12] [14]	[7] [12] [17] [14]

[a] Intrinsic viscosity.

[b] Melt Viscosity.

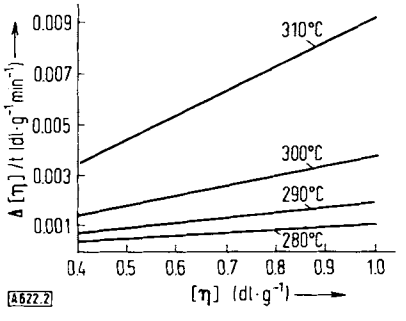


Fig. 2. The thermal degradation of PET per minute as a function of $[\eta]$ at different temperatures.

3. Oxidation

The degradation of PET in various oxygen-nitrogen mixtures between 280 °C and 325 °C has been investigated by *Marshall* and *Todd* [12]. The rate of degradation (measured by the decrease in the melt viscosity) increased linearly with increasing oxygen content. Passing oxygen through molten polyester causes rapid degradation, noticeable by color formation, an increase in carboxyl content and a decrease in molecular weight [14].

3.1. Course of Oxidation

No generally accepted concept for the course of the oxidation of PET has been reported. In previous studies, the mechanism developed by *Bolland et. al* [19] for the oxidation of hydrocarbons has generally been referred to and adopted in the interpretation of the oxidation of polymers [18].

The high molecular weight of PET and the influence of the physical structure make it difficult to study the oxidation of the polymer directly. Consequently,

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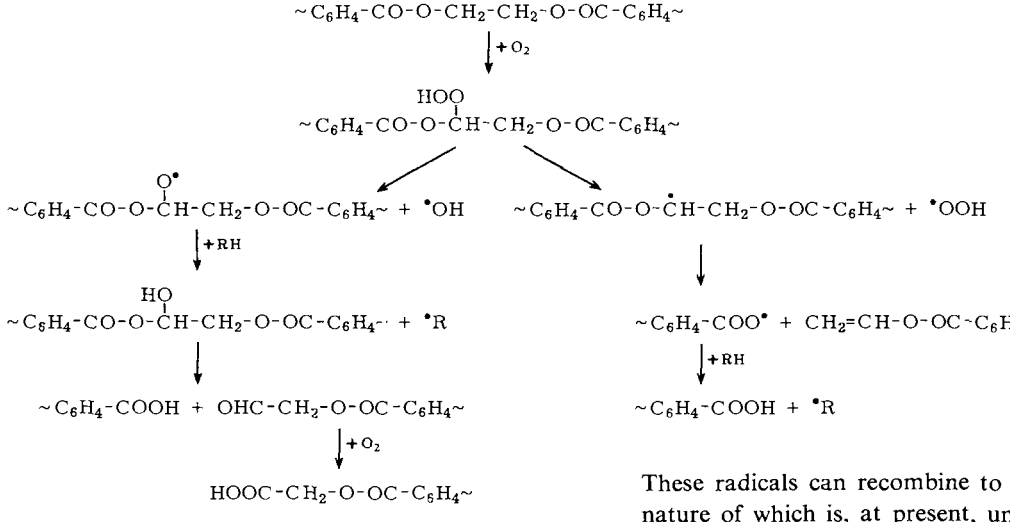
[18] *W. L. Hawkins*, SPE Trans. July *1964*, 187.

[19] *J. L. Bolland*, Quart. Rev. chem. Soc. (London) *3*, 1 (1949).

studies with model compounds have provided most of the mechanistic information available. 3-Oxapentylene dibenzoate *(4)* oxidizes readily at 130 °C[20] to give 2-benzoyloxyethyl benzoyloxyacetate, 2-benzoyloxyethyl formate, benzoyloxyacetic acid, benzoic acid, formic acid and water. Ethylene dibenzoate *(2)*, and 2-hydroxyethyl benzoate, *(3)*, can not be oxidized at 130 °C; above 200 °C decomposition occurs, but this is probably a combination of oxidative and thermal degradation. The mechnism of the oxidation of these two model compounds is therefore inaccessible to direct study. When comparing the degradation of these compounds under oxygen and under nitrogen at 210 °C, the higher carboxyl-group content and the darker color of the samples heated under oxygen suggest a breakdown to acidic and color forming species similar to those obtained from *(4)*.

The results from these model compound studies are in good agreement with results obtained with PET.

Diethylene glycol links lower the stability of polyester toward oxidation. The reaction sequences shown in Scheme 3 have been proposed as an interpretation of the oxidation of PET:



Scheme 3. RH = PET

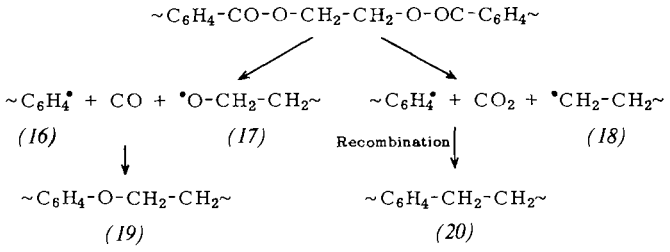
4. Degradation by Radiation

4.1. Photolysis

Generally speaking poly(ethylene terephthalate) is very stable toward ultraviolet light; however, some long term degradation occurs especially when it is exposed to light of wavelength 3000–3300 Å[21a]. There seems to be a threshold photon energy of about 3 eV below which no damage is done[21].

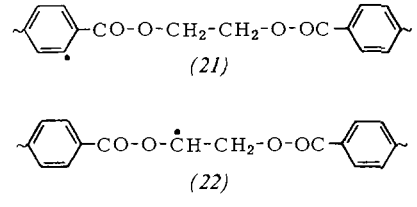
The present understanding of the photodegradation of polyesters is very rudimentary since most reports on this subject are of "weathering" experiments, in which oxygen and moisture play an important role in the degradation.

Stephenson et al.[21] and *Marcotte et al.*[21a] showed that the polymer turns to an amber color, becomes brittle, evolves gas (mainly CO and CO_2), and becomes partly insoluble in trifluoroacetic acid, after it has been exposed to monochromatic light of wavelengths 2537 and 3130 Å. From their results the reaction sequences shown in Scheme 4 seem probable:



Schema 4.

Hydrogen abstraction from neighboring molecules leads to the formation of radicals such as *(21)* and *(22)*.



These radicals can recombine to form crosslinks, the nature of which is, at present, unknown. The formation of polyphenyl systems, in which reactions involving the radical *(22)* (see section 4.2.) seem to be of little importance, has also been suggested[22].

For practical purposes, "weathering" experiments give a good picture of the performance of PET in specific outdoor applications. Under these conditions the ether content of the polymer is of extreme importance. *Coleman*[22] exposed copolymers of PET containing polyoxyethylene glycol to ultraviolet light. After 300 hours of exposure, a yarn containing 17% by weight of polyoxyethylene glycol (MW = 2800) showed a 40% decrease in intrinsic viscosity while pure PET was not affected. Therefore this copolymer was not

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accepted on the market even though the dyeability of fibers of this material was much superior to that of fibers prepared from the homopolymer.

4.2. Degradation by High Energy Ionizing Radiation

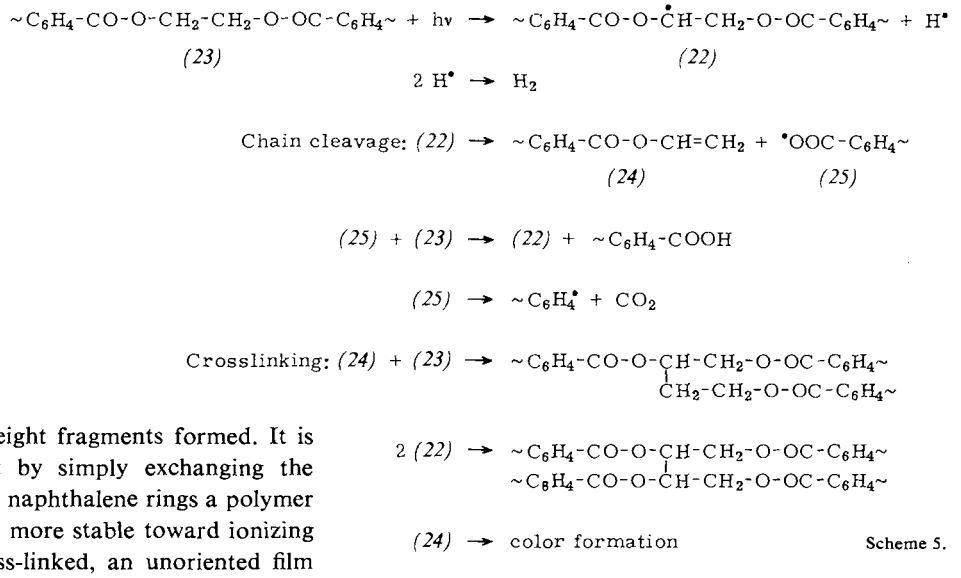
The mechanical properties of PET fibers are relatively unchanged by moderate doses of high energy radiation. When subjected to doses of more than 50 Mrad the tensile strength and ultimate elongation of the PET begin to decrease considerably and deteriorate rapidly when the dose reaches the 100–500 Mrad range. Radiation doses exceeding 1000 Mrad [23] lead to the lowering of the glass transition temperature, which probably results from the lowering of the molecular weight by chain cleavage and from plasticization by the low molecular weight fragments formed. It is interesting to note that by simply exchanging the benzene rings in PET for naphthalene rings a polymer is formed which is much more stable toward ionizing radiation. Although cross-linked, an unoriented film of poly(ethylene 2,6-naphthalene dicarboxylate) was still tough and flexible after 1000 Mrad of gamma radiation [40].

Rather contradictory results have been reported concerning the reactions occurring during high energy irradiation. Both crosslinking [24,26] and chain cleavage [25] have been claimed to be predominant; the former claim was based upon partial insolubilization of the polymer, while the latter was based upon complete solubility, a steady decrease in molecular weight with increasing dose, and physical evidence of chain cleavage.

More recent evidence suggests that both chain cleavage and crosslinking occur and that the reaction conditions determine which process is predominant. Dose rate, kind of radiation, temperature, crystallinity, and impurities, such as water [26] or oxygen, are examples. At low dose rates of gamma-rays, carboxyl groups are formed – and no gel formation has been observed. At higher dose rates (over 5000 Mrad) a network is formed in the polymer [29] and fewer carboxyl groups are formed.

Some investigations have been carried out using high speed electrons [26,28] instead of gamma-rays [27]. The results of these experiments were expected to be different since electrons are known to cause a temperature increase in the polymer (electron microscopy) and are reported to destroy crystallinity in PET by changing the steric conformation of the chain [28]. No gel formation has been observed at temperatures up to 175 °C for doses of up to 2000 Mrad [29a]; at temperatures above 200 °C rapid gelation occurs even with low doses.

ESR studies of free radicals formed by gamma-irradiation of PET [29] support the suggestion of the reaction sequences shown in Scheme 5 as being the primary steps in the degradation:



Scheme 5.

The differences between photolysis of PET and degradation by high energy radiation can be summarized as follows:

Photolysis:

Primary reaction products:

$\sim C_6H_4\cdot + CO + {}^{\bullet}OCH_2-CH_2-O-OC-C_6H_4 \sim$;
Only few carboxyl groups, and no hydrogen, are formed.

Crosslinking occurs.

Degradation by high energy radiation:

Primary reaction products:

$\sim C_6H_4-CO-O-\dot{C}H-CH_2-O-OC-C_6H_4 \sim + H^{\bullet}$
Hydrogen and carboxyl groups are formed.

No gelation occurs (up to 2000–5000 Mrad).

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5. Hydrolytic Degradation

In contrast to other polyesters, PET is very resistant to attack by water, acids, and bases; this is due, presumably, to its aromatic character and to the tight packing of its chains. Nevertheless, it does hydrolyze at temperatures above 100 °C. Of the forms of degradation discussed thus far, hydrolysis is by far the most troublesome reaction. The hydrolysis of PET at 100°–120 °C and 100% relative humidity proceeds 10000 times faster than that of thermal degradation and 5000 times faster than that of oxidation in air in the same temperature range [31].

It is known that dry PET adsorbs moisture rapidly and that the extent of adsorption is dependent upon the time of exposure, the particle size, crystallinity, and relative humidity.

5.1. Neutral-, and Acid-Catalyzed Hydrolysis

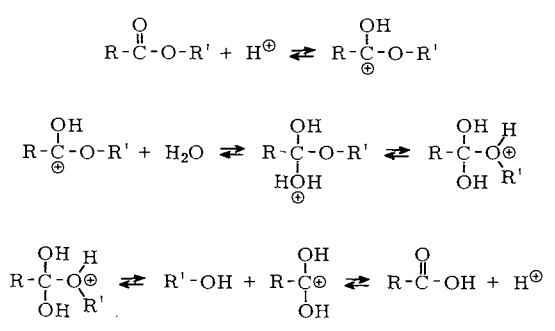
5.1.1. Adsorption and Diffusion of Water

The hydrolysis of ester bonds must proceed *via* (i) the adsorption of water on the surface of the polymer and (ii) diffusion to the interior of the polymer from the point of attack. Knowledge of the rates of adsorption and diffusion are of practical and theoretical importance. The adsorption of water by dry PET cubes of length 3/16″ (or 0.4762 cm) amounts to 0.025% after $^1/_2$ h, and, by dry PET powder (40 mesh), to *ca.* 0.125%.

The influence of the diffusion of moisture on the rate of hydrolysis has been considered by several groups of workers, but the results are contradictory. *Golike* and *Lasoski* [30] and *McMahon et al.* [31] assume that the diffusion of moisture into the polymer is the rate-controlling step. However, the rate of diffusion of water into PET at temperatures above 100 °C is at least 1000-fold higher than the rate of hydrolysis [32, 33]. The observed differences are probably due to differences in morphology and molecular geometry of the polymers studied.

5.1.2. Course of Hydrolysis

The hydrolysis of esters in neutral or acid media generally proceeds according to the reactions shown in Scheme 6:



Scheme 6.

The reaction rate depends on both the proton concentration and the amount of water. This is in agreement with the observation that the hydrolysis rate for PET depends on the relative humidity. The adsorption isotherm [33] shows that the rate of hydrolysis is directly proportional to the concentration of water in the polymer.

The influence of proton concentration on the hydrolysis rate is evident in the hydrolysis of PET in hydrochloric acid [33–36,42–44]. The rate is only slightly influenced by acid concentrations below 3 N but increases rapidly at concentrations above this value. *Ravens* [34] explains this by considering the acid concentration not in the aqueous phase, but in the polymer itself. Because of the low dielectric constant of PET (< 4), one can assume that the acid in the polymer is only slightly dissociated. This is in agreement with the work of *Sheard* [35], who observed that ammonia will diffuse through films of PET whereas ammonium ions will not. The importance of the dielectric constant is further emphasized by the fact that the rate of acid hydrolysis is slower in drawn fibers than it is in undrawn fibers.

In drawn fibers the crystallinity is of a higher order than it is in undrawn fibers. During crystallization, the molecules assume a *trans*-configuration; hence, the polymer has a smaller dipole moment and therefore a smaller dielectric constant. This in turn leads to a decrease in the degree of dissociation of the hydrochloric acid, so that the proton concentration within the polymer is lower than that in the surrounding medium.

Organic acids, *e.g.* adipic acid [45], also catalyze the hydrolysis of PET [36]. Terminal carboxyl groups of a polyester, which enter into all reactions characteristic of carboxylic acids, also have a catalytic effect. From investigations on polymers with initial carboxyl-group concentrations of from 8 to 97 equiv./10^6 gram of polymer, *Ravens* and *Ward* [33] concluded that the hydrolysis rate can be expressed by

$$d[-COOH] / dt = k[-COOH]^{1/2}$$

where the square root term arises from the weakly acidic nature of the carboxyl group of the polymer. This is a catalytic effect and is not due to adsorption of water in the polymer at carboxyl end groups only, since the adsorption isotherm is independent of the carboxyl end group concentration [33].

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5.2. Base Catalyzed Hydrolysis

Very little has been published about the base catalyzed hydrolysis of PET. This is especially important in view of the potential interactions between polyester fibers and various organic and inorganic bases used in dyeing, aftertreatment, and washing.

Sodium or potassium hydroxide solutions normally attack only the surface of a PET fiber; however, changes in the fine structure of the inner part of the fiber after such treatment have been observed recently [37]. The dielectric properties of the polymer and the formation of carboxylate ions on the fiber surface presumably present a barrier to the penetration of the polymer by hydroxyl ions. The formation of a skin around the fiber and the fact that the rate constant for base catalyzed hydrolysis of esters of dibasic acids is smaller than the rate constant for acid hydrolysis is taken as further evidence for the greater stability of polyester fibers in alkaline solutions than in acid solutions.

The degradation of PET in the presence of amines is accompanied by the formation of amide bonds. The final formation of the terephthalic acid diamide takes place *via* oligoester amides and oligoamides [37, 38]. The morphology of the polymer is again of great importance. Thus *Farrow*, *Ravens*, and *Ward* [39] have shown that a fiber sample with high orientation and crystallinity was unattacked after 16 hours in aqueous methylamine, whereas samples having other morphological properties were considerably degraded. The attack by methylamine takes place in three stages: The initial attack is in the amorphous regions; in the second stage, scission produces more low molecular weight material and gives rise to an increase in the degree of crystallinity of the polymer; the third stage, distinguished by a gradual decrease in the rate of reaction, is attributed to a decrease in the rate of attack on both crystalline and amorphous regions.

The rate of aminolysis in the presence of primary and secondary amines is of the same order of magnitude as the rate of alcoholysis [37]. Tertiary amines react with polyester only at higher temperatures; but these reactions are not, as yet, fully understood. For example, the products of the thermal degradation of PET seem to react with the tertiary amine; the products of this reaction and the amine itself are subject to further thermal and oxidative degradation. The known catalytic effect of hydroxyl compounds on the aminolysis of esters [41] further complicates the picture.

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Formation and Properties of Solvated Electrons

BY U. SCHINDEWOLF [*]

In the formulation of many chemical reactions, electrons are regarded as readily transferable particles, though their participation in these reactions cannot be directly observed. However, the discovery that electrons can be produced in various ways in suitable solutions and that they are stabilized by solvation and can thus be studied directly has recently led to a rapid growth of interest in these, the simplest and most reactive particles of chemistry. The solvated electron has physical properties that permit its detection by various methods even at very low concentrations, so that it is also possible to follow its many reactions, most of which are extremely fast.

1. General

It has been shown in recent years that dissolved electrons [1, 2] occur as reaction intermediates in the course of many energy-consuming chemical processes. They are formed on radiolysis, photolysis, and electrolysis of aqueous and other polar systems. They also occur in the base-promoted ionization of hydrogen in solution, and probably in some redox processes. However, dissolved electrons are by no means a very recent discovery, but were observed more than a hundred years ago on dissolution of alkali metals in

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liquid ammonia [3]; they were recognized as such and some of their properties established fifty years ago as a result of investigations on such metal solutions.

In view of the many ways in which dissolved electrons are formed, it is likely that they take part in numerous chemical processes, such as metabolism, photosynthesis, and biological radiation damage.

It is not easy to detect the participation of dissolved electrons in these processes, since the high reduction potential of the electrons makes them extremely reactive toward many dissolved ions, free radicals, and neutral molecules, as well as toward the solvent molecules themselves, so that they are generally short-lived (lifetime in pure water < 1 msec) and are consequently present in the solutions only in very low concentrations. The electrons can be stabilized, however, by inhibition of their reactions in frozen solvents. In the absence of impurities, they have a relatively long life even at room temperature in solutions of metals in ammonia, so that these solutions are particularly suitable for the study of the physical properties of dissolved electrons (rate of decomposition of highly purified sodium-ammonia solutions $< 1\%$ per day).

The electrons naturally do not exist in solution as free particles, but, as the common term "solvated electron" implies, they are solvated, *i.e.* bound by the solvent; they therefore possess properties similar to those of ions in solution. Nevertheless, the solvation of electrons must be distinguished from that of ions. For example, with a hydrogen ion, which is localized within a small volume element because of its great mass, ion-dipole interactions lead to the firm attachment of one or more solvent molecules (H_3O^+ or $H_9O_4^+$). The dissolved electron, on the other hand, has a small mass and a low momentum, and is therefore "smeared out" over a large volume in accordance with the uncertainty principle. The field extending from the small spatial charge density of the "smeared out" electron is too weak for the formation of a firm solvation sheath; it is nevertheless sufficient to polarize the surrounding solvent molecules (electronic and orientation polarization) to such an extent that the electron is trapped in the resulting polarization field of the solvent.

Repulsion between the captured electron and the electrons of the solvent molecules leads to a displacement of the latter with formation of a cavity [9, 10] (in ammonia this cavity has a volume of 110 to 180 Å^3, corresponding to a radius of 2.95 to 3.40 Å). The electron is naturally not confined to this cavity, but the probability of its being found outside the cavity is small; this probability decreases with increasing distance.

According to the above model, which was developed in general terms by *Landau* [11] and was applied to dissolved electrons by *Davydov* [12] and *Deigen* [13], and finally in a refined form by *Jortner* [14], there is a resemblance between dissolved electrons and F centers in ionic crystals [15], *i.e.* electrons trapped in anion vacancies. Since the ions in the crystal are immobile, the electrons, produced *e.g.* by irradiation, cannot create space for themselves, and stabilization of these electrons consequently depends on the presence of anion vacancies in the crystal.

The most outstanding physical property of dissolved electrons is their high light absorption in the red to infrared region of the spectrum, as a result of which they appear blue and can be detected in concentrations as low as 10^{-8} mole/l. They are paramagnetic, give a one-line ESR spectrum, and have a mobility three to four times as high as that of normal solvated ions in an electric field.

The electrons exist in this state only at low concentrations. At higher concentrations they tend to undergo spin compensation with formation of diamagnetic electron pairs (e_2^{2-}) analogous to the F′ centers in ionic crystals. If the concentration of the electrons can be further increased, the solutions assume a metal-like character (free electrons), with high conductivities and metallic luster. These transitions can be represented by the equilibria (1a,1b), which are displaced toward the right with increasing concentration.

$$e^- \rightleftharpoons 1/2\, e_2^{2-} \rightleftharpoons e_{met}^- \qquad (1a, 1b)$$

2. Formation

2.1. Solutions of Metals

Solutions of electrons in ammonia and its derivatives (methylamine, dimethylamine, ethylamine, ethylenediamine, hexamethylphosphoramide) can be relatively easily prepared by dissolution of alkali metals, alkaline earth metals, and certain rare earth metals, which spontaneously dissociate:

$$M \rightarrow M^+ + e^- \qquad (2)$$

The equilibria (1) between the solvated electrons (which predominate at concentrations lower than 0.001 M), the spin-compensated electron pairs, and the

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free electrons of the near-metallic state (above 1 M) can be followed particularly readily in solutions of alkali metals in ammonia, since a wide range of concentrations can be covered owing to the high solubility of the metal (cf. the phase diagram of the sodium-ammonia system in Fig. 1). The transition to the metallic state is associated at low temperatures with a miscibility gap [16–19].

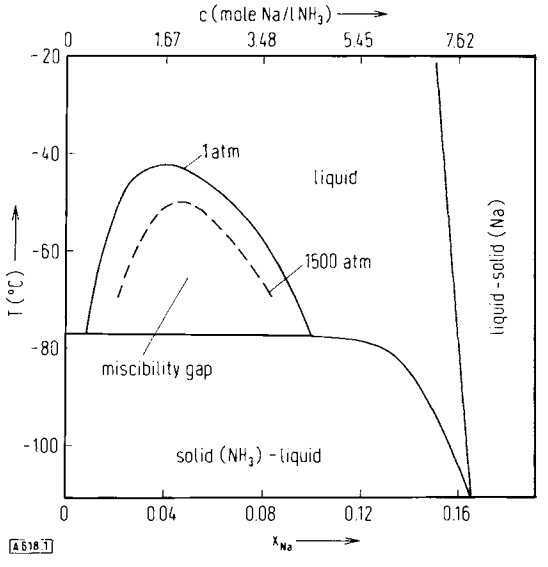

Fig. 1. Part of the phase diagram of the system sodium-ammonia with eutectic and miscibility gap (cf. [8]); the miscibility gap is displaced toward lower temperatures and higher concentrations by increased pressure (broken curve) [19].

In amines, in which the solubility of the metals is generally considerably lower, probably ion pairs such as $(Na^+ \cdot e^-)$, $(Na \cdot e_2)^-$, and $(Na^+ \cdot e^-)_2$ also occur, as deduced from light absorption and ESR spectra of these solutions.

The solubility of alkali metals in some aliphatic ethers such as tetrahydrofuran, dimethoxyethane, and dioxane is three to five orders of magnitude lower than that in ammonia [20–22]. Like the solutions in ammonia and in amines, these solutions are blue; however, they are diamagnetic, probably because of the formation of higher ion pairs or spin-compensated electron pairs. Above 0 °C these solutions become colorless.

Solutions of alkali metals in water and in alcohols cannot be obtained, owing to the fast reaction of the solvated electrons that are probably formed during the dissolution process. However, evidence of the formation of electrons on dissolution of alkali metals in water is provided by the chemical behavior of dissolved nitrous oxide [23], a specific reagent for dissolved electrons ($N_2O + e^- + H_2O \rightarrow N_2 + OH + OH^-$). Attempts to confirm the observation [24] that supercooled water-alcohol mixtures turn blue when metallic sodium is added have been unsuccessful.

However, it is possible to obtain condensates that are blue owing to solvated electrons by condensation of water or alcohol vapor together with alkali metal vapor on a cold surface at 70 °K [25–26]. Solvated electrons can be produced in solid ammonia in the same way [27], whereas liquid metal-ammonia solutions separate on cooling into solid metal and solid ammonia [28].

2.2. Radiolytic Processes

Many radiation-chemical reactions in water, alcohols, and other polar solvents proceed *via* solvated electrons (which are formed after thermalization of the high-energy electrons produced by the Compton effect, the photoelectric effect, and by electron impact) [1, 2, 29–32], *e.g.* in accordance with,

$$H_2O \rightarrow H_2O^+ + e^- \qquad (3)$$

in which the relaxation time of solvation is less than 5×10^{-10} sec [32a]). The radiolytic yield on irradiation of aqueous solutions with X-rays or with electrons is 2.5 electrons per 100 eV of energy absorbed [33a]. It follows that the absorption of 1 rad (1 rad = 6.25×10^{13} eV of energy absorbed per g of irradiated substance) is sufficient for the formation of 1.56×10^{12} electrons per ml of aqueous solution.

If, by means of pulse techniques, this dose is supplied in an interval of time that is short (< 10 μsec) compared with the lifetime of the solvated electrons, one obtains an initial electron concentration of 2.6×10^{-9} M. Doses of more than 10^4 rad can be produced within a few μsec by pulsed operation of electron accelerators, so that the dissolved electrons formed can be detected by fast-recording optical methods and their reactions can be followed kinetically. A schematic representation of an arrangement suitable for the production of solvated electrons by pulse radiolysis and for their optical detection is given in Fig. 2.

The doses obtainable with continuous radiation sources (irradiation times > lifetime of dissolved electrons) are much smaller because of the strong heating effect, so that the electron concentrations attainable are also much lower (with an arrangement of favorable geometry, a 15000 curie

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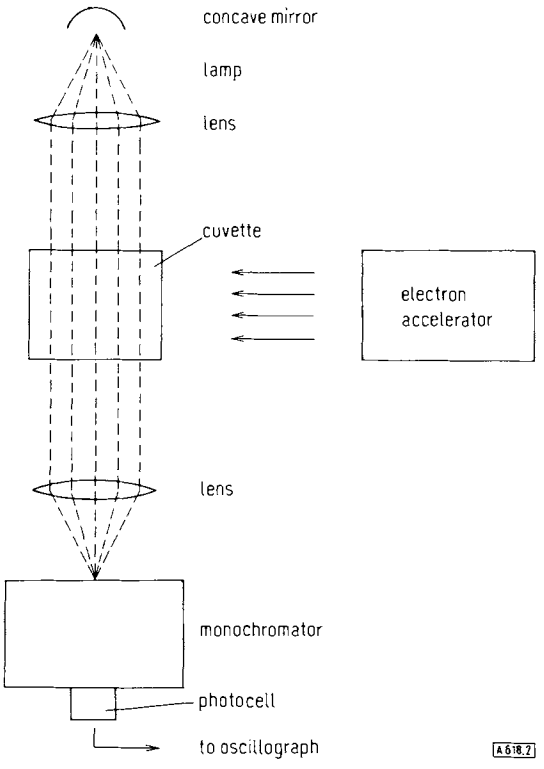

Fig. 2. Arrangement for the production of solvated electrons by pulse radiolysis with fast electrons. The solvated electrons are detected with a quick-response photocell, which records the change in the optical density of the irradiated solution in the red part of the spectrum.

^{60}Co γ source produces, in pure water, a stationary electron concentration of 10^{-8} M [34]).

The secondary reactions of the electrons are so strongly inhibited in vitrified solvents below 100 °K that the electrons can accumulate during irradiation until the glass turns blue [26, 30, 35–37]. According to recent observations, when large radiation doses are absorbed, *i.e.* at high electron concentrations, the electrons form electron pairs [38] according to eq. (1a).

The vitreous state is essential for the stabilization of electrons in frozen solvents [26, 35–37]; in a crystalline matrix electron can also be detected but the attainable concentrations are much lower [37a].

2.3. Photochemical Processes

Solvated electrons also take part in many photochemical reactions in aqueous and alcoholic solutions [39]. However, the electrons in photochemical reactions, unlike those in radiolytic reactions, are formed, not by ionization of the solvent, but by ionization of photochemically active solutes (*e.g.* Hal^- [40–42], OH^- [40–42], $[Fe(CN)_6]^{3-}$ [42,43], SO_4^{2-}, CO_3^{2-} [43a], and many aromatic compounds having electron-donating groups [44]).

Within wide limits, the yield of electrons produced in this way is proportional to the intensity of the light used and to the concentration of the photochemically active solutes. The yield increases with rising temperature [39], suggesting that the electron is emitted thermally from the excited state, *e.g.*

$$I^- \underset{}{\overset{h\nu}{\rightleftharpoons}} I^{*-} \xrightarrow{\text{therm.}} I + e^- \qquad (4)$$

As a result of solvation, the energies involved are changed in such a way that the emission of electrons often requires less energy in solution than in the gas phase.

The UV illumination of metals, *e.g.* mercury, in aqueous solutions leads to the formation of solvated electrons which can be traced by the photocurrent [44a,44b].

2.4. Dissociation of Hydrogen

The pH-dependence of the chemical behavior of dissolved electrons and of dissolved hydrogen atoms in water [45–49] shows that the equilibrium

$$H \rightleftharpoons H^+ + e^- \qquad (5)$$

is established between the two particles; this corresponds to an acid-base equilibrium with the hydrogen atom as the acid and the solvated electron as the base. The dissociation constant is approximately 10^{-10} mole/l [50, 51]. In alkaline solution the hydrogen atoms are completely dissociated:

$$H + OH^- \rightarrow H_2O + e^- \qquad (6a)$$

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The corresponding reaction of fluoride ions

$$H + F^- \rightarrow HF + e^- \qquad (6b)$$

also yields solvated electrons [51a].

Not only hydrogen atoms, but also hydrogen molecules, can dissociate in the presence of strong bases to give solvated electrons [52, 53].

The reaction in liquid ammonia,

$$1/2\ H_2 + NH_2^- \rightleftharpoons NH_3 + e^- \qquad (7)$$

which is very fast, has an equilibrium constant of 2×10^{-5} $(mole/l)^{1/2}$. At constant hydrogen concentration, the equilibrium is displaced to the right with rising temperature and to the left with rising pressure (Fig. 3).

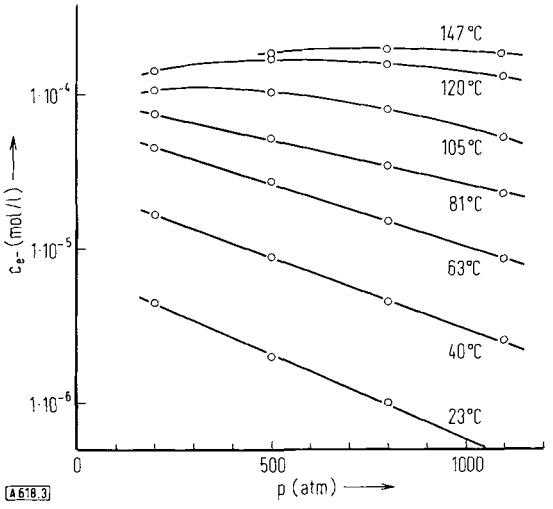

Fig. 3. Pressure-dependence and temperature-dependence of the equilibrium concentration of the solvated electrons in a 0.23 M solution of potassium amide in liquid ammonia saturated with 100 atm of hydrogen [53].

The heat of reaction as calculated from the temperature-dependence of the equilibrium constant is 12–16 kcal/mole, while the pressure-dependence gives a value of 64 ± 3 ml/mole for the volume increase associated with the reaction [53].

The equilibrium reaction (7) permits the investigation of dissolved electrons at extremely low concentrations even at high temperatures (up to the supercritical state of ammonia [53]), at which the electrons are normally no longer stable owing to reactions with the solvent or with impurities.

2.5. Electrolysis

It was observed some 70 years ago [54] that when solutions of alkali metal salts in ammonia are electrolyzed they attain the blue color of solvated electrons at the cathode. The thermodynamically favored formation of hydrogen at the cathode is completely suppressed because of the high overvoltage. The reaction inhibition leading to the hydrogen overvoltage may be due to the slow reaction of dissolved electrons with ammonia.

Electrolysis of aqueous solutions of alkali metal salts probably also results initially in the formation of solvated electrons, but these have not yet been definitely detected, owing to fast secondary reaction with water. Indication of the electrolytic production of solvated electrons is provided from the presure dependence of the discharge current of a hydrogen electrode at constant overvoltage [54a]. The reduction behavior of dissolved nitrous oxide on electrolysis [23] and the change in the light absorption at the cathode [55] also indicate the intermediate formation of dissolved electrons. Definite spectroscopic detection should be possible with the aid of pulse electrolysis (discharge of a highly charged condenser through an electrolyte solution having a low ohmic resistance), in which high concentrations of dissolved electrons should be present for short periods.

3. Physical Properties

3.1. Apparent Molar Volume

The cavity model mentioned in the introduction is based mainly on the observation that solutions of metals in ammonia occupy a volume greater than the sum of the volumes of the pure components, *i.e.* that the volume of the metals is greater in the dissolved state than in the solid state [56–60]. For example, the apparent molar volume of sodium at −33 °C and at concentrations between 0.05 M (at lower concentrations the density measurements are too inaccurate) and 0.5 M is 61 ± 1 ml/mole (Fig. 4), whereas the molar volume of solid sodium is 23 ml/mole.

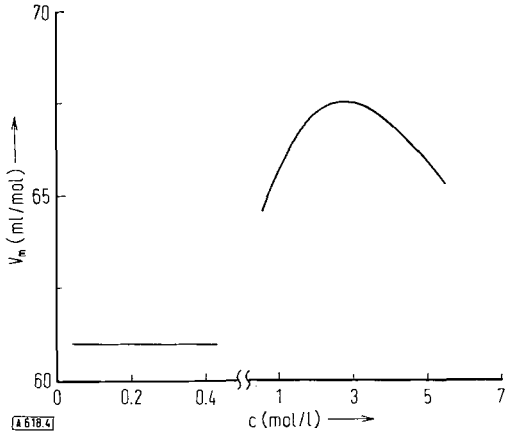

Fig. 4. Apparent molar volume (V_m) of sodium dissolved in liquid ammonia as a function of concentration at −33 °C [56–60].

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This increase in the apparent molar volume must be due to the special state of the electrons in solution, since positive volume effects of this order of magnitude are not found in solutions of other substances; on the contrary, the volume frequently decreases in the case of ionic solutes because of electrostriction.

The volume occupied by the dissolved electrons as calculated from the apparent molar volume of dissolved sodium, taking into account the molar volume of the sodium ions and the electrostriction effects due to these ions (which cannot be determined directly by experiment), is 65 to 95 ml/mole [5, 14a, 61]. This value, however, is valid only for electron pairs, since the density measurements, on which this calculation was based, were carried out on relatively concentrated solutions in which the electrons are mainly in the spin-compensated state.

Values found from density measurements for the volume of electrons in more dilute solutions, in which unpaired electrons predominate, are inconsistent (the molar volume of dissolved sodium, according to *Ogg* [10], is 700 ml/mole; according to *Evers* [59] it passes through a minimum value of 50 ml/mole at 0.02 M; according to *Gunn* [60], the value is 60 ml/mole, and is independent of the concentration).

However, the volume can be estimated indirectly from the volume change associated with the equilibrium reaction (7) between hydrogen and electrons (concentration $< 10^{-4}$ M), which can be calculated from the pressure-dependence of the equilibrium constant [53]. From this volume change and the molar volumes of the other substances taking part in the reaction, the volume occupied by the unpaired electrons at −33 °C is found to be 84 ± 15 ml/mole.

According to these measurements, the electrons in the unpaired state have the same volume as the spin-paired electrons. This is supported by the observation, based on magnetic measurements, that the equilibrium between unpaired and paired electrons is practically independent of pressure [62]. On the other hand, electrons in the metallic state have a greater volume, as is shown not only by density measurements on metallic solutions [56–58] (Fig. 4), but also by the displacement of the equilibrium (1b) toward the nonmetallic state by pressure. This displacement is revealed by the decrease in the electric conductivity of concentrated metal solutions [63] and by the shift of the miscibility gap of these solutions under the influence of pressure [19] (Fig. 1).

The value of 65 to 95 ml/mole for the volume of electrons dissolved in ammonia, which corresponds to 110 to 160 Å^3/electron, naturally has nothing to do with the size of the electrons. It simply indicates the loosening of the structure of ammonia by the electron, which is interpreted in the cavity model by displacement of the ammonia out of reach of the short-range forces of the electron. The average radius of the cavity as given by the above volume is 2.95 to 3.40 Å. *Jortner*'s theoretical treatment [14] of the solvated electron by the cavity model leads, in conjunction with optical measurements, to similar values. As is also shown by optical measurements, an increase in pressure leads to compression of the cavity and a rise in temperature to expansion of the cavity [64].

No reliable data can be given for the size of the electron cavities in water and in alcohols, since solutions of sufficiently high concentrations for density measurements cannot be prepared. Optical measurements indicate that the cavities in these systems are smaller than those in ammonia.

The observation that solvated electrons can readily be obtained radiolytically in vitreous frozen solvents, but only to a small extent in crystalline frozen solvents [26, 35–37a], also indicates that space is required for the stabilization of the electrons. The regular structure of the crystals does not provide cavities of sufficient size, nor can they be created by the electrons owing to the immobility of the structural units of the crystal. Amorphous glasses, on the other hand, already contain enough vacancies to accommodate electrons, and the presence of these vacancies may be favored by the addition of electrolytes.

3.2. Light Absorption

Dilute solutions of the alkali metals in ammonia and its derivatives, in some ethers, and in vitreous frozen aqueous and alcoholic solutions are blue because of their absorption of light in the red part of the spectrum. Similar colors are seen in metal-free deep-frozen water and alcohol glasses on irradiation with X-rays or with electrons. Irradiation of liquid water, alcohol, ammonia, *etc.* leads to a similar, though transient, blue color. The obvious explanation for the blue color in all these systems is the absorption of light by dissolved electrons.

As can be seen from Figure 5 for water [31, 34, 65–68] (on irradiation with electrons) and ammonia [69–73] (with low concentrations of dissolved alkali metals) and from Table 1 for a number of other solvents, the absorption spectra are found to exhibit certain characteristic features. The spectrum of dissolved electrons consists of a single asymmetric absorption region extending from the blue to the near infrared region, with a half-width of *ca.* 0.5 to 1 eV. The area under the absorption curve yields an oscillator strength of nearly unity. The position and height of the absorption maximum depend on the solvent.

The absorption maximum occurs at lower energies for ammonia and its derivatives than for water and alcohols. Mixed

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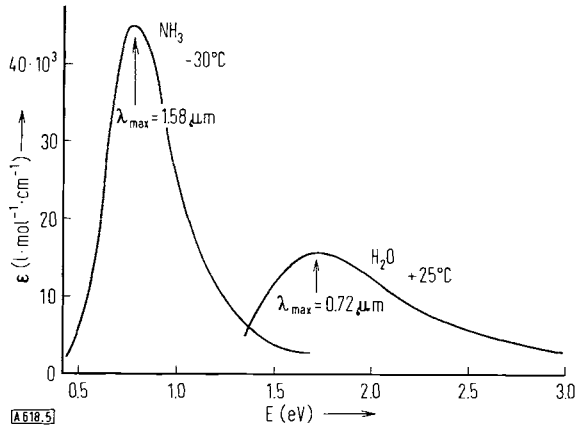

Fig. 5. Absorption spectrum of solvated electrons in liquid ammonia (dilute solutions of alkali metals) [69—73] and in water (radiolysis with electron beams) [34, 65—68]; ε = extinction coefficient.

solvents, *e.g.* water-ammonia, exhibit, not the two absorption maxima characteristic of the two solvents, but only one maximum in an intermediate position, this position depending on the composition of the solvent [31, 70, 71, 77]. The absorption maximum is displaced toward higher energies by deuteration [35, 78, 79] and by the addition of electrolytes [73, 80], as well as by an increase in pressure or by a decrease in temperature.

In solutions of metals in ammonia or in amines, an increase in concentration leads to a small displacement of the absorption maximum toward lower energies [72, 73]; in the case of the amines, this is accompanied by the appearance of further maxima in the higher energy range, the positions and heights of which depend on the metal [70, 71, 74, 81, 82]. The displacement is attributed to the formation of electron pairs, which absorb at a longer wavelength, and the new maxima to the formation of ion pairs. The metallic solutions of high concentration are highly reflecting [83] to light of the infrared to red region of the spectrum, thereby appearing bronze-colored. The high reflectivity gives support to the contention that free electrons are present in the solutions.

The absorption of the solvated electron, like that of F centers, is interpreted as being due to a $1s \rightarrow 2p$ transition of a caged electron [14]; the transition energy is a function of the size of the cavity and of the potential that acts on the electron. With the simplified assumption of a square-well potential, the transition energy is inversely proportional to the square of the cavity radius R:

$$E_{2p} - E_{1s} = h\nu \approx R^{-2} \qquad (8)$$

This relationship is very satisfactorily obeyed in F centers, in which the size of the lattice vacancies occupied by the electrons is defined by the lattice parameters [84].

Some of the characteristics of the spectrum of dissolved electrons can be qualitatively explained with the aid of eq. (8). Since no rigid structure and hence no uniform radius can be assumed for the cavity containing the electron, no sharp spectral line should be expected according to eq. (8). The fact that the spectrum extends over a wide range of energies is probably due to a wide scatter of the size of the cavities about a preferred mean value. The absorption spectrum of F centers is considerably narrower than that of solvated electrons, since the size of the cavities in the former case varies only with the vibration of the lattice points, whereas the size in the case of solvated electrons is influenced, not only by the vibration, but also by the rotation of the solvent molecules.

According to eq. (8), the displacement of the absorption maximum toward higher energies with increasing

Table 1. Absorption of light by solvated electrons.

Origin of solv. electrons	Solvent	Conditions	Maximum of absorption		Maximum absorption coefficient ($l \cdot mole^{-1}\ cm^{-1}$)	Ref.
			Energy (eV)	Wavelength (µm)		
Dissolved alkali metals	ammonia	+ 150 °C	0.67	1.85	—	[53]
	ammonia	− 50 °C	0.80	1.55	46000	[64]
	ammonia	− 50 °C 1000 atm	0.87	1.43	—	[64]
	ammonia	vitreous frozen, −196 °C	1.08	1.15	—	[27]
	methylamine	− 50 °C	0.93	1.33	—	[70, 71]
	ethylamine	− 50 °C	0.87	1.42	—	[70, 71]
	ethylenediamine	room temp.	0.97	1.28	—	[74]
Radiolysis	water	95 °C	1.51	0.82	15800	[75]
	water	10 °C	1.76	0.70	15800	[75]
	water	vitreous frozen, −196 °C	2.12	0.58	18000	[26, 35, 36]
	methanol	room temp.	1.97	0.63	17000	[76, 77]
	ethanol	room temp.	1.77	0.70	15000	[76, 77]
	propanol	room temp.	1.68	0.74	15000	[76, 77]
	i-propanol	room temp.	1.51	0.82	13000	[76, 77]
	ethylene glycol	room temp.	2.14	0.58	14000	[76, 77]
	glycerin	room temp.	2.34	0.53	—	[77]

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pressures is due to compression of the cavity, and the displacement toward lower energies with rising temperature is due to the thermal expansion of the cavity.

Application of eq. (8) to the position of the absorption maximum in various solvents leads to the conclusion that the size of the cavities depends mainly on the solvating groups $-OH$ or $>NH$ of the solvent, whereas the substituents on these groups (H, CH_3, *etc.*) exert only a small effect. This means that the size of the cavities is independent of the size or bulk of the solvent molecules and of their macroscopic dielectric constants or their surface tension. In solvent mixtures, the cavity size assumes a value intermediate between the values for the pure solvents; this shows that the cavity is formed from the molecules of all the solvent components, *i.e.* that there is no preference for solvation by any one solvent.

The assumption on which eq. (8) is based, *i.e.* that the electrons move in a square-well potential, is an oversimplification. However, a more accurate treatment of the cavity model based on a coulombic potential also predicts that the energy of the optical transition increases with decreasing size of the cavity [14].

3.3. Magnetic Properties

The experimental evidence for the equilibrium (1a) between single electrons and spin-compensated electron pairs is based primarily on the concentration-dependence of the molar paramagnetic susceptibility of dissolved alkali metals in ammonia (Fig. 6) [57,85].

In very dilute solutions, in which the dissolved metal may be assumed to be completely dissociated into metal cations and electrons, the molar susceptibility, χ, is about 1500×10^{-6} cm³/mole at -33 °C; this is the value expected for paramagnetic particles having a magnetic moment $\mu = 1$ Bohr magneton ($\chi = N\mu^2/kT$, N = Avogadro's number). Since the cations are diamagnetic, the paramagnetism must be attributed to the electrons (spin paramagnetism). The molar susceptibility decreases rapidly with increasing concentration (to 50×10^{-6} cm³/mole in 0.5 M solution) because of the formation of spin-paired electron pairs. The temperature-dependence of the molar susceptibility at concentrations up to 0.5 M shows that the dissociation equilibrium $e^{2-} \rightleftharpoons 2\,e^-$ is displaced toward the right with rising temperature, *i.e.* that energy is absorbed during the dissociation (4.5 kcal/mole) [86]. On the other hand, the dissociation equilibrium is not affected by pressure, as is shown by the fact that the magnetic properties are independent of the pressure [62].

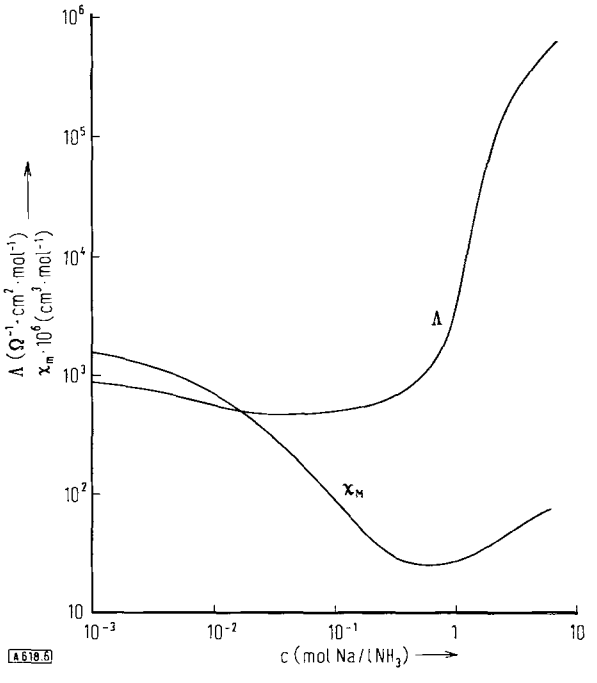

Fig. 6. Magnetic susceptibility χ_m [56, 82] and equivalent electric conductivity Λ [4, 90] of solutions of sodium in liquid ammonia at -33.5 °C as a function of concentration.

The magnetic measurements and their interpretation are confirmed by ESR measurements [87]. The ESR spectrum of the dissolved electrons contains a single, extremely sharp line (half-width 0.05 gauss; g-factor 2.0012). The absence of any hyperfine splitting, and the line sharpness, indicate that there is no strong magnetic interaction between the electron and the solvent molecules of an ordered solvation sheath, but that the solvation sheath forming the cavity must instead be very loosely bound. The spin-compensated electron pairs do not give an ESR signal.

Numerous magnetic measurements have also been carried out on solutions in other amines [82,88–90]. The interpretation of these measurements is complicated because of the additional occurrence of electron-ion pairs in these solutions. It has not yet been possible to carry out measurements on irradiated liquid systems, owing to the short lifetime of the electrons.

Blue condensates of alkali metal vapor and water- or alcohol vapor and irradiated vitreous frozen solvents in which the electrons have accumulated sufficiently to turn the glass blue exhibit essentially the same magnetic behavior [25, 26, 30, 35–37]; the ESR spectra contain several lines, but only one of these can be assigned to the captured electrons, the others probably being due to free radicals formed from the solvent. The signal assigned to the electrons decreases in intensity at the same rate as does the blue color on heating and on exposure to light. When the material is heated, the electrons are taken up by the solvent or by free radicals; on exposure to light, they are probably promoted into a higher energy level, since the blue color and the ESR signal of the electrons return when the exposed sample is carefully heated [36].

Ortho-para hydrogen conversion. Like all paramagnetic particles, dissolved electrons catalyze the ortho-para

[85] *S. Freed* and *N. Sugarman*, J. chem. Physics *11*, 354 (1943).

[86] *J. Kaplan* and *C. Kittel*, J. chem. Physics *21*, 1429 (1953).

[87] *C. A. Hutchinson* and *R. C. Pastor*, J. chem. Physics *21*, 1959 (1953).

[88] *K. D. Vos* and *J. L. Dye*, J. chem. Physics *38*, 2033 (1963).

[89] *K. Bar-Eli* and *T. R. Tuttle*, J. chem. Physics *40*, 2508 (1964).

[90] *J. Dye* and *L. R. Dalton*, J. physic. Chem. *71*, 184 (1967).

hydrogen conversion [91,92]. However, measurements on highly purified, amide-free solutions of sodium in ammonia show that the rate of conversion is several orders of magnitude higher than would be expected from *Wigner*'s theory [93] for paramagnetic particles having a radius of about 3 Å (rate constant of the conversion by paramagnetic particles proportional to r^{-4}; r = collision radius).

3.4. Electric Mobility

Data on the mobility of dissolved electrons can be obtained from conductivity studies of their solutions [4, 94]. The limiting value of the equivalent conductivity of highly dilute solutions of sodium in ammonia is about 1020 Ω^{-1}cm^{2}mole^{-1} at −33 °C (Fig. 6). Taking into account the mobility of the sodium ions (130 Ω^{-1} cm^{2}mole^{-1}), we find that the mobility of the dissolved electrons is about 900 Ω^{-1}cm^{2}mole^{-1} [95]. When the concentration is increased to the range in which electron pairs are formed, the equivalent conductivity of the solutions decreases slightly. Thus the marked decrease in the molar magnetic susceptibility on formation of electron pairs has no parallel in the conductivity behavior; the course of the curve shows that the mobility of the electron pairs is only slightly lower than that of the unpaired electrons, if the slight decrease in conductivity is not entirely due to slight ion-pair formation.

The transition to the metallic state is marked by the strong increase in conductivity above 0.5 M. The equivalent conductivity of a saturated solution of sodium in ammonia is comparable to that of mercury or of pure sodium. Over the entire concentration range, the conductivity increases with rising temperature [94] and decreases with rising pressure [63].

Solutions of metals in amines [96,97] and in ethers [22] have much lower equivalent conductivities, owing to incomplete dissociation. Data on the mobility of the electrons in these solutions are not available.

On pulse radiolysis of aqueous solutions a transient increase in conductivity is observed which may be attributed to the radiolytically generated electrons and the ionic decomposition products of water [98,99]. The mobility of electrons in water at room temperature, as found from the increase in conductivity, taking into account the conductivity component of the ions, is 177 ± 20 Ω^{-1}cm^{2}mole^{-1} [44a,99]. Thus the mobility of electrons in water is only about one fifth of the mobility in ammonia.

If a normal migration mechanism (*i.e.* movement of the charged particle with its solvation sheath through the viscous solvent) is assumed, this difference in the mobilities of dissolved electrons in water and in ammonia could be due to the difference in the viscosities of the two solvents (η_{H_2O} (25 °C) = 0.894 cP; η_{NH_3} (−33 °C) = 0.255 cP) in accordance with the Walden rule $l \sim 1/\eta \cdot r$ (l = mobility, r = radius of the charged particle, η = viscosity of the solvent). However, since the mobility of charged particles is also inversely proportional to their size, the mobility of the large solvated electron should be lower than that of normal ions, whereas the mobility of electrons in water and ammonia is two to five times as great (for comparison, the mobilities of Na^+ and Cl^- ions in water at 25 °C are 50 and 76 resp.; in ammonia at −33 °C they are 130 and 179 Ω^{-1}cm^{2}mole^{-1} resp.). It therefore seems unlikely that the electrons migrate exclusively by a normal mechanism.

In view of the small mass of the electron, tunneling may be a possible explanation for the high mobility [100]. Thus it is conceivable that the electron "jumps" from its cavity into an adjacent solvent zone in which a chance arrangement of the molecules provides the conditions required for the accommodation of an electron. The anomalous thermoelectric properties [101] of dilute solutions of metals in ammonia (direction of heat transport opposite to that of the electron movement, owing to the polarization energy released on the collapse of an abandoned cavity) support the assumption that tunneling is involved.

The effects of temperature and pressure on the conductivity of dilute solutions can be interpreted in this context by a change in the probability of tunneling due to dilatation or compression of the solvent.

Further information about the mechanism of conduction by dissolved electrons should be provided by transport measurements on dilute solutions of metals [102,103] and by conductivity measurements on deep-frozen condensates of metal vapor and water- or ammonia vapor, in which the contribution of the metal ions and the ions of the solvent itself to the conductivity should be negligible.

3.5. Thermodynamic Quantities

The thermodynamic data for dissolved electrons are not known very accurately, since they are generally obtainable only indirectly, *e.g. via* cyclic processes, and their determination involves more or less arbitrary assumptions. They can therefore be used only with certain reservations for further calculations.

[91] *Y. Claeys, C. F. Baes,* and *W. K. Wilmarth,* J. chem. Physics *16*, 425 (1948).

[92] *U. Schindewolf,* unpublished.

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[94] *C. A. Kraus,* J. Amer. chem. Soc. *43*, 749 (1921); *C. A. Kraus* and *W. W. Lucasse,* J. Amer. chem. Soc. *45*, 2551 (1923).

[95] *E. C. Evers* and *P. W. Frank,* J. chem. Physics *30*, 61 (1959).

[96] *A. J. Panson* and *E. C. Evers,* J. Amer. chem. Soc. *79*, 5118 (1957); *82*, 4468 (1960).

[97] *R. R. Dewald* and *L. J. Dye,* J. physic. Chem. *68*, 128 (1964).

[98] *J. W. Boag, G. E. Adams,* and *E. J. Hart* in *L. Augstein, R. Mason,* and *B. Rosenberg*: Physical Processes in Radiation Biology. Academic Press, New York 1964.

[99] *K. H. Schmidt* and *W. L. Buck,* Science (Washington) *151*, 70 (1966).

[100] *E. Arnold* and *A. Patterson* [7], p. 160.

[101] *J. F. Dewald* and *G. Lepoutre,* J. Amer. chem. Soc. *76*, 3369 (1954); *78*, 2956 (1956).

[102] *C. A. Kraus,* J. Amer. chem. Soc. *36*, 864 (1914).

[103] *J. L. Dye* [7], p. 137.

Standard potential. The standard potential of dissolved electrons E_e^0 in ammonia, with respect to the standard hydrogen electrode, was determined polarographically[104], and is -1.95 ± 0.1 V at 25 °C (overall reaction $H^+ + e^- \rightarrow {}^1/_2\,H_2$). It is more positive than the standard potentials E_M^0 of metals (overall reaction $H^+ + M \rightarrow 1/2\,H_2 + M^+$) that dissolve in ammonia to form solvated electrons (*e.g.* $E_{Li}^0 = -2.24$ V, $E_K^0 = -1.98$ V[105]). The dissolution of these metals ($M \rightarrow M^+ + e^-$) is associated with a loss of free energy ($E_M^0 - E_e^0 < 0$). Metals having a more positive standard potential (*e.g.* Mg; $E_{Mg}^0 = -1.74$ V[105]) have very low solubilities or are insoluble since the dissolution process is accompanied by an increase of free energy ($E_M^0 - E_e^0 > 0$). However, if the required free energy is supplied from an external source, *e.g.* in the form of electric energy, then Mg, Be, and Al[106] as well as Sm, La, and Ce[107] also dissolve with formation of dissolved electrons (anodic dissolution).

For aqueous solutions, the standard potential is given by the sum of the free enthalpies of the various reaction steps[108]

$(e^-)_s + (H_2O)_l \rightarrow$	$(H)_s + (OH^-)_s$	$\Delta G° =$	8.4 kcal/mole
$(H)_s \rightarrow$	$1/2\,(H_2)_g$	$\Delta G° =$	−53.1 kcal/mole
$(H^+)_s + (OH^-)_s \rightarrow$	$(H_2O)_l$	$\Delta G° =$	−19.1 kcal/mole
$(e^-)_s + (H^+)_s \rightarrow$	$1/2\,(H_2)_g$	$\Delta G° =$	−63.8 kcal/mole

(the subscripts g, s, and l denote the gaseous, solvated, and liquid states). The free enthalpy of the first reaction is found from the equilibrium constant which is calculated from the ratio of the rate constants of the forward[50] and reverse[51] reactions ($k_{forw.} = 16$ l·mole^{-1}·sec^{-1}, $k_{rev} = 1.8 \times 10^7$ l·mole^{-1}·sec^{-1}). The free enthalpy of the second reaction consists of the free enthalpy of dissociation of hydrogen and the free enthalpy of solvation of hydrogen atoms[109]. The free enthalpy of the third reaction is given by the dissociation equilibrium of water. The value found from the free enthalpy of the overall reaction for the standard potential of electrons dissolved in water at 25 °C is −2.78 V.

Since the standard potential of electrons in aqueous solutions is more positive than those of most of the alkali and alkaline earth metals, the formation of solvated electrons during the dissolution of these metals in water is possible, at least thermodynamically.

Heat of solvation. The heat of solvation of electrons, *i.e.* the energy liberated when an electron passes from a vacuum into a solution, can be calculated for ammonia by means of a Born-Haber cycle applied to solutions of metals in liquid ammonia ($(M)_{solid} \rightarrow (M)_g \rightarrow (M^+)_g + (e^-)_g \rightarrow (M^+)_s + (e^-)_s \rightarrow (M)_{solid}$) involving the heat of sublimation and the heat of ionization of the metal, the estimated heat of solvation of the metal ions, and the experimental heat of solution of the metal[14a]. The heat of solvation of electrons in ammonia is found from the data for the alkali and alkaline earth metals to be $\Delta H_{e^-} = -36 \pm 4$ kcal/mole. In agreement with this, a value of −34 kcal/mole is obtained from a similar cycle including the exothermic reaction[110]

$$(e^-)_s + (NH_4^+)_s \rightarrow (NH_3)_l + 1/2\,(H_2)_g \quad \Delta H = -43 \text{ kcal/mole}$$

as well as the dissociation and ionization of hydrogen and the solvation of the protons (heat of solvation ≈ −285 kcal/mole). A value of $\Delta H_{e^-} = -39$ kcal/mole is found by another route for the heat of solvation of electrons in water.

The heats of solvation of electrons in water and in ammonia are considerably lower than those of simple monovalent negative ions. This is due to the low charge density of electrons in the solvated state. The empirical relationship between the heat of solvation and the radius of simple negatively charged ions in water gives a radius of about 3 Å for the mean charge distribution of the electron[109].

The standard potential and the heat of solvation of electrons can be used to determine the equilibrium constant and the heat of reaction for certain reactions. Thus the standard potential of electrons in ammonia and the self-dissociation constant of ammonia give a value of 4×10^{-6} (mole/l)$^{1/2}$ for the equilibrium constant of reaction (7) at 25 °C. Though this is approximately three orders of magnitude lower than the experimental value[52,53], one could scarcely expect a better agreement in view of the uncertainty in the standard potential of electrons and in the dissociation constant of liquid ammonia (uncertain by a factor of 100). The heat of reaction is found by calculation to be $\Delta H = 17$ kcal/mole, in fairly good agreement with experiment.

The equilibrium constant found in this way for the corresponding reaction in water

$$1/2\,H_2 + OH^- \rightarrow H_2O + e^- \qquad (9)$$

is so small that it seems pointless to try to detect the electrons formed at room temperature. However, since the heat of reaction is probably very high, *i.e.* the equilibrium is displaced to the right with rising temperature, it may be possible to obtain and to study solvated electrons in equilibrium with hydrogen at elevated temperatures even in water[*].

The reverse reactions (7) and (9) formally describe the exothermic decomposition reactions of electrons (at low concentrations) with the pure solvents. The reaction is relatively fast in water, but extremely slow in ammonia. This difference in behavior of the electrons in the two solvents is due to the different enthalpies of the respective endothermic first reaction steps leading to atomic hydrogen.

$$(e^-)_s + (NH_3)_l \rightarrow (H)_s + (NH_2^-)_s \quad \Delta H = 33 \text{ kcal/mole} \qquad (10)$$

$$(e^-)_s + (H_2O)_l \rightarrow (H)_s + (OH^-)_s \quad \Delta H = 6 \text{ kcal/mole} \qquad (11)$$

The heat of reaction in ammonia is so high that the reaction cannot proceed at, or below, room temperature.

4. Models

The theoretical treatment of the solvated electron is not strictly possible unless its structure is known. The treatments published so far[14,111,112] are based on

[104] *H. A. Laitinen* and *C. J. Nyman*, J. Amer. chem. Soc. *70*, 2241 (1948).

[105] *H. Strehlow* in *J. J. Lagowski*: The Chemistry of Non-Aqueous Solvents, Vol. 1 of [8].

[106] *A. D. McElroy, J. Kleinberg*, and *A. W. Davidson*, J. Amer. chem. Soc. *72*, 5178 (1950).

[107] *W. Rüdorff*, Chimia *19*, 489 (1965).

[108] *J. H. Baxendale*, Radiat. Res. Suppl. *4*, 139 (1964).

[109] *J. Jortner* and *R. M. Noyes*, J. physic. Chem. *70*, 770 (1966).

[110] *L. V. Coulter*, J. physic. Chem. *57*, 533 (1953).

[*] Note added in proof: Preliminary experiments up to 300 °C gave no indication for reaction (9).

[111] *M. Natori* and *T. Watanabe*, J. physic. Soc. Japan *21*, 1573 (1966).

[112] *L. Raff* and *H. A. Pohl* [1], p. 173.

various, sometimes contradictory assumptions regarding the structure of the solvation sheath; however, they all include the assumption that the electron is not strongly localized, but moves within a relatively large volume.

Jortner's model [14], which was mentioned earlier, will now be described in somewhat greater detail, since it copes well with the diffuse structure deduced for the solvation sheath on the basis of experimental results. According to this model the electron is bound in the polarization field due to the solvent molecules, which have been oriented and polarized by the field of the electron.

By means of the SCF theory the energy of the electron in the 1s ground state and in the optically excited 2p state, and hence the energy of the transition responsible for the absorption of light ($h\nu = E_{2p} - E_{1s}$) can be calculated as a function of the diameter of the cavity. This relates two quantities that can be determined experimentally, at least in the case of liquid ammonia, so that the theory can be checked. Alternatively, if the energy of the optical transition in other solvents is known, the theory can be used to obtain a rough estimate of the size of the cavities occupied by the electrons.

According to the rules of quantum mechanics, the total energy of the system consisting of a dissolved electron and the polarized dielectric (in relation to the energy of the resting electron in a vacuum and the unpolarized dielectric) is equal to the expectation value of the Hamiltonian operator of the Schrödinger equation given by the electronic wave

$$E_i = \int \psi_i^* \left[-\frac{h^2}{8\pi^2 m} \nabla^2 + \frac{e}{2}\left(1 - \frac{1}{D}\right) f_i \right] \psi_i \, d\tau \qquad (12)$$

function ψ. (The subscript i refers to the i-th state of the electron; D = static dielectric constant of the solvent, h = Planck's constant, m = mass of the electron, e = electronic charge, ∇^2 = Laplace operator; the integration is to be carried out over the entire space.) The potential f_i due to the diffuse electronic charge without the dielectric is given by the Poisson equation

$$\nabla^2 f_i = 4\pi e |\psi_i|^2 \qquad (13)$$

The polarization field acting on the electron as a result of the polarization of the dielectric is $(1 - 1/D) f_i$.

The potential f_i and the wave function ψ_i are consistent with each other only if ψ_i is an eigenfunction of the Schrödinger equation formed with $f_i(\psi_i)$. E_i then assumes a minimum value.

A hydrogen-like, one-parameter wave function

$$\psi_{1s} = \left(\frac{\lambda^3}{\pi}\right)^{1/2} e^{-\lambda r} \qquad (14)$$

is assumed for the ground state (1s state) of the electron. The parameter λ (dimension cm^{-1}) is the reciprocal of the radius of maximum charge density. Equations (13) and (14) lead to the potential f_{1s}

$$f_{1s} = -\frac{e}{r} + \frac{e(1 + \lambda r)\exp(-2\lambda r)}{r} \qquad (15)$$

For large distances r, f_{1s} is a pure Coulomb potential, but it shows positive deviations at small distances. The potential is assumed to be constant inside the cavity ($f_{r < R} = f_R$, R = radius of the cavity).

Insertion of (14) and (15) in (12) gives the energy of the 1s electron as a function of the size of the cavity and the parameter λ. The value of λ to be used is found from $(dE/d\lambda)_R = 0$ by the variation method.

The energy of the excited 2p state is calculated in the same way with the aid of the assumed wave function:

$$\psi_{2p} = \left(\frac{\mu^5}{\pi}\right)^{1/2} r\, e^{-\mu r} \cos\Theta$$

In this case, however, it must be remembered that the excited state is not an equilibrium state, since the orientation polarization of the solvent cannot adapt itself to the changed charge distribution of the 2p state on excitation (Franck-Condon principle): the orientation polarization of the 2p state is therefore determined by the charge distribution of the electron in the ground state. Electronic polarization, of course, follows the change in the charge distribution on excitation.

The calculations were carried out for two values of the radius of the cavities, *i.e.* for the value $R = 3.3$ Å estimated from density measurements on solutions of metals in liquid ammonia and for the limiting value $R = 0$ Å. The transition energies found for these two cases from the macroscopic data for water (dielectric constant and refractive index) are 0.93 and 1.35 eV. As expected, the transition energy increases with decreasing cavity size, though not so rapidly as is suggested by eq. (8) on the assumption of a square-well potential. In agreement with experiment, calculations of the oscillator strength in both cases give values of the order of 1, as is to be expected for allowed transitions.

Since the energies found in this way depend only slightly on the macroscopic data for the solvent (they differ by less than 5% for water and ammonia), they can be compared directly with the transition energies found experimentally in various solvents. The calculated results for ammonia and its derivatives (for $R = 3.3$ Å) agree fairly well with experiment (cf. Table 1). Thus in conjunction with theory, the optical measurements confirm the value found by another route for the cavity size. For water and alcohols, comparison indicates an infinitesimally small cavity for the dissolved electrons (but according to the theory, the electron is still distributed over a finite volume; the radius of maximum charge density $1/\lambda$ is about 1.7 Å for $R = 0$ and about 2.6 Å for $R = 3.3$ Å).

It is probably an exaggeration to say that the cavities in water and in alcohols are infinitesimally small. However, this result cannot be refuted so long as the volume occupied by the solvated electrons in these solvents cannot be measured either directly or indirectly (determination of the densities of suitable solutions, the pressure-dependence of the position of the absorption maximum, the pressure-dependence of the position of the equilibrium or of the rate of suitable reactions). However, it is necessary to refute the assumption that the infinitesimally small cavity in water is due to the surface tension of water, which is high in comparison with that of liquid ammonia, and which must be overcome in the formation of the cavity. Thus in spite of the lower or even negligible surface tension, the cavity sizes found from optical measurements are approximately the same in methanol [76, 77] as in water, and the same in supercritical ammonia [53] as in liquid ammonia.

Jortner's cavity model, in which the solvation sheath has a diffuse structure, contrasts with two other models, which involve distinct short-range order. *Natori* and *Watanabe* [111] assume a tetrahedral structure of the cavities in water, which would follow from the regular structure of ice if a central water molecule were replaced by an electron, the four water molecules at the vertices of the tetrahedron being arranged with one hydrogen atom of each pointing toward the center. In the model proposed by *Raff* and *Pohl* [112], two oppositely oriented solvent dipoles, in which the positive pole is a hydrogen atom, are held together by the charge of the electron situated between them, *e.g.*

$H-O-H\cdots e^-\cdots H-O-H$

This structure can be described more simply by a hydrogen molecule-ion interacting with two anions of the solvent, *i.e.* in this case OH^- ions:

$HO^-\cdots H_2^+\cdots OH^-$

The transition energies calculated from both of these models roughly agree with those found experimentally. However, the assumed short-range order should give a multiline ESR spectrum, owing to the magnetic interaction with the protons bound in a fixed geometric arrangement, whereas such a spectrum has not yet been observed (except in the case of alkali metal-water condensates at −140 °C)[25,113]. Moreover, these two models cannot explain the broad absorption spectrum, which can be readily interpreted in *Jortner*'s model as being due to a broad radius distribution.

5. Chemical Properties

As is to be expected from their strongly negative redox potential, solvated electrons can react with many substances in solution. The reactions are generally so fast that they can be followed only with the aid of special methods (*e.g.* pulse radiolysis or flash photolysis to produce the electrons and flash spectroscopy to detect them). Though the rate constants have been measured for most of the reactions studied[114], the primary products are still largely uncertain, so that conclusions regarding the reaction mechanism can be reached in only a few cases.

Some characteristics of the reactions of solvated electrons are illustrated by the following examples.

Highly purified solvents. The instability of solvated electrons in water can be attributed to the following reactions, all of which yield hydrogen:

	Rate constant ($l \cdot mole^{-1} \cdot sec^{-1}$)	Activation energy ($kcal \cdot mole^{-1}$)	
$e^- + H_2O \rightarrow H + OH^-$	16 [50]	—	(16)
$2\,e^- + 2\,H_2O \rightarrow H_2 + 2\,OH^-$	4.5×10^9 [49, 115]	5.2 [75]	(17)
$e^- + H^+ \rightarrow H$	2.1×10^{10} [65, 115, 116]	3.2 [117, 118]	(18)

(The electrons formed *e.g.* by radiolysis also react with the other primary and secondary products OH, O^-, H_2O_2, *etc.*) Reaction (18) predominates in acidic to neutral solutions. In alkaline solution, the main reaction at low electron concentrations is reaction (16), which is first order with respect to the electrons, while the second-order reaction (17) becomes predominant at higher electron concentrations. Molecular hydrogen is formed directly only in reaction (17).

Reaction (16), which has also been studied in aqueous ethylenediamine containing dissolved alkali metal[119], is the slowest reaction of electrons in water that has been studied so far. The rate constant given may be only an upper limit, since contamination with reactive compounds even at a concentration of 10^{-8} M interferes with the kinetic measurements. For the same reason, 4.55 $kcal \cdot mole^{-1}$ [117] is probably only a lower limit for the activation energy of this reaction, particularly since the reaction enthalpy is about 6 $kcal \cdot mole^{-1}$ according to eq. (11).

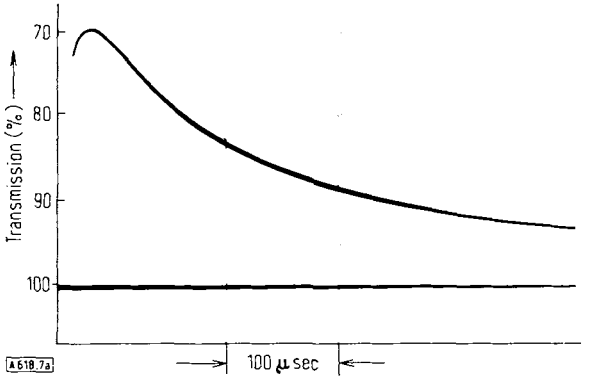

Fig. 7a. Change in the light transmission at 0.7 µ as a result of the formation and reaction of solvated electrons in heavy water (0.01 M NaOD, saturated with D_2 at 1 atm) on pulse radiolysis with fast electrons (10 MeV, 0.5 A, 5 µsec; optical path 6 cm) [79]. Owing to secondary processes, the maximum concentration of solvated electrons is reached only 50 µsec after the end of the pulse.

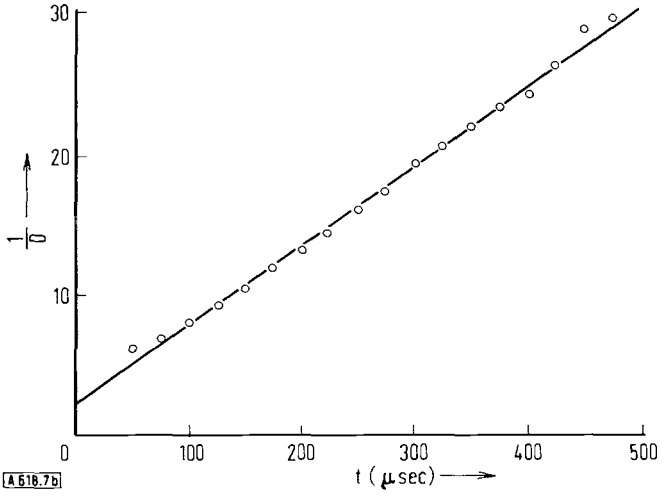

Fig. 7b. A plot of the reciprocal of the optical density *D* from Fig. 7a against time gives a straight line (second-order reaction according to eq. (17)), whose slope gives the rate constant (5.4×10^9 $l \cdot mole \cdot sec^{-1}$) and whose intercept on the ordinate gives the total concentration of the solvated electrons formed (6×10^{-6} M).

Few details are available as yet concerning the reactions corresponding to equations (16) to (18) in other solvents[25,119a]. In the absence of H^+ ions, the life-

[113] *F. Fueki*, J. chem. Physics *45*, 183 (1966).

[114] Reviews on the reactions studied, with rate constants: *M. Anbar* and *P. Neta*, Int. J. appl. Radiat. Isotopes *16*, 227 (1965); *18*, 493 (1967); *M. Anbar* [1], p. 55; *E. J. Hart* [2].

[115] *S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani*, and *J. K. Thomas*, J. Amer. chem. Soc. *85*, 1375 (1963); Discuss. Faraday Soc. *36*, 193 (1963).

[116] *L. M. Dorfman* and *I. A. Taub*, J. Amer. chem. Soc. *85*, 2370 (1963).

[117] *J. K. Thomas, S. Gordon*, and *E. J. Hart*, J. physic. Chem. *68*, 1524 (1964).

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[119] *R. R. Dewald, J. L. Dye, M. Eigen*, and *L. de Maeyer*, J. chem. Physics *39*, 2388 (1963).

[119a] *D. M. J. Compton, J. F. Bryant, R. A. Cesena*, and *B. L. Gehman* in *M. Ebert, J. P. Keene, A. J. Swallow*, and *J. H. Baxendale*: Pulse Radiolysis. Academic Press, London 1965.

time of the electrons in solution decreases in the order liquid ammonia, amines, water (lifetime < 1 msec) methanol (< 5 μsec)[120]. Since the volume occupied by the electrons also decreases in this order (cf. Table 1 in conjunction with eq. (8)), the dependence of the lifetime of the electrons on the solvent may be attributed to the solvent-dependence of the cavity size. When an electron reacts with a solvent molecule, the cavity disappears, so that the formation of the activated complex is associated with a decrease in volume, the change in volume increasing with the size of the cavity.

Thus the activation volume, *i.e.* the difference in volume between the activated complex and the starting materials, is much more negative in the reaction of electrons with ammonia than in the reaction with water. The empirically observed[121] and theoretically justifiable linear relationship between the activation volume and the entropy of activation $\Delta S^{\neq}$, which, according to the transition state theory, determines the activation energy E_a along with the rate constant k_r of a chemical reaction

$$k_r = \frac{kT}{h} \cdot e^{\Delta S^{\neq}/R} \cdot e^{-E_a/RT}$$

consequently shows that the stability of the electrons is many orders of magnitude greater in ammonia, and a few orders of magnitude less in alcohols, than in water. The difference in the activation volumes suggests that the reaction in ammonia should be much more strongly accelerated by pressure than the reaction in water[*].

Simple neutral molecules. The reaction of solvated electrons with simple molecules, such as $O_2 \rightarrow O^-$, $I_2 \rightarrow I_2^-$, $CO \rightarrow CHO$, $CO_2 \rightarrow COOH$, $H_2O_2 \rightarrow HO + OH^-$, $N_2O \rightarrow N_2 + OH$, $NO \rightarrow NHO$, $CS_2 \rightarrow CS_2H$, $CCl_4 \rightarrow CCl_3 + Cl^-$, $C(NO_2)_4 \rightarrow C(NO_2)_3 + NO_2^-$, have rate constants $> 10^9$ l·mole^{-1}·sec^{-1} [66, 115, 117, 122, 123]. They are therefore close to the limit of diffusion-controlled reactions. Hydrogen, nitrogen, and the noble gases are inert to solvated electrons.

Cations. All metal cations apart from alkali, alkaline earth, and bivalent rare earth metal ions[66, 117] are reduced by solvated electrons to an oxidation state one unit of charge lower, *e.g.* $Ag^+ \rightarrow Ag$, $Cd^{2+} \rightarrow Cd^+$, $Tm^{3+} \rightarrow Tm^{2+}$. The resulting unstable ions react further. In the series of bivalent metal ions[66] Mn^{2+}, Fe^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cr^{2+}, Cd^{2+} and the trivalent rare earth metal ions[117] Lu^{3+}, Pr^{3+}, La^{3+}, Tb^{3+}, Dy^{3+}, Gd^{3+}, Nd^{3+}, Tm^{3+}, Sm^{3+}, Yb^{3+}, Eu^{3+}, the rate constant increases from 10^8 to 4×10^{10} l·mole^{-1}·sec^{-1}. It is not yet possible to establish any clear relationship between the rates of these reactions and the properties of the ions.

The rate of reaction of metal ions with solvated electrons is sometimes considerably increased by complexing of the metal ions[66, 124]; the promotion of the reaction by the ligands is attributed partly to their ability to capture an electron and pass it on to the central cation, and partly to the change in the electron density of the cation due to complex formation. The effectiveness of ligands for such processes increases in the order OH^-, CN^-, NH_3, H_2O, F^-, Cl^-, and I^- [124].

Anions. Anions with completely filled valence shells, such as F^-, Cl^-, Br^-, I^-, CN^-, CNO^-, CNS^-, N_3^-, and OH^-, do not react with solvated electrons[117]. The following nonmetallic oxo anions are also inert to solvated electrons in their highest oxidation state[117]: $B_4O_7^{2-}$, CO_3^{2-}, HCO_3^-, ClO_4^-, HPO_4^{2-}, PO_4^{3-}, SO_4^{2-}. On the other hand, the oxo anions of metals[117], *e.g.* MnO_4^- and $Cr_2O_7^{2-}$, as well as all the oxo anions of nitrogen, bromine, and chlorine (except ClO_4^-)[117, 124] are highly reactive.

For a number of the above mentioned reactions, the rate constants obtained by pulse radiolysis are confirmed by electrochemical measurements[44a].

Aliphatic compounds. Saturated hydrocarbons, alcohols, amines, ethers, and their fluorine derivatives show little tendency to react with solvated electrons in water ($k < 10^7$ l·mole^{-1}·sec^{-1})[122]. The anions of lower fatty acids and simple hydroxy acids, as well as some of the acids themselves, do not react (formate, acetate, lactate, succinate ions; oxalic, citric, and lactic acids)[122]. Some of these compounds are also stable to solutions of metals in liquid ammonia. Olefins (particularly those with conjugated double bonds), aldehydes, and ketones (but not their hydrates) are mostly very reactive[115, 122, 124, 125].

Halogenated hydrocarbons and fatty acids (except fluorinated compounds) react extremely rapidly with solvated electrons[126]. The reaction rate increases in the order Cl, Br, I derivatives. The reactions result in the removal of halide ions:

$$R{-}X + e^- \rightarrow R\cdot + X^-$$

The reactivity of the halogen substituent is further increased by adjacent electron-attracting substituents; this effect can be very satisfactorily described by the Taft substituent constant σ^* [127], which characterizes the efficiency of the substituents in withdrawing electrons from the halogen through the aliphatic chain (inductive effect). This supports the assumption that the electrons attack at the halogen atom.

Aromatic compounds. In contrast to the saturated aliphatic hydrocarbons, the aromatic hydrocarbons,

[120] *J. J. Myron* and *G. R. Freeman*, Canad. J. Chem. *43*, 381 (1965).

[121] *K. J. Laidler* and *D. T. Y. Chen*, Canad. J. Chem. *37*, 599 (1959); *K. J. Laidler*: Reaction Kinetics. Pergamon Press, London 1963.

[*] Note added in proof: According to preliminary pulse radiolysis experiments under pressures of up to 1000 atm, the activation volume of reaction (17) is negligible.

[122] *E. J. Hart, J. K. Thomas*, and *S. Gordon*, Radiat. Res. Suppl. *4*, 74 (1964).

[123] *K. D. Asmus* and *A. Henglein*, Ber. Bunsenges. physik. Chem. *68*, 348 (1964).

[124] *M. Anbar* and *E. J. Hart*, J. physic. Chem. *69*, 973 (1965).

[125] *E. J. Hart, S. Gordon*, and *J. K. Thomas*, J. physic. Chem. *68*, 1271 (1964).

[126] *M. Anbar* and *E. J. Hart*, J. physic. Chem. *69*, 271 (1965).

[127] *R. W. Taft* in *M. S. Newman*: Steric Effects in Organic Chemistry. Wiley, New York 1956.

owing to their particular electron system, can readily accept an additional electron. This results in the formation of aromatic radical-anions, which are very stable, at least in nonaqueous solutions. They can be prepared in solutions of alkali metals in liquid ammonia [128], amines [129], and ethers [130–132] by the addition of aromatic compounds. The rate of the addition reaction is again appreciable. Rate constants of 1×10^7 to about 5×10^9 l·mole^{-1}·sec^{-1} [125, 126, 133] have been found by pulse radiolysis for the addition of solvated electrons to benzene, naphthalene, anthracene, biphenyl, and terphenyl in aqueous and alcoholic solutions.

As in the halogenated hydrocarbons, substitution in the aromatic ring leads to variation of the reaction rate within wide limits [126] (phenol $k = 4 \times 10^6$, fluorobenzene 6×10^7, chlorobenzene 6×10^8, iodobenzene 4×10^9, nitrobenzene 3×10^{10} l·mole^{-1}·sec^{-1}). This variation of the reactivity of substituted aromatic compounds toward solvated electrons is similar to that shown by the aromatic compounds toward nucleophilic reagents, which can be described by the Hammett σ function [134]. This parallelism suggests that dissolved electrons attack the ring system in exactly the same way as nucleophilic reagents.

The activation energies of about 20 exothermic reactions with rate constants between 10^5 and 10^{11} l·mole^{-1}·sec^{-1} are all about 4 ± 1 kcal/mole [118, 135–137], so that the rates of these reactions, like those of the reactions with the pure solvents, are determined by the change in entropy on formation of the activated complex. This result cannot be generalized until a greater number of slow reactions of electrons have been studied. However, it appears to be of general significance to the reactions of dissolved electrons.

The investigation of reactions of electrons with rate constants $< 10^7$ l·mole^{-1}·sec^{-1} in water is unfortunately very difficult because of the reaction of the electrons with the water molecules. Consequently, further studies should be carried out on substances that react only slowly in liquid ammonia, in which the electrons are stable but in other respects react in the same way as in water.

It can be seen from these examples that the reactions of electrons have been more thoroughly studied, from the kinetic point of view, than those of any other reactive particle. Nevertheless, there is still much ground to be covered before it will be possible to explain the many reactions of electrons on the basis of a single consistent theory. However, it is to be hoped that the evaluation of the kinetic studies, supplemented by investigations in other solvents, will lead to a deeper understanding of the relationship between the structure or electron distribution of molecules and their chemical reactivity.

I am grateful to Prof. Dr. E. W. Becker, Dr. K. W. Böddeker, Dr. R. W. Kessler, Dipl.-Phys. G. Eisenbeiss, and Dozent Dr. D. Schulte-Frohlinde for interesting discussions and valuable advice.

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The Discovery, Isolation, Elucidation of Structure, and Synthesis of Antamanide [1]

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Dedicated to Professor A. Butenandt on the occasion of his 65th birthday

Antamanide is the name we have given to a constituent of the fungus Amanita phalloides. This substance counteracts the lethal action of the Amanita toxins phalloidine and α-amanatine if administered to the white mouse before, or simultaneously with, the poisons. Its concentration in the fungus is, however, so low that the toxic action of the latter predominates. Antamanide is a cyclic decapeptide formed from the L-amino acids alanine, phenylalanine, proline, and valine in the molar ratio 1:4:4:1. The amino-acid sequence was determined by a combination of gas chromatography and mass spectrometry. The structural formula assigned was confirmed by synthesis according to a classic route of peptide chemistry.

1. Discovery

Since the summer of 1962 we have been busy with the investigation of the extremely small amounts of lipophilic components of the constituents of the bulbous leaf fungus, *Amanita phalloides*. By consequential chromatography we were able to obtain two hitherto unknown materials in pure form, phallin B, a toxic component belonging to the phallotoxine family, and a non-poisonous cyclopeptide, phallin A, which consists[3] of alanine, glycine, proline, phenylalanine, and valine (in the molar ratio 1:1:1:2:1). The fraction 1b mentioned in reference[3], which was obtained by a complicated purification procedure followed by chromatography on silica gel, was found to be non-poisonous when administered to mice despite its content of the poisonous phallin B. This led us to consider the possibility of the fraction 1b containing an antitoxic principle, which neutralized the toxic action of phallin B. With doses of 50 mg of the fraction 1b per kg of white mouse, the absolute lethal action of 5 mg of phalloidine per kg (LD_{50} = 2.0 mg/kg) could be completely counteracted. All attempts to enrich the antitoxin resulted in a preparation, whose thin layer chromatogram showed the presence of six components. 5 mg of this mixture per kg of white mouse was found to be a sufficient dose for complete protection against 5 mg phalloidine per kg. The amount of the antitoxic preparation available was, at this stage of our investigations, too small to permit further enrichment and characterization experiments to be carried out. This limitation and lack of time, compelled us to momentarily shelve our investigations.

2. Isolation

At this point in time *D. Rempel*[4] began his working up of the fungus harvest of 1963. Like his predecessors he used chromatographic methods for the separation of the numerous components, but instead of using a cellulose powder chromatographic column, as was used by previous workers, he used a column of dextran gel Sephadex G-25. Partition chromatography on such a column with a mixture of butanone, acetone, and water (20:6:5 v/v = solvent F) permitted the separation of the toxic and the non-toxic peptide constituents, the non-toxic components, because of their lipophilic character, leaving the chromatographic column ahead (pre-toxic fraction) of the toxic components.

At a later date, our group utilized the solubility of the non-toxic peptides in acetone in that we extracted the part of "primary material" LA that is soluble in solvent F with acetone and used the acetone-soluble LLA for the further working up of these peptides. From 125 kg of *A. phalloides*, approx. 40 g of the lipophilic non-toxic mixture could be obtained, which on being administered to a white mouse at a dose of

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[4] *Th. Wieland, D. Rempel, U. Gebert, A. Buku*, and *H. Boehringer*, Liebigs Ann. Chem. *704*, 226 (1967).

[5] *G. Lüben*, Dissertation, Universität Frankfurt a.M., 1965, D 30.

50 mg/kg proved sufficient to prevent certain death from 5 mg/kg of phalloidine. Further enrichment of the antitoxic principle[5] was achieved by column chromatography using methanol, or a methanol/water mixture, on Sephadex G-25 in earlier experiments and on Sephadex LH-20 in later work.

The anti-toxic substance absorbs in the UV-region and therefore its presence in the eluate from the chromatographic column is registered by a Uvicord; however, it does not give a specific color reaction and each of the fractions from the column had to be tested in experiments with mice in order to establish their preventative action against phalloidine.

Because of the large number of similar products present in the mixture, thin layer chromatography proved most effective after a certain degree of enrichment had already been achieved. At the same time the peptides were rendered visible (dark blue coloration) by *N*-chlorination with *tert*-butyl hypochlorite followed by treatment with tolidine[6]. After the first run, using methanol, the total activity was contained in a tenth of the amount by weight of the starting material; its concentration was found to be such that a dose of 5 mg/kg was sufficient protection against 5 mg/kg phalloidine. After a second run in methanol/water (1:1) (see Fig. 1) the amount by weight of the active portion had been reduced by a factor of 10 % resulting

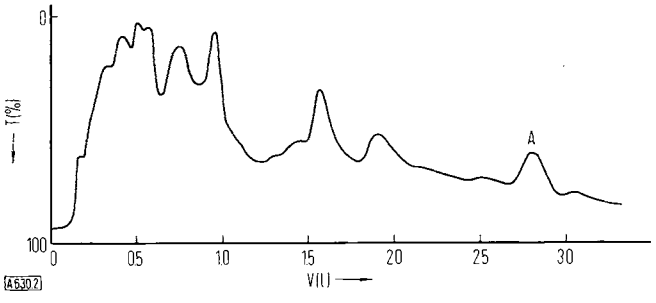

Fig. 1. Uvicord chart obtained on chromatographing [Sephadex LH-20 column (4 × 200 cm); eluant: methanol-water (1:1 v/v)] crude antamanide (1.5 g) isolated by preliminary chromatography. Antamanide at A.
Ordinate: Transmission T (%).
Abscissa: Volume V (l).

in an increase in activity such that a dose of 0.5–1 mg/kg proved to be sufficient protection against 5 mg/kg phalloidine. The thin layer chromatogram showed the presence of an almost pure active substance.

Preparative thin layer chromatography, on silica gel HF_{254} and using a mixture of *sec*-butanol/ethyl acetate/water (13:12:5) as solvent, formed the last purification step. After elution of the layer (at $R_F \approx 0.5$) containing the antitoxic substance, traces of dissolved silica gel could be removed by passage of the solution through a Sephadex LH-20 column. By using the above purification technique *ca.* 250 mg of pure antamanide were obtained from 40 g of a mixture of the acetone-soluble lipophilic components extracted from *A. phalloides*. The pure antamanide crystallized out on rubbing with acetone or butanone and was recrystallized from these solvents (see Fig. 2). It sinters at 167 °C and melts at 172 °C, is extremely soluble in methanol, acetone, ethyl acetate or pyridine, is readily soluble in higher alcohols and butanone, moderately soluble in ethyl acetate, slightly soluble in benzene, and almost insoluble in water and in paraffins.

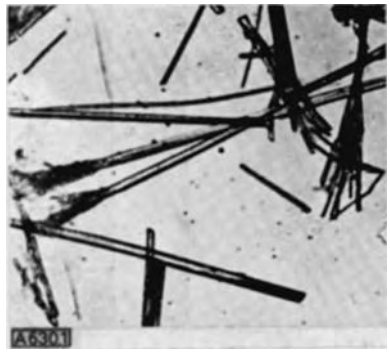

Fig. 2. Antamanide, crystallized from butanone.

In the white mouse the protective dose (PD) of pure antamanide against 5 mg/kg phalloidine amounts to 0.5 mg/kg. If the amount of poison is increased to 10 mg/kg (*i.e.* 4 × LD_{50}), complete protection can be achieved with 1.5 mg/kg of antamanide. A dose of 5 mg/kg of antamanide is sufficient protection against 25 mg/kg phalloidine. Whilst phalloidine administered to unprotected mice leads to the destruction of the endoplasmic reticulum of the liver cells within 15–30 minutes after injection (*O. Wieland* and *F. Miller*, *L. Fiume*, and *R. Laschi*; see ref.[7]), the liver of mice protected by antamanide remains completely normal. The slowly operating action of 1 mg (per kg body weight) of the ten times more poisonous α-amanitine, which attacks the nucleus of the liver cell, can be offset by repeated doses of 10 mg/kg of antamanide administered over a period of a few days.

3. Elucidation of Structure

3.1. Attempted Elucidation of Constitution by Classical Means

On hydrolysis with acetic acid/hydrochloric acid (1:1) for 12 h at 110 °C antamanide decomposes to the amino acids alanine, phenylalanine, proline, and valine in the molar ratio 1:4:4:1. Further, since antamanide is electrophoretically neutral and gives a negative ninhydrin test it must be considered as being a cyclopeptide. Mass spectrographic analysis showed the presence of a molecular ion at $m/e = 1146$, which is in accord with a cyclic decapeptide derived from the above mentioned amino acids in the given ratio. A new micromethod[8] was used for establishing the con-

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[7] *Th. Wieland*, Fortschr. Chem. org. Naturstoffe *25*, 214 (1967).

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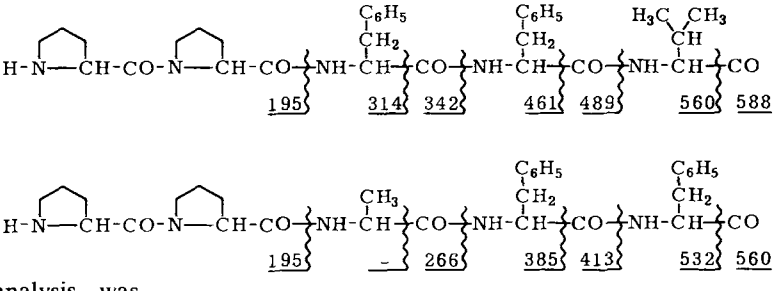
figuration of the structural units. This involved the micro-chromatographic, or electrophoretic isolation of the amino acids to be investigated from the hydrolyzate and their subsequent coupling with the azide of a suitable benzyloxycarbonyl-(= Z-) L-amino acid to form the Z-dipeptide. The presence of the L-forms gives rise to the formation of isochiral (L-, L-) Z-dipeptides; if a D-amino acid is present then a diachiral L-D-compound is also formed. A good separation [9] of the diastereoisomers can be obtained on a cellulose powder layer using pyridine/water (82:18 v/v) as solvent, provided that the group Z is first removed. This can be achieved on the micro-scale by gently applying spots of a 0.1 % solution of $PdCl_2$ in methanol to the initial drops of Z-dipeptide on the thin-layer plate and then placing the plate in a hydrogen atmosphere whereupon catalytic reduction occurs. It was subsequently established by chromatography, using the solvents mentioned above, that every one of the amino acids derived from the antamanide hydrolyzate gave rise to a spot of the L-L dipeptide only, thus suggesting that all the structural units have the L-configuration. The determination of the amino acid sequence presented hitherto unknown difficulties. The first step in our investigations was the examination of the possibility of cleaving the peptide ring in only one position by acid hydrolysis. *G. Lüben* obtained a mixture of peptides that gave a positive ninhydrin test (*i.e.* a mixture of linear peptides) together with the unchanged cyclopeptide, by treatment with glacial acetic acid /12 N hydrochloric acid at 40 °C for 24 h. This mixture could be separated by preparative thin layer chromatography. The quickest migrating component, which, according to the amino acid analysis, was composed of two phenylalanine, one alanine, one valine, and four proline units, was stepwise degraded (in a way that was modified in order to take into account the lipophilic nature) according to the method of *Edman*. The results obtained indicated the series Phe–Phe–Ala–Val–Pro–Pro–(Pro–Pro). Since the two missing phenylalanine units can only be accommodated at the beginning of the chain, we proposed the structural formula (–Phe_4–Ala–Val–Pro_4–) for antamanide and proceeded to synthesize a corresponding linear decapeptide. On chromatographic analysis of the synthetic product, a large discrepancy appeared between the R_F value of the synthesized octapeptide Phe–Phe–Ala–Val–Pro–Pro–Pro–Pro and that of the degradation peptide of the same assumed formula that had been subjected to sequence analysis; the latter migrated considerably farther. The unexpected lipophilic nature of the degradation peptides from antamanide was quite remarkable, and yet there seemed no reason to doubt the results of the Edman degradation, which had been carried out in the customary manner. It was not until later that we ascertained that the degradation peptide investigated, as well as other peptides isolated from the product of partial hydrolysis of antamanide, exhibited a certain peculiarity insofar as they all yielded two ninhydrin-positive products on incubation with methanolic ammonia; these products proved separable on thin-layer chromatography. This peculiarity has not yet been explained.

After it had become clear that the classic methods of sequence analysis could not be applied to the problem in hand, we resorted to mass spectrometric analysis.

3.2. Elucidation of the Structure by Mass Spectrometry

In agreement with the amino acid structure, the molecular ion of antamanide appears in the mass spectrum at *m/e* 1146. Its high intensity is suggestive of a cyclopeptide. A remarkable feature of the spectrum is the absence of intense fragment ions above *m/e* 588 and *m/e* 560, the only exception being an ion at M–91 (91 = benzyl). On the basis of these ions it was possible to derive formally two pentapeptide sequences, each containing the sequence Pro–Pro at their N-terminal end. This derivation takes into consideration the majority of the fragment ions that are observed (Scheme 1).



Scheme 1. Suggested fragmentation patterns for two pentapeptides.

The formation of analogous fragment ions with an N-terminal H–Pro–Pro sequence had already been observed during the mass-spectrometric decomposition of a cyclononapeptide [10]. The absence of characteristic fragment ions between *m/e* 588 and *m/e* 1055 (M–91) is readily explained by the immediate decomposition of the antamanide molecule into two pentapeptides, which then proceed to decompose stepwise. The structure of antamanide should thus result from the coupling of the two sequences Pro–Pro–Phe–Phe–Val and Pro–Pro–Ala–Phe–Phe.

A combination of gas chromatography and mass spectrometry was used to confirm the sequence [11].

[9] *Th. Wieland* and *H. Bende* Chem. Ber. *98*, 504 (1965).

[10] *F. Weygand* and *A. Prox*, unpublished.

[11] *A. Prox* and *F. Weygand*: Peptides. Proc. 8th Europ. Peptide Sympos., Nordwijk 1966. North-Holland Publ. Comp., Amsterdam 1967, p. 158.

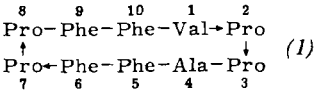
Since fragments were detected that had been formed by transannular transpeptidation, the procedure adopted in this part of the structure elucidation is briefly described below.

Antamanide (10 mg) was partially methanolized by treatment with 8.5 N methanolic hydrogen chloride solution for 5 h at 70 °C. The methyl esters of the peptides were separated gas chromatographically as the *N*-trifluoroacetyl compounds and were then analyzed mass spectrometrically. Over 30 components were obtained, a characteristic selection of which is given in sequence form in Table 1.

Table 1. Sequence derivation from the partial sequences of the N-trifluoroacetyl peptide methyl esters separated by gas chromatography.

1	2	3	4	5	6	7	8	9	10	(11	12)
Val	Pro	Pro	Ala								
		Ala	Phe	Phe							
			Phe	Phe	Pro						
				Phe	Pro	Pro					
					Pro	Pro	Phe				
							Phe	Phe	Val		
									Phe	Val	Pro
Val	Pro	Pro	Ala	Phe	Phe	Pro	Pro	Phe	Phe	(Val	Pro–)

The results of this precise analysis thus indicate the new structure *(1)* for antamanide (see also Scheme 2).

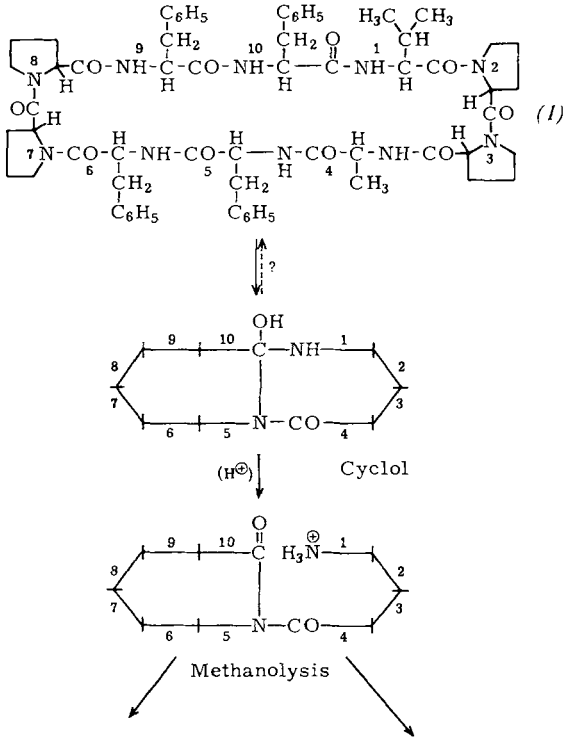


(1)

In addition to the peptide methyl esters listed in Table 1, others were found whose sequences were not consistent with the series given above, *e.g.*, Phe–Val–Phe, Phe–Phe–Ala, Phe–Val–Ala, and Phe–Phe–Phe. Their occurrence can be explained by the assumption of transannular interactions during the process of H^+-catalyzed methanolysis. A cyclol structure[12], formed by the reaction of an amide group with a CO group, can undergo ring cleavage thus giving rise to a peptide ring of reduced size that bears a linear polypeptide side chain. The side chain is split off from the resulting diacylimide by methanolysis and is degraded further. (If the side chain consists of only two units, it can be cleaved off as the diketopiperazine.) On partial methanolysis of the contracted peptide ring, peptide esters can be formed whose sequence is not present in the original peptide but arises as a result of rearrangement. This process is formulated in Scheme 2 for the "artificial" tripeptide Phe–Phe–Phe, but it can apply – *mutatis mutandis* – for the other three new peptides.

4. Synthesis of Antamanide

The synthesis of antamanide was accomplished *via* the cyclization of a linear decapeptide. Of the ten isomers that are possible in principle, we prepared one in a way that readily permitted variations to be made. On the basis of recent findings it proved unnecessary to observe the basic approach that had previously been adopted. Hitherto, the danger of racemization had prohibited the use of the usual activation methods[13] except in the case of amino acids protected by urethane groups; the only method permitted was the azide method. According to the latest work of *G. W. Anderson et al.*[14], the simplest method of peptide synthesis (with mixed alkyl carboxylic anhydrides[15]), however,



Phe-Phe-Phe-OCH_3 (9 10 5)

Val-Pro-Pro-Ala-OCH_3 (1 2 3 4)

+ Phe-Pro-Pro-OCH_3 (6 7 8)

and other esters

Scheme 2. Possible rearrangement in acid-catalyzed degration of antamanide *(1)*.

proceeds without racemization if certain bases, *e.g.* *N*-methylmorpholine, are used in place of triethylamine. Our synthesis of the methyl ester of the *N*-*tert*-butyloxycarbonyl-(BOC) compound from pentapeptides I (6–10) and II (1–5), as shown in Scheme 3, was conducted mainly according to the anhydride method although other common coupling methods[13] were also used.

The ester of pentapeptide I was converted into the acid by hydrolysis with sodium hydroxide solution in dioxane, and the derivative of pentapeptide II was converted into the ester having a free amino group by acid-catalyzed removal of BOC. The two components could then be coupled by the anhydride method to form the methyl ester of the BOC-decapeptide.

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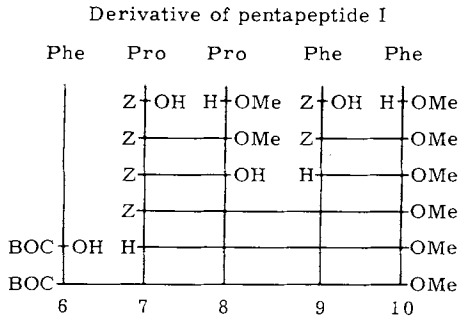
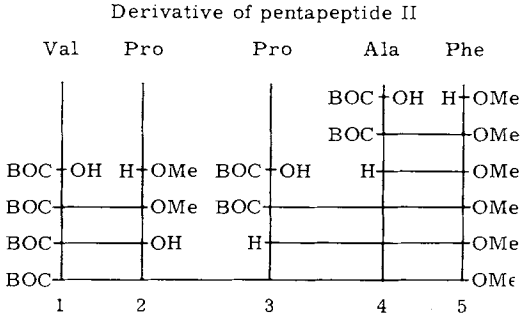
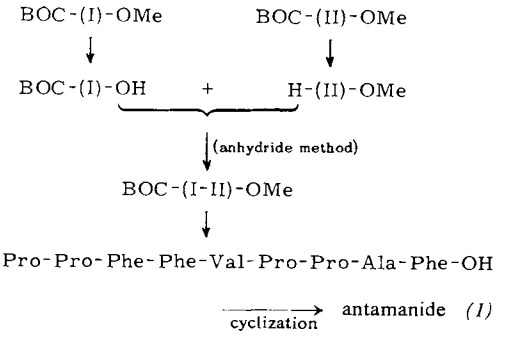




Scheme 3. Synthesis of the derivatives of pentapeptides I and II. Z = benzyloxycarbonyl group, BOC = *tert*-butoxycarbonyl group, Me = CH_3.

The terminal protecting group was removed from the decapeptide and cyclization of the free decapeptide was then accomplished by means of the anhydride method [16]. The yield was improved by additional protonation of the free amino terminal during anhydride formation [17]. Antamanide was obtained in *ca.* 30 % yield (with reference to the linear zwitterionic decapeptide). The compound crystallized out when its solution was seeded with the natural substance. In mouse experiments a dose of 0.5 mg per kg body weight, administered subcutaneously, was found to be effective against 5 mg of phalloidine per kg.



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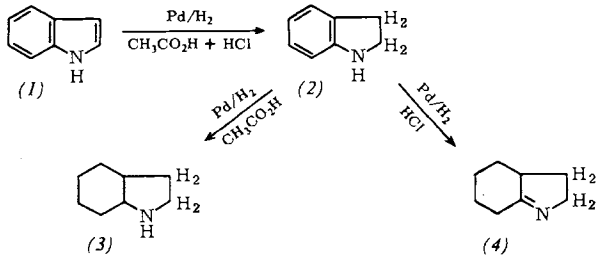
COMMUNICATIONS

Catalytic Hydrogenation of Indole

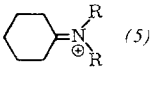
By *I. Butula* and the late *R. Kuhn* [*]

Willstätter and *Jaquet* [1] hydrogenated indole *(1)* over platinum in glacial acetic acid, obtaining octahydroindole *(3)*. If the hydrogenation was interrupted after absorption of one molar equivalent of hydrogen, then indoline *(2)* was isolated as well as *(3)*. *Adkins* and *Leonradt* [2] obtained *(2)* in 60% yield on hydrogenation of *(1)* over copper chromite at 170–190 °C and 250 atm, and *(3)* from *(1)* in 80% yield on hydrogenation over Ni at 250 °C and 250 atm.

If indole is hydrogenated in glacial acetic acid over $Pd(OH)_2/BaSO_4$ at 18 or 60 °C, dark products are formed with an H_2-absorption of 3–4 molar equivalents. If hydrochloric acid is added and hydrogenation is effected at 60 °C, 1 molar equivalent of hydrogen is taken up rapidly and reduction then ceases. Indoline can be isolated in 80% yield. This product is hydrogenated in glacial acetic acid over the same catalyst at 60 °C to give octahydroindole *(3)* (80%). However, if *(2)* is hydrogenated in 1 N hydrochloric acid at 60 °C, 3,3a,4,5,6,7-hexahydro-2*H*-indole *(4)* is obtained in 64% yield.



Under these conditions *Kuhn* and *Haas* [3] obtained cyclohexanone from aniline and suggested that the hydrogenation proceeds by way of the immonium compound *(5)*. If *(2)* is regarded as a substituted aniline, the appearance of the



(5)

imine *(4)* confirms *Kuhn* and *Haas*' suggestion. The structure of *(4)*, which was prepared by a different route *i.e.* as intermediate in the synthesis of erythrinane [4], was proved by IR [5] and NMR spectra.

Indoline (2): 2 g of $Pd(OH)_2/BaSO_4$ [6] was prereduced in 50 ml of glacial acetic acid, then 2.34 g of indole in 20 ml of 2 N HCl was added, and the mixture was hydrogenated in a shaking-apparatus at 60 °C and atmospheric pressure for

1.5 h. The catalyst was filtered off, the filtrate evaporated to dryness, and the residue dissolved in dilute sodium hydroxide solution and extracted with chloroform. After removal of the solvent and distillation of residue, 2.1 g (90%) of *(2)* was obtained. The IR spectrum was in accord with the Sadtler spectrum No. 22446.

Octahydroindole (3): 2.1 g of compound *(2)* was hydrogenated in 40 ml of glacial acetic acid over 2 g of $Pd(OH)_2/BaSO_4$ for 14 h at 60 °C. Working up as above afforded 1.7 g (80%) of *(3)*. Picrate, m.p. 135–137 °C ([1]: 137–139 °C).

3,3a,4,5,6,7-Hexahydro-2H-indole (4): 4 g of $Pd(OH)_2/BaSO_4$ was prereduced in 50 ml of distilled water, 3.6 g of *(2)* in 100 ml of 1 N HCl was added, and the mixture was hydrogenated at 60 °C and atmospheric pressure for 20 h (H_2 uptake: 2.4 molar equivalents). The crude product (strong $-\overset{\oplus}{H}N=C\diagdown$ absorption band at 1684 cm^{-1} in the IR spectrum) was dissolved in dilute aqueous sodium hydroxide, extracted with $CHCl_3$, and distilled. 64% (2.3 g) of compound *(4)* was obtained alongside a little *(3)*. Picrate, m.p. 132–133 °C ([4]: 132–133 °C).

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[1] *R. Willstätter* and *D. Jaquet*, Ber. dtsch. chem. Ges. *51*, 777 (1918).

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A New Alkenynylamine Synthesis

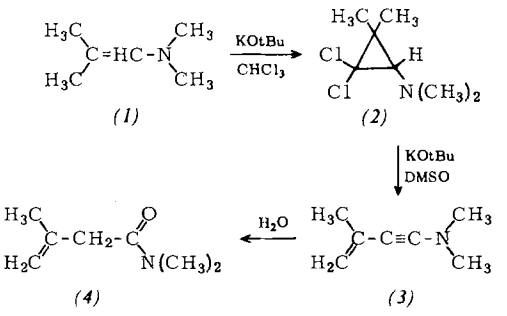
By *T. C. Shields*, *W. E. Billups*, and *A. N. Kurtz* [*]

Alkynylamines have been prepared [1] and stimulated considerable interest recently. We wish to report the extension of a simple route for alkenynes [2] to the synthesis of alkenynylamines.

Treatment of isobutenyldimethylamine *(1)* with chloroform and an excess of potassium *tert*-butoxide in pentane results in (2,2-dichloro-3,3-dimethylcyclopropyl)dimethylamine *(2)* in 32% yield [3]. Its NMR spectrum consists of four sharp singlets at τ = 7.73 (6 H, $(CH_3)_2N$ group), 8.38 (1 H, cyclopropyl proton), and 8.73 and 8.77 (3 H each, $C(CH_3)_2$ group).

Dehydrochlorination of *(2)* with potassium *tert*-butoxide in dimethyl sulfoxide at 25–40 °C for five hours affords a 20–30% yield of dimethyl-(3-methylbut-3-en-1-ynyl)amine *(3)*. The NMR spectrum of *(3)* shows a multiplet at τ = 5.24 (2 H, $=CH_2$ group), a sharp singlet at 7.30 (6 H, $(CH_3)_2N$ group), and a three line pattern centered at 8.23 (3 H, $C(CH_3)$ group). The molecular weight was determined mass spectrometrically (molecular ion at *m/e* = 109 with other significant fragments at *m/e* = 94, 79, and 53). The ultraviolet spectrum ($\lambda_{max.}^{C_6H_{12}}$ = 257 nm, ε = 8100, in cyclohexane) and infrared absorption [4.53 μ, $-C\equiv C-N(CH_3)_2$], along with elemental analysis, confirm the structure of *(3)*.

In water, compound *(3)* is hydrolyzed to *N,N*-dimethyl-3-methylbut-3-enamide *(4)* which shows NMR multiplets at τ = 5.19 and 5.31 (1 H each, $=CH_2$ group), a singlet at τ = 7.03 (6 H, $(CH_3)_2N$ group), and multiplets at 7.14 (2 H, CH_2 group) and 8.25 (3 H, $C(CH_3)$ group).



The mechanism of the conversion of compound *(2)* into *(3)* is not clear; however, attempts to trap a cyclopropene intermediate with nucleophiles have failed [4].

Synthesis of compound (2):

Isobutenyldimethylamine (121.0 g; 1.22 moles) in *n*-pentane (500 ml) is combined with chloroform (150.4 g; 1.26 moles) and cooled to 5 °C. Potassium *tert*-butoxide (179.5 g; 1.6 moles) is added slowly with stirring under a nitrogen atmosphere. Additional *n*-pentane (100 ml) is added during this period to reduce the viscosity of the reaction mixture. After an additional 1.6 hour's stirring, the mixture is quenched in ice water and the organic phase dried over Na_2SO_4. The *n*-pentane is removed and the product rapidly distilled through a short-path column whereupon 71 g (32% yield) of product, b.p. ~22 °C/0.7 torr, are obtained. The kettle temperature should be kept below about 60 °C since the contents are liable to explode if overheated. Redistillation of the product is uneventful except for a small amount of decomposition. Analysis by VPC is not practical due to extensive decomposition in the instrument; however, the compound is shown to exist in a very high state of purity by NMR spectroscopy.

Synthesis of compound (3):

Compound *(2)* (18.2 g; 0.10 mole) is added slowly to a solution of potassium *tert*-butoxide (44.9 g; 0.40 mole) in dimethyl sulfoxide (300 ml), with stirring, under nitrogen. The temperature (exothermic reaction) is maintained below 40 °C. After five hours total reaction time the mixture is quenched in ice water and extracted with *n*-pentane. The extract is dried over Na_2SO_4, concentrated, and distilled through an 8″ Vigreaux column. About 3.5 g of product (20–30% yield) is obtained. Purification is easily accomplished *via* preparative gas chromatography using an 8 ft. 10% SE-30 silicone gum rubber column.

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[1] *H. G. Viehe*, Angew. Chem. *79*, 744 (1967); Angew. Chem. internat. Edit. *6*, 767 (1967), and literature cited there.

[2] *T. C. Shields*, *B. A. Loving*, and *P. D. Gardner*, Chem. Commun. *1967*, 556.

[3] *M. Ohno*, Tetrahedron Letters *1963*, 1753, has also described the addition of dichlorocarbene to alkenylamines.

[4] *T. C. Shields*, *B. A. Shoulders*, *J. F. Krause*, *C. L. Osborn*, and *P. D. Gardner*, J. Amer. chem. Soc. *87*, 3026 (1965).

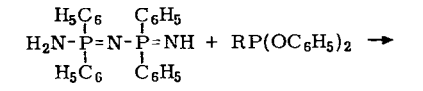
Hydrogen-substituted Cyclotriphosphazenes Formed by NH→PH Tautomerization [1]

By *A. Schmidpeter* and *J. Ebeling* [*]

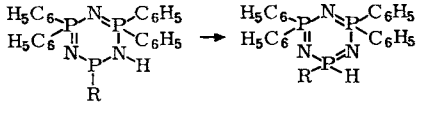
1-Amino-3-iminodiphosphazenes [**] condense readily with compounds that contain two replaceable nucleophilic substituents on the central atom, yielding six-membered phosphazene heterocycles [2]. 1-Amino-3-imino-1,1,3,3-tetraphen-

yldiphosphazene removes 2 molar equivalents of phenol from triphenyl phosphite *(2a)*. The diphenyl alkylphosphonites *(2b)* [3] and *(2c)* react similarly.

The products correspond in composition to the expected cyclotriphosphazadienes *(3)* but do not have the sensitivity to oxidation expected for such compounds; they are unchanged by atmospheric oxygen. The couplings that occur in the ^{31}P- and ^{1}H–NMR spectra, especially the high P–H coupling show unambiguously that the reaction products are the tautomers *(4)* that have arisen by migration of the proton from nitrogen to phosphorus.



(1) *(2)*



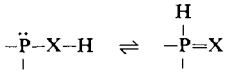
(3) *(4)*

(a), R = OC_6H_5
(b), R = CH_3
(c), R = C_2H_5

	(4a)	*(4b)*	*(4c)*
Temp. of prepn. (°C)	100–200	50–100	60–120
M.p. (°C)	153	152	127–129
νPH (cm^{-1})	2410 m 2350 sh	2360 m 2310 sh	2350 m 2300 sh
Chem. shifts (ppm)			
δ^{31}P (Ph_2P)	−14.5	−12.9	−15.5
(RHP)	−5.8, doublet	−6.9, doublet	−12.5, doublet
δ^{1}H (PH)	−7.36, double triplet	−7.65, 2·3·4 lines	−7.58, 2·2·3 lines
(R)	−7.05, pseudosinglet	−1.57, 2·2·3 lines	−1.72, multiplet (CH_2) −1.03, double triplet (CH_3)
Spin-spin couplings (Hz)			
J_{PH}	676	509	506
J_{PNPH}	10.0	3.9	4.6 (?)
J_{HCPH}		2.8	6.4 (?)
J_{PCH}		15.1	*ca.* 14
J_{PNPCH}		2.0	1.8 (?)
J_{HCCH}			*ca.* 7
J_{PCCH}			*ca.* 22

A direct P–H coupling from phosphorus bound to nitrogen has not hitherto been known. However, values for coupling constants can be estimated from $L_{PH} \approx 100\ (\Sigma\chi_S - 3)$ Hz. χ_S are here the electronegativities of the substituents (other than the hydrogen) bound to the phosphorus. Agreement of the calculated values [670 Hz for *(4a)*; 570 Hz for *(4b)* and *(4c)*] with the experimental values can be taken as confirmation of structure *(4)*.

Whereas for X = O the tautomeric equilibrium



always lies exclusively to the right-hand side, all the amino and imino derivatives so far prepared from phosphorus in the oxidation state +3 (X = N–) are stable only in the NH form, and not in the phosphazene form [4]. The compounds *(4)* are thus also the first hydrogen-substituted cyclophosphazenes. The factors governing the phosphazane/phosphazene tautomerism are currently being investigated.

Experimental:

An equimolar mixture of the diphosphazene *(1)* and the phosphonite *(2)* is slowly heated at 0.2 torr for one hour in a flask arranged for distillation. The phenol released distills into the receiver. The residue is recrystallized from benzene or acetonitrile, affording the cyclotriphosphazene *(4)* as colorless needles in 70–80 % yield.

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[**] IUPAC rules for the nomenclature of phosphazenes are not yet available. According to *R. A. Shaw et al.* (Chem. Reviews *62*, 247 (1962)), compound *(1)* can be named 4-amino-2,2,4,4-tetraphenyldiphosphazene.

[1] Part 15 of Phosphazenes. – Part 14: *A. Schmidpeter* and *J. Ebeling*, Chem. Ber. *101*, 815 (1968).

[2] *A. Schmidpeter* and *J. Ebeling*, Angew. Chem. *79*, 534 (1967); Angew. Chem. internat. Edit. *6*, 565 (1967).

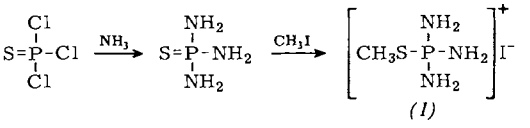
[3] B.p. 88–89 °C/0.06 torr, $\delta^{1}H(CH_3) = -0.88$ ppm, $\delta^{31}P = -178.5$ ppm, $J_{PCH} = 10.3$ Hz, prepared in accordance with directions in *Houben-Weyl*: Methoden der organischen Chemie. Thieme, Stuttgart 1963, Vol. XII/1, p. 325.

[4] *H. Nöth* and *L. Meinel*, Z. anorg. allg. Chem. *349*, 225 (1967).

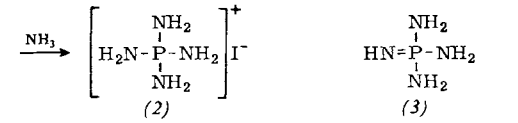
Preparation of Tetraaminophosphonium Salts by Ammonolysis of the Triamino(methylthio)-phosphonium Ion [1]

By *A. Schmidpeter* and *C. Weingand* [*]

Ammonolysis of PCl_5 is always accompanied by condensation and leads to amino-di- [2], -tri- [3,4], -tetra- [3], and -polyphosphazenes [3]. The imidophosphoric triamide *(3)* that is assumed as unstable monophosphazene intermediate [5] cannot be isolated in such experiments. It is obtained as its hydriodide *(2)* if the trifunctional $SPCl_3$ is used as starting material, instead of the tetra- or penta-functional PCl_5, for the ammonolysis, the sulfur function that remains in the resulting $SP(NH_2)_3$ [6] is activated by alkylation [7], and the fourth amino group is introduced by further, mild, ammonolysis.

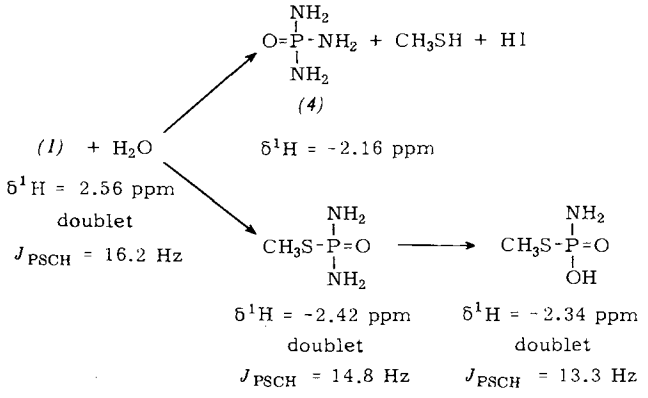


(1)



(2) *(3)*

The compound *(1)*[8] obtained from thiophosphoric triamide and methyl iodide is insoluble in organic solvents except aniline. In contrast to $SP(NH_2)_4$ it is rapidly decomposed by aliphatic amines, alcohols, and water. The half-reaction time for hydrolysis at 0 °C was determined by ^1H–NMR spectroscopy as approximately 20 minutes for a 40% solution in D_2O. The hydrolysis does not proceed uniformly; the methylthio group is only partly removed from the phosphorus atom, a somewhat smaller proportion remaining attached thereto. At room temperature hydrolysis is complete within a few minutes.



Chemical shifts in D_2O relative to TMS as external standard.

NH_3 reacts less fast, but removes methanethiol quantitatively. In methylene chloride ammonolysis of *(1)* leads smoothly to *(2)*, no condensation accompanying the substitution. This compound is unexpectedly stable thermally: it is altered only above 210 °C, and then without melting. It is soluble only in liquid ammonia (6 g/100 ml) and water. When warmed, the cation is rapidly hydrolyzed to $OP(NH_2)_3$, but in cold water it is stable to a considerable extent in contrast to the middle members[9] of the series $[(C_6H_5)_nP(NH_2)_{4-n}]^+$. It can be precipitated from aqueous solution as reineckate $[P(NH_2)_4]Cr(SCN)_4(NH_3)_2$ (pink, analytically pure) and as tetraphenylborate $[P(NH_2)_4]B(C_6H_5)_4$ [containing $NH_4B(C_6H_5)_4$ as impurity]. Further, by reaction with BiI_3 and HgI_2, pale red $[P(NH_2)_4]BiI_4$ and yellow $[P(NH_2)_4]_2HgI_4$ were obtained from *(2)*, and brown $[CH_3SP(NH_2)_3]BiI_4$ and yellow $[CH_3SP(NH_2)_3]_2HgI_4$ from *(1)*.

It has not yet been possible to obtain the underlying base *(3)*, the aza analog of phosphoric acid, from *(2)*. The base *(3)* does not come into question as an intermediate in the ammonolysis of PCl_5 since it is apparently a stronger base than NH_3. But use of an extremely high NH_3/PCl_5 ratio might lead to formation of its hydrochloride $[P(NH_2)_4]Cl$.

Triamino(methylthio)phosphonium iodide (1):

$SP(NH_2)_3$ (28 g, 0.25 mole) was stirred for 6 days at room temperature with CH_3I (45 g, 0.32 mole) and CH_3Cl (60 ml). The deposit was sucked off and washed with ether. The yield (63 g) is quantitative and the product is analytically pure. M.p. 161–162 °C with loss of CH_3SH lit.[8]: 159–160 °C.

Tetraaminophosphonium iodide (2):

A fast stream of NH_3 is passed into a vigorously stirred suspension of *(1)* (2.00 g) in CH_2Cl_2 (30 ml) for 2 h. On removal of the solution there remained 1.71 g of pure *(2)* (yield 98%). Incompletely reacted products can be purified by washing quickly with methanol warmed to 40 °C.

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[1] Part 16 of Phosphazenes. – Part 15: *A. Schmidpeter* and *J. Ebeling*, Angew. Chem. *80*, 197 (1968); Angew. Chem. internat. Edit. *7*, 209 (1968).

[2] *M. Becke-Goehring* and *B. Scharf*, Z. anorg. allg. Chem. *353*, 320 (1967).

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[8] *H. Tolkmith*, US.-Pat. 3074993, Dow Chemical Co.; Chem. Abstr. *59*, 1542b (1963).

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Radiospirometric Determination of the Oxidation *in vivo* of [17α-^{3}H]Testosterone and its Esters at C-17

By *M. Wenzel*, *L. Pitzel*, and *P.-E. Schulze*[*]

With the aid of "metabolism-labile" labeling by deuterium or tritium it has proved possible to elucidate the oxidation in a specific position of organic compounds within an organism by measuring the activity of the water in the expired air[1,2]. We used this method to determine the minimal oxidation of [17α-^{3}H]-testosterone and the minimal oxidation and rate of hydrolysis of its 17β-esters, testosterone acetate and heptanoate, in rats. The determination is based on the following reactions:

$$\text{[17α-}^3\text{H]Testosterone} + \frac{\text{DPN}}{\text{TPN}} \xrightarrow[\text{dehydrogenase}]{\text{17β-Steroid-}}$$

$$\text{4-Androstene-3,17-dione} + \frac{^3\text{H-DPN}}{^3\text{H-TPN}} \xrightarrow[\text{cycle}]{\text{Respiration}}$$

H^3HO in body water

The [17α-^{3}H]testosterone esters must be hydrolyzed in the organism before the testosterone can be oxidized.

If the amount of radioactivity injected, the weight of the experimental animal, and thus the total body water[2a] are known, then measuring the specific tritium activity in a distilled sample of body water permits the amount of steroid oxidized to be determined by means of the following calculation:

$$\frac{\mu\text{Ci per ml of distilled body water}}{\mu\text{Ci of injected steroid per ml of body water}} \cdot 100 = \text{minimal oxidation in \%}$$

Fig. 1 shows the rate of oxidation of [17α-^{3}H]testosterone[3], and of its 17β-acetate and 17β-heptanoate, determined in this way in an apparatus described previously[1,2].

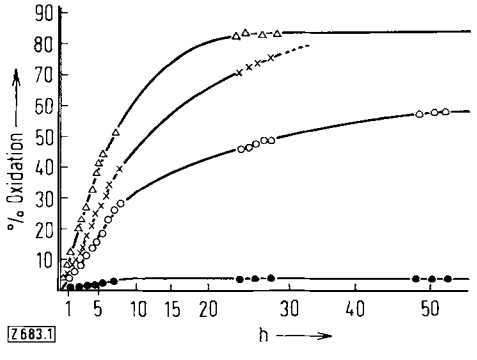

Fig. 1. Oxidation, *in vivo*, of [17α-^{3}H]testosterone (—Δ—Δ—), its acetate (—×—×—) and heptanoate (—O—O—), and of [7-^{3}H]testosterone (—•—•—) in male rats.
Injection of the steroids dissolved in propylene glycol and physiological saline (1:1); 0.5 ml intramuscularly.
Ordinate: % oxidation at C-7 or C-17.

According to these results, testosterone (at a dosage of 0.4 μmole/kg rat) is oxidized to the 17-ketone to the extent of at least 85% within 24 hours, whereas the acetate (0.35 μmole/kg) and heptanoate (0.6 μmole/kg) are hydrolyzed and oxidized to the 17-ketone only to the extent of 70 and 40%, respectively, during the same period.

These results are difficult to reconcile with concepts about the extended duration of action of hormone esters (*e.g.*, 28–30 days for testosterone heptanoate). The cause may be that in *Junckmann* and *Witzel*'s experiments[4] 1 to 5 mg of hormone per animal (12 to 60 μmole/kg) were injected, sometimes in oily suspension. It is possible that resorption, hydrolysis, and oxidation are reduced under these circumstances. We showed previously that the proportion oxidized decreases with increasing steroid dosage, even before the capacity of the 17β-hydroxysteroid dehydrogenase is exhausted[2].

If [7-^{3}H]testosterone (0.11 mg/kg) is injected into rats, no oxidation occurs at C-7 and therefore very little tritium is found in the body water (Fig. 1). This low labilization of tritium may be caused by a partial hydroxylation at C-7[5].

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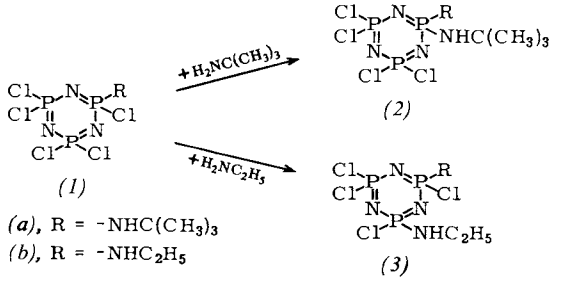
The Structure of the Products of Aminolysis of Aminopentachlorocyclotriphosphazenes

By *R. Keat*[*] and *R. A. Shaw*[**]

The pattern of replacement of the chlorine atoms in hexachlorocyclotriphosphazene by a number of different primary and secondary amines has been studied in some detail[1]. Widely differing replacement patterns have been observed with different alkylamines, even when members of the same class of amine were involved. In this connection we have studied the factor which determines the structure of the aminolysis product in the case of the amino derivatives *(1)*. The *tert*-butylamino-derivative *(1a)* gives with further *tert*-butylamine the geminal diamino-derivative *(2a)*[1f] whilst the monoethylamino-derivative *(1b)* yields with further ethylamine a non-geminal compound *(3b)*[1d].

On treatment of compound *(1a)* with ethylamine, a diamino-derivative, m.p. 68–70 °C, is obtained. When these two substituents are introduced in the reverse order, *i.e.* when *(1b)* is treated with *tert*-butylamine a diamino-derivative having m.p. 104–105 °C results. If the amino group already attached to the ring determines the point of entry of the second amino group then the lower melting isomer should be the geminal, and the higher melting isomer the non-geminal compound. In fact, the opposite is the case, *i.e.* the compound having m.p. 68–70 °C has the structure *(3a)* whilst the substance of m.p. 104–105 °C has the structure *(2b)*. This suggests that the nature of the nucleophile is, at least in the reactions reported here, a major structure determining factor.



(a), R = $-NHC(CH_3)_3$
(b), R = $-NHC_2H_5$

All compounds reported here had satisfactory analyses and their structures were determined by ^{1}H–NMR spectroscopy (cf. ref.[2]). Thin-layer chromatography showed that, in general, the compounds reported could be obtained in yields of more than 85%. Methods for the synthesis, the separation, and the determination of structure of this type of compound have been described previously[1e–1h, 2].

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Trimethylsilyl Derivatives of Germanium and Tin. — Electron-balance Bonds of Silicon

By *H. Bürger* and *U. Goetze*[*]

Investigation of the electron-excess compounds of type $(R_3Si)_2E(VI)$ *(1)* and $(R_3Si)_3E(V)$ *(2)* [R = H or CH_3; E(VI) = O, S, Se, or Te; E(V) = N, P, As, or Sb] by structural analysis or spectroscopy has shown that the elements O and N use approximately sp- and sp^2-hybridized orbitals, respectively, whereas the other elements use preponderately p-orbitals for their bonds with the Si atom[1]; thus the valence parameters in the series *(1)* and *(2)* cannot be compared directly. However, in the electron-balance compounds $(R_3Si)_4E(IV)$ *(3)* the E atom is sp^3-hybridized; comparative observations for compounds of type *(3)* are thus not falsified by differences in the s-character of the Si–E bonds.

We have completed the series *(3)* by preparing the compounds $[(CH_3)_3Si]_4Ge$ *(3c)* and $[(CH_3)_3Si]_4Sn$ *(3d)* and have examined them by IR, Raman, and ^{1}H–NMR spectroscopy in conjunction with $[(CH_3)_3Si]_4C$ *(3a)*[2] and $[(CH_3)_3Si]_4Si$ *(3b)*[3]. Compounds *(3c)* and *(3d)* were prepared similarly to *(3a)*[2] and *(3b)*[3]:

$$Cl_4E(IV) + 8\,Li + 4\,(CH_3)_3SiCl \xrightarrow{THF} 8\,LiCl + (3)$$

When E(IV) = Ge or Sn the reduction

$$Cl_4E(IV) + 4\,Li \rightarrow E(IV) + 4\,LiCl$$

also occurs, so that 50% of the Ge used or 80% of the Sn used is recovered as metal. Calculated on the proportion of reaction that leads to linkage, the yields are 70% for *(3c)* and 50–60% for *(3d)*. Like *(3a)* and *(3b)*, the compounds *(3c)* and *(3d)*, which are spherical top molecules, colorless, crystallizing well from CH_3CN, and subliming at 60 °C/10^{-4} torr, have unusually high melting points and volatility. They are decomposed by KOH to $(GeH_2)_x$ and Sn, respectively. Alcohol and H_2O attack them more slowly than in the case of *(3b)*.

	$[(CH_3)_3Si]_4E$(IV) E(IV) =	M.p. (°C) [a]	^{1}H–NMR $\delta \pm 0.01$	$J(^1H^{13}C) \pm 0.5$ (Hz)	$J(^1H^{29}Si) \pm 0.1$ (Hz)	$J(^1HE(IV))$ (Hz)
(3a)	C	305–307 [2]	0.23 [b] 0.2 [2]	119.5	6.3	^{13}C (1.4 [c])
(3b)	Si	319–321 [3]	0.21	120.0	6.5	^{29}Si: 2.2 ± 0.1
(3c)	Ge	295	0.24	120.5	6.7	—
(3d)	Sn	235–236	0.29	120.7	6.7	^{119}Sn: 22.2 ± 0.2 ^{117}Sn: 21.5 ± 0.2

[a] In molten capillaries.
[b] 25% Solution in CCl_4, TMS and cyclohexane as internal standards, Varian A 60.
[c] Limit of resolution power.

The ^{1}H–NMR spectra show a steady progression of all δ- and *J*-values and no irregularities as for compounds *(1)* and *(2)*. The vibrations of the Si_4E(IV) skeleton obey the selection rules for ideal tetrahedrons. The fundamentals ν_1 to ν_4 are at the following frequencies (in $cm^{-1} \pm 2\ cm^{-1}$):

	ν_1	ν_2	ν_3	ν_4
(3a)	382	151	673	176
(3b)	328	90	457	101
(3c)	319	68	361	89
(3d)	311	58	330	73

The positions of the stretching vibrations confirm qualitatively that, in spite of the lower polarity, the (sp^3)Si-(sp^3)Sn σ-bond in *(3d)* (ν = 326 cm^{-1}) is stronger than the (sp^3)Si-(sp^3)Sb bond in $[(CH_3)_3Si]_3Sb$ (ν = 319 cm^{-1}), whereas the Si–C bond in *(3a)* is appreciably weaker than the Si–N bond in $[(CH_3)_3Si]_3N$ because the former has less s-character and less polarity and no π-contribution to strengthen it. We shall report the force constants of *(3a)–(3d)* together with the complete analysis of the vibration spectra in a future communication.

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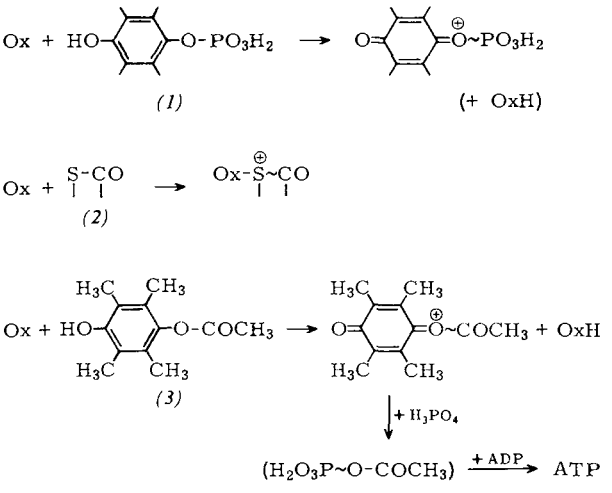
Formation of Adenosine Triphosphate (ATP) from Adenosine Diphosphate (ADP) and Phosphate during Oxidation of Durohydroquinone Monoacetate[1]

By *Th. Wieland* and *H. Aquila*[*]

We have demonstrated the conversion of oxidation energy into a high group-transfer potential[2] for the case of formation of an energy-rich phosphoryl linkage, H_2O_3P–X, during oxidation of *S*-phosphoryl thiols[3] or hydroquinone monophosphoric esters *(1)*[4]. Energy-rich acyl groups (which can transfer their acyl group to phosphoric acid) are formed similarly during the action of oxidizing agents on *S*-acyl compounds such as thiolactones *(2)*[2,5].

The use of hydroquinone for oxidative formation of activated acyl groups also makes it possible to obtain ATP from ADP and phosphate. In our reaction system the energy-rich acetyl group produced by oxidizing durohydroquinone monoacetate *(3)* with bromine or tetrabromo-*o*-benzoquinone reacts with phosphate (or ADP) to give acetyl phosphate (or acetyl-ADP), which reacts with ADP (or phosphate) to give ATP.



Formation of acetic anhydride on oxidation of 2-methyl-1,4-naphthohydroquinone-1-acetate by *N*-bromosuccinimide in glacial acetic acid has recently been described by *Thanassi* and *Cohen*[6].

We obtained durohydroquinone monoacetate *(3)* in *ca.* 35% yield by acetylation of durohydroquinone at 0 °C with acetyl chloride in pyridine, together with the diacetate from which it was separated by utilizing its slower rate of migration on chromatography on silica gel with chloroform as eluant. Recrystallization from ethanol/water and then from benzene gave material melting at 146.5–147.5 °C.

For oxidative phosphorylation 48 mg (0.1 mmole) of ADP·$3H_2O$ (C.F. Boehringer und Soehne, Mannheim-Waldhof), 0.87 ml of a 0.115 M solution of 85% phosphoric acid in dioxane, and 5 ml of a 0.1 M solution of tetrabutylammonium hydroxide in propan-2-ol (Merck, Darmstadt) were placed in a 50-ml flask and evaporated on a rotary apparatus in a vacuum. The residue was moistened with ethanol and the latter was then removed. After this procedure had been repeated several times, the residue was dried for 5 h at oil-pump vacuum over P_2O_5 and solid KOH in a desiccator; it was then dissolved in 5 ml of pyridine (dried over CaH_2) and, after addition of 20.8 mg of durohydroquinone monoacetate, treated with 0.014 ml (0.25 mmole) of bromine or 47 mg (0.11 mmole) of tetrabromo-*o*-benzoquinone with ice cooling and magnetic stirring. The mixture was stirred in the ice-bath for half an hour and for a further 1.5 h at 20 °C then evaporated in a vacuum. The residue dissolved wholly in 2.0 ml of methanol. 0.5 ml of this solution was placed on a 20 cm × 20 cm thin-layer plate (0.5 mm of silica gel HF_{254}, Merck), and the chromatogram was developed first with chloroform/methanol (10:3), then dried with a fan, and fur-

ther developed with propan-1-ol/conc. ammonia/water (6:3:1). After drying, the lower fluorescence-quenching ATP zone was removed and the silica gel was eluted with 25 ml of 0.05 M Tris buffer (pH = 7.55). The yields of ATP determined enzymically [7] and referred to the ADP used were: on oxidation with bromine 6.0 and 6.8%; on oxidation with tetrabromo-*o*-benzoquinone 9.5%; without oxidizing agent 0.0%; and without acetyldurohydroquinone monoacetate 0.0%.

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Syntheses by Means of 1-Alkylidene- and 1-(Arylalkylidene)-3-pyrazolidone *N,N*-Betaines, a New Type of Stable Azomethine Imine

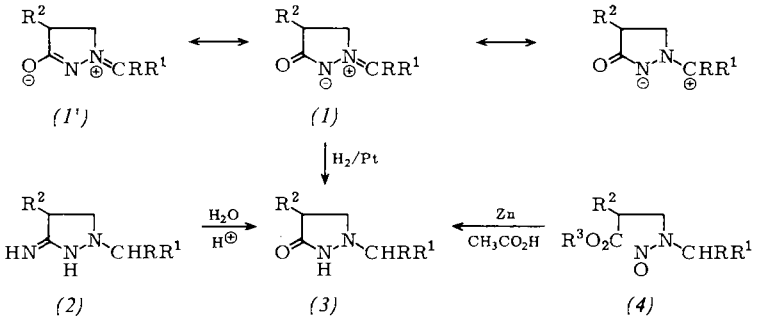
By *H. Dorn* and *A. Otto*

Azomethine imines have, it is true, been postulated as intermediates in the formation of hexahydro-1,2,4,5-tetrazines from 1,2-disubstituted hydrazines and aldehydes [1], but they have been isolated in only two cases, namely, as deep blue "anhydro bases" from *N*-(arylamino)pyridinium iodides [2] and as orange-red products from arenediazo cyanides and diazofluorene [3]. We have found that stable azomethine imines are obtained very simply from 3-pyrazolidone and carbonyl compounds in 80–90% yield. This reaction is generally applicable; it takes place exothermally and either without a solvent or in methanol. The crystalline azomethine imines *(1)* are dried in a vacuum over P_4O_{10} and then recrystallized from alcohols or dioxane. They are colorless unless substituents R^1 are introduced that deepen color (NO_2, 4-dialkylamino).

Because of their molecular weights and their chemical behavior the products *(1)* cannot be either hexahydro-1,2,4,5-tetrazines or β-lactams. Their acid-catalyzed hydrolysis regenerates the starting materials quantitatively. Catalytic hydrogenation (methanol, Adams Pt, atmospheric pressure) leads to quantitative yields of 1-substituted 3-pyrazolidones *(3)*. Since 3-pyrazolidone [4] and its *C*-alkyl derivatives [5] have recently become readily accessible, this reaction offers a very simple synthesis of 1-substituted 3-pyrazolidones [6].

The position of CRR^1 in *(1)* and *(3)* follows from synthesis of *(3a)* and *(3b)* by way of the 3-amino-*N*-nitrosopropionic ester *(4)* and of *(3c)* by acid hydrolysis of 1-benzyl-3-iminopyrazolidine *(2c)* which is obtained by cyclization of 1-benzyl-1-(2-cyanoethyl)hydrazine [7].

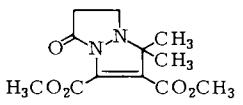
In agreement with the azomethine imine structure, the IR spectra of *(1)* contain intense bands at 1670 and 1600 cm^{-1}, of which the latter, more intense, band is to be assigned to the carbonyl vibration. Their shift to lower frequencies compared with the bands of the corresponding pyrazolidones indicates participation of the limiting structure *(1')*. The NMR spectra of *(1a)*, *(1c)*, and *(1e)*, and of compounds analogous to *(1b)* that are synthesized from 2,2,6,6-tetradeuteriocyclohexanone correspond to the azomethine imine structure *(1)*; *(1a)* (in $CDCl_3$) shows two singlets at $\tau = 7.62$ and 7.73 for the two methyl groups.



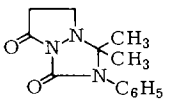
(1') *(1)* *(2)* *(3)* *(4)*

	R	R^1	R^2	M.p. (°C)	ν (CO) (cm^{-1})	ν (C=N) (cm^{-1})
(1a)	CH_3	CH_3	H	156–160	1600 [a]	1665 [a]
(1b)	Cyclohexylidene		H	155–160	1605 [a]	1660 [a]
(1c)	H	C_6H_5	H	205–208	1600 [a]	1680/1655 [a]
(1d)	H	*p*-Cl–C_6H_4	H	214–217	1600 [a]	1675/1660 [a]
(1e)	H	*p*-H_3CO–C_6H_4	H	187–189	1610 [b]	1687/1667 [b]
					1613 [a]	1680/1662 [a]
(1f)	H	2-Furyl	H	213–216	1608 [b]	1680/1655 [b]
					1604 [a]	1678/1658 [a]
(1g)	H	5-Nitro-2-furyl	H	Decomp. from 230	1600 [a]	1680/1660 [a]
(1h)	H	C_6H_5	CH_3	139–141	1596 [a]	1668 [a]
(3a)	CH_3	CH_3	H	80–81	1700 [b]	
(3b)	H	C_6H_{11}	H	90–91	1700 [b]	
					1685 [a]	
(3c)	H	C_6H_5	H	86–87	1705 [b]	
(3d)	H	*p*-Cl–C_6H_4	H	105–106	1695 [b]	
(3e)	H	*p*-H_3CO–C_6H_4	H	57–58	1695 [b]	
(3f)	H	2-Furyl	H	59–60.5	1688 [b]	
					1696 [a]	
(3h)	H	C_6H_5	CH_3	72–72,5	1698 [b]	

[a] In KBr; [b] In $CHCl_3$.



(5)



(6)

With dipolarophiles the azomethine imines *(1)* give azapyrrolizidines in very good yields, *inter alia*, dimethyl 1,5,6,7-tetrahydro-1,1-dimethyl-5-oxopyrazolo[1,2-*a*]pyrazole-6,7-dicarboxylate *(5)* [m.p. 138–139 °C] and perhydro-3,3-dimethyl-2-phenylpyrazolo[1,2-*a*]-[1,2,4]-triazole-1,7-dione *(6)* [m.p. 135–137 °C].

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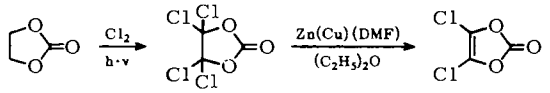
Syntheses by Means of Dichlorovinylene Carbonate (4,5-Dichloro-1,3-dioxol-2-one) as Dienophile and Photocyclophile [**]

By *H.-D. Scharf*, *W. Droste*, and *R. Liebig* [*]

We have prepared the hitherto unknown dichlorovinylene carbonate (4,5-dichloro-1,3-dioxol-2-one) *(3)* in good yield by the following route:

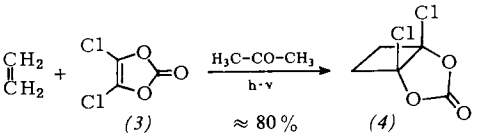


(1) *(2)* *(3)*

Exhaustive chlorination of the readily accessible ethylene carbonate *(1)* by *Ellingboe* and *Melby*'s method [1] leads to the tetrachloro-derivative *(2)* which reacts with a copper-zinc couple in ether in presence of catalytic amounts of dimethylformamide to give the compound *(3)* with loss of chlorine. This product is a colorless, lachrymatory liquid of b.p. 39–40 °C/10 torr, $n_D^{28} = 1.4602$, which crystallizes below room temperature. Its IR carbonyl vibration [2] is at 1890 cm^{-1}. The molecular weight, determined mass-spectrometrically, is 154, corresponding to the formula $C_3O_3Cl_2$ for the chlorine isotope 35.

Photocycloaddition to ethylene:

On irradiation [3], *(3)* reacts with ethylene [4] in acetone at room temperature, giving the cycloadduct *(4)* smoothly:

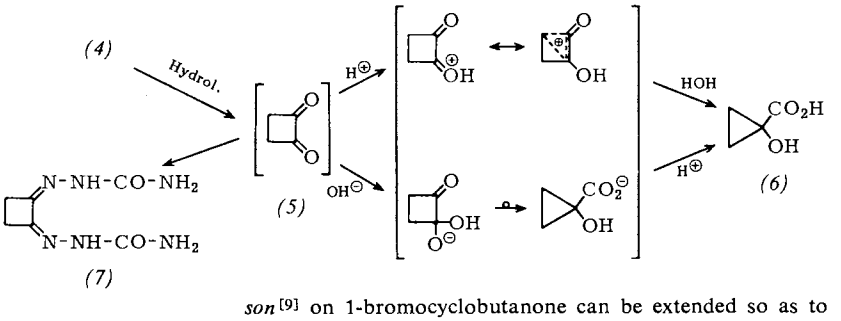


(3) ≈ 80 % *(4)*

1,2-Dichloro-1,2-cyclobutylene carbonate (3a,5a-dichloro-3a,4,5,5a-tetrahydrocyclobuta[*d*]-[1,3]-dioxol-2-one) *(4)* forms colorless crystals (m.p. 50 °C). The expected AA'BB' NMR spectrum of the four protons [5] collapses to a singlet at $\tau = 7.05$ because the shielding of the proton pairs above and below the ring is apparently comparable. The spin coupling type [6] can be recognized by scale expansion of the signal. IR absorption [2] (CCl_4): γ_{CO} at 1885 cm^{-1}. The C–H skeletal vibrations correspond to the values given by *Mery* and *McCleon* [7] for the cyclobutane ring; namely, C–H stretching vibration at 3010 and 2960 cm^{-1}, deformation vibration of the H–C–H angle at 1420 cm^{-1}, deformation vibration of the four-membered ring at 1230 cm^{-1}.

On dissolution of *(4)* in cold dilute KOH and subsequent acidification, or on its dissolution in HCl, 1-hydroxycyclopropanecarboxylic acid *(6)* is formed as sole product.

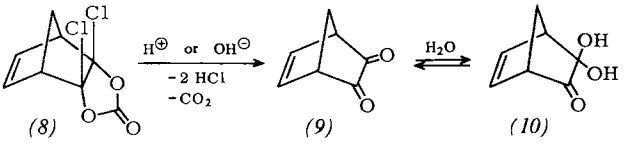
Since this reaction corresponds formally to a Favorskii rearrangement but takes place in both pH ranges, the observations made by *Conia* and *Ripoll* [8] and by *Rappe* and *Knutson* [9] on 1-bromocyclobutanone can be extended so as to indicate that the dione *(5)* is formed as intermediate and rearranges in acid by way of a dicyclobutonium ion but in alkali by the benzilic acid mechanism. The diketone *(5)* can be trapped as bissemicarbazone *(7)* [10], which is in agreement with the above assumptions.



(4) *(5)* *(6)* *(7)*

Compound *(6)* has m.p. 106 °C. Its structure was proved by comparison of its ^1H–NMR spectrum with the data of *Wiberg* and *Nist* [11].

Diels-Alder reaction with cyclopentadiene:



(8) *(9)* *(10)*

The thermal diene reaction of *(3)* with cyclopentadiene in boiling dioxane gives the *endo*-bicyclo[2.2.1]heptene derivative *(8)*, which forms colorless crystals of m.p. 147 °C. Its structure follows from the ^1H–NMR spectrum [5]. This spectrum shows three triplets of equal area at $\tau = 3.6$, 6.4, and 7.85, which are to be assigned to the olefinic, tertiary, and methylene protons. The methylene protons here do not constitute an AB system because of the comparable shielding.

Treating *(8)* with hydrochloric acid or alkali affords the hitherto unknown bicyclo[2.2.1]heptene-2,3-dione *(9)*, which

is formally a homo-*ortho*-quinone. After distillation, the dione *(9)* is a yellowish-red oil which slowly crystallizes. The yellow crystals melt at 35 °C[12]. The ^{1}H–NMR spectrum[5] of the diketone shows a triplet at $\tau = 3.55$ for the two olefinic protons, a quintuplet at $\tau = 6.8$ for the two tertiary protons, and for the two methylene protons an AB system with shielding parameters $\tau = 7.1$ and 7.5 and a geminal coupling of 11 Hz; the B part of the system is split by 2-Hz coupling with the tertiary protons.

In D_2O the signals are changed in a characteristic way. The olefinic protons now form an AB system, whose components are centered at $\tau = 3.35$ and 3.73. The vicinal coupling of the two protons amounts to 6 Hz. Each component is again split by a 3-Hz coupling, which one finds again in the two, now separated multiplets for the tertiary protons at $\tau = 6.73$ and 6.85. The two methylene protons appear as a singlet at $\tau = 7.6$, which is split by a long-range coupling (*ca.* 1 Hz) with the two tertiary protons and the A component of the olefinic protons.

On addition of water a hydroxyl-proton signal appears at $\tau = 5.15$, which indicates that a carbonyl group of the diketone *(9)* is hydrated in aqueous solution, giving compound *(10)*. In this way we explain the reversible thermochromic behavior of dilute aqueous solutions of *(9)*, which are colorless *(10)* at 0–5 °C but deep yellow *(9)* at 80 °C.

The dione *(9)* is formally a Diels-Alder adduct of cyclopentadiene with dicarbon dioxide O=C=C=O, which is so far known only in derivatives[13]. This unknown carbon oxide occurs masked in the dichlorovinylene carbonate *(3)*, so that its thermal and photochemical cycloadditions can be simulated by *(3)*.

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[**] We wish to thank the Deutsche Forschungsgemeinschaft for generous financial support. We are also grateful to Prof. *F. Korte* for the interest he has shown in this work.

[1] *E. K. Ellingboe* and *L. R. Melby*, US.-Pat. 2816287 (Dec. 10, 1957), Chem. Abstr. *52P*, 12899g (1958). The preparative method of Chem. Werke Hüls [Fr. Pat. 1363740 (June 12, 1964); Chem. Abstr. *61P*, 11896e (1964)] proved less profitable.

[2] Measured in the condensed phase.

[3] Mercury lamp HPK 125 W, Philips, Pyrex glass as filter.

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[5] CCl_4 as solvent.

[6] The spectrum corresponds to that in *K. B. Wiberg* and *B. J. Nist*: Interpretation of NMR Spectra, Benjamin, New York 1962; spectrum No. 5-92 on page 363.

[7] *H. E. Mery* and *J. R. McCleon*, Tetrahedron *19*, 749 (1963).

[8] *J. M. Conia* and *J. L. Ripoll*, Bull. Soc. Chim. France, *1963*, 755, 773.

[9] *C. Rappe* and *L. Knutsson*, Acta chem. scand. *21*, 163 (1967).

[10] M.p. 267–269 °C (from ethanol), comparison with the preparation referred to on p. 759 of ref [8].

[11] *K. B. Wiberg* and *E. J. Nist*, J. Amer. chem. Soc., *85*, 2788 (1963).

[12] The crystals liquefy in a short time with decomposition.

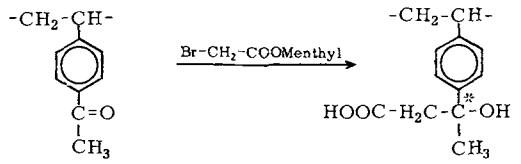
[13] The bisdiketal was prepared and examined by *R. W. Hoffman et al.*, Chem. Ber. *99*, 1892 (1966). Tetra(dimethylamino)-ethylene according to *H. Bredereck et al.*, Angew. Chem. *78*, 984 (1966); Angew. Chem. internat. Edit. *5*, 972 (1966).

Asymmetric Reduction of Polyvinylacetophenone[**]

By *Rolf C. Schulz*[***] and *H. Mayerhöfer*[*]

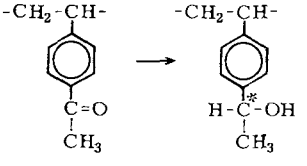
Asymmetric syntheses have so far been described only for compounds of low molecular weight. We have applied such reactions to macromolecular substances, in order to obtain optically active polymers.

The Reformatsky reaction between menthyl bromoacetate and acetophenone described by *Reid* and *Turner*[1] was applied to polyvinylacetophenone *(1)*. It could be shown by IR spectroscopy that the reaction took the expected course; however, since only insoluble polymers resulted, no value for the optical rotation or the optical yield could be determined.



(1)

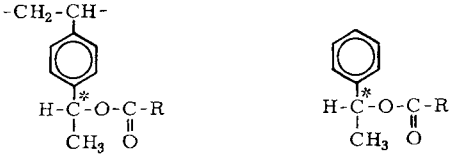
Since reduction of *(1)* by lithium aluminum hydride led to soluble poly-[4-(2-hydroxyethyl)styrene] *(2)*, an attempt was made to direct this reaction sterically. Products from $LiAlH_4$ and chiral alcohols [2,3] came into consideration as reducing agents. We used 1,2-*O*-cyclohexylidene-α-D-glucofuranose[2a] or quinine. In model reactions with acetophenone the optical yields of α-methylbenzyl alcohol were 15 % and 48 %, respectively.



(1) *(2)*

Spectroscopy and elemental analysis of derivatives of the reduction product *(2)* showed that all the keto groups were reduced. The asymmetric reagents could be separated by dialysis or precipitation from the polymers that were soluble in tetrahydrofuran or methanol. When the glucose derivative was used, the polymer *(2)* obtained was levorotatory. Reduction with $LiAlH_4$/quinine proved more advantageous; it afforded a dextrorotatory polymer *(2)*: $[\alpha]_{589} = +3.86$, $[\alpha]_{500} = +5.92$ ($c = 3.000$ in THF). If one assumes that the optically pure polymer has the same rotation as (+)-α-methylbenzyl alcohol ($[\alpha]_{589} = +43.3$, homogeneous; $[\alpha]_{500} = +65.5$, homogeneous)[4], then an optical yield of 9 % can be calculated.

To confirm this finding, derivatives of *(2)* and (+)-α-methylbenzyl alcohol were prepared. The *p*-nitrobenzoate *(3a)* of the polymer and of (+)-α-methylbenzyl alcohol *(4a)* have small negative rotations. However, the rotation of the polymer and of (+)-α-methylbenzyl alcohol are approximately doubled on reaction with phenyl isocyanate.



(3) *(4)*

(a), R = *(b)*, R =

(3b): $[\alpha]_{589} = +6.58$ ($c = 1.0$ in THF)
$[\alpha]_{500} = +9.8$ ($c = 1.0$ in THF)

(4b): $[\alpha]_{589} = +101.5$ ($c = 4.864$ in benzene) [5]
$[\alpha]_{589} = +40.8$ ($c = 4.88$ in benzene) 40.3 % optical purity
$[\alpha]_{500} = +57.4$ ($c = 4.88$ in benzene) 40.3 % optical purity
$[\alpha]_{500} = +39.8$ ($c = 4.88$ in THF) 40.3 % optical purity

From the rotations of the urethanes *(3b)* and *(4b)* the optical yield for the asymmetric reduction of polyvinylacetophenone *(1)* is 9.8 %. The agreement between the optical yields leads

to the conclusion that an asymmetric synthesis of the polymer has in fact been achieved.

These results demonstrate a new method for the synthesis of optically active polymers.

Experimental:

Polyvinylacetophenone was prepared according to *Kenyon*[6], and (+)-α-methylbenzyl alcohol according to *Červinka*[3] with $[\alpha]_{589} = +19.5°$ (homogeneous), in 45–48 % optical yield.

(+)-Poly-[4-(2-hydroxyethyl)styrene] *(2)*:

$LiAlH_4$ (2.112 g, 0.0553 mole) was suspended in tetrahydrofuran (250 ml), quinine ($[\alpha]_D = -172°$; 16.2 g, 0.05 mole) was added, and the mixture was boiled for 10 min. A solution of *(1)* (4 g, 0.0274 unit mole) in tetrahydrofuran (50 ml) was added dropwise during 10 min and the whole boiled under reflux for 6 h. The polymer was precipitated by pouring the mixture into 3 % sulfuric acid and was reprecipitated from tetrahydrofuran by 3 % sulfuric acid and then from tetrahydrofuran by saturated sodium hydrogen carbonate solution and water. Yield 2.5 g.

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[**] Part of the dissertation by *H. Mayerhöfer*, Mainz D 77.

[***] We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

[1] *J. A. Reid* and *E. E. Turner*, J. chem. Soc. (London) *1949*, 3365; *1950*, 3694.

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Formation of Polymethyl(methylene)aluminum

By *H. Sinn*[*], *H. Hinck*[*], *F. Bandermann*[*], and *H. F. Grützmacher*[**]

Complex formation between biscyclopentadienyltitanium(IV) compounds (Cp_2TiCl_2 and $Cp_2TiClCH_3$) and trimethylaluminum has a half-reaction time of $< 10^{-2}$ seconds even at −45 °C. In both cases the complex formation is accompanied by a very slow reaction. This is indicated by development of an absorption band at 460 nm which is at first synchronous with an evolution of methane. It thus seemed likely that the reaction should be considered as formation of the compounds with CH_2 bridges between Ti and Al that *C. Feay*[1] had isolated.

However, we observed that further methane was evolved after the band at 460 nm had developed; the reaction was therefore studied without use of a solvent and with a large excess of $Al(CH_3)_3$. The rate of initial evolution of methane followed the rate law:

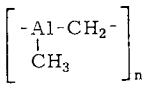
$$d[CH_4]/dt = k[Ti][Al(CH_3)_3]^{0.5}$$

If the initial molar ratio $Cp_2TiCl_2/Al(CH_3)_3$ was 1:100, the evolution of methane increased after *ca.* 100 hours at room temperature. The viscosity of the mixture increased from 0.9 cp to > 100 cp; after 350 hours the reaction mass solidified, yet slowly evolved more methane. In sum, almost 1 mole of methane was liberated per mole of $Al(CH_3)_3$.

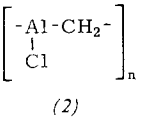
The solidified mass does not dissolve in petroleum ether, and swells in benzene; components of low molecular weight and products formed from the titanium compound are removed by extraction in a glass Soxhlet apparatus with benzene. The residue is a pale greyish powder with the composition C_2H_5Al. It reacts quantitatively with deuterium chloride:

$$C_2H_5Al + 3\,DCl \rightarrow AlCl_3 + D_2CH_2 + DCH_3$$

We therefore propose formula *(1)*, where *n* is probably about 100. (If this were not so, more DCH_3, would be formed by reaction with the end groups.)



(1)



(2)

In this connection the compound *(2)* that was obtained by *H. Lehmkuhl* and *R. Schaefer*[2] by a quite different route should be noted.

Before the extraction, the reaction mass evolves only traces of $Al(CH_3)_3$ in a high vacuum. It dissolves in tetrahydrofuran. Viscosity determination (on the basis of the Staudinger relation that is valid for polystyrene) gave a mean degree of polymerization $P_n = 1/(1-p) = 20$, corresponding to a degree of reaction $p = 0.95$, whereas we expected $p = 0.85$ to 0.90 on the basis of the amount of methane evolved.

The extraction residue, swollen and suspended in benzene, reacts with titanium tetrachloride with formation of a voluminous, almost black, mass. A suspension of this compound in hydrocarbons is an efficient catalyst for the polyreaction of ethylene and α-olefins.

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[1] *D. C. Feay*, Belg. Pat. 635987 (Feb. 10, 1964); Belg. Pat. 635988 (Feb. 10, 1964); *D. C. Feay* and *G. S. Fujioka*, Lecture, 10th International Conference on Coordination Chemistry, Sept. 1967.

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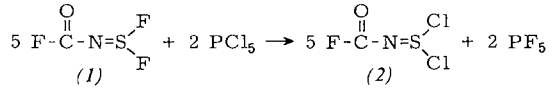
N-(Fluoroformyl)iminosulfur Dichloride and *N*-(Chloroformyl)iminosulfur Dichloride

By *H. W. Roesky* and *R. Mews*[*]

As part of our study of sulfur-nitrogen compounds[1] we have prepared iminosulfur dichlorides $-N{=}SCl_2$ from the corresponding fluoro derivatives. *N*-(Fluoroformyl)iminosulfur difluoride *(1)* [2] reacts with phosphorus pentachloride at room temperature, giving *N*-(fluoroformyl)iminosulfur dichloride *(2)* and phosphorus pentafluoride.



(1) *(2)*

33 g of *(1)* is added dropwise with ice cooling to 23.1 g of PCl_5. The mixture is then stirred for 2 h at 0 °C and for 24 h at room temperature. The volatile products are removed in a

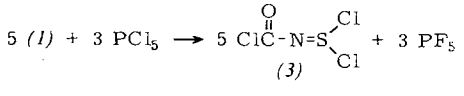
high vacuum at room temperature and trapped at −80 °C (acetone/Dry Ice) and −196 °C (liquid nitrogen). The contents of the (−80 °C)-trap (31.6 g) were fractionated at water-pump vacuum through a 25-cm packed column: b.p. 42 to 44 °C/12–14 mm; yield 26 g (61 %); molecular weight 162 (cryoscopic in benzene; theor. 164).

Compound *(2)* is a pale yellow liquid, which reacts with V4A steel with decomposition. The compound *(1)* reacts also with aluminum trichloride to give *(2)*, but in this case only a low yield of product is obtained.

The IR spectrum (capillary film) in the NaCl and KBr region includes bands at 1800 (vs), 1240 (vs), 1120 (with shoulder, vs), 838 (vs), 760 (vs), 655 (m), 628 (w), 590 (w), 535 (w), 495 (m), and 440 (vs) cm^{-1}.

The ^{19}F–NMR spectrum includes a singlet at $\delta_F = -19.8$ ppm against CCl_3F as external standard.

Reaction of *(1)* with PCl_5 at 40 to 60 °C gives *N*-(chloroformyl)iminosulfur dichloride *(3)*:



$$5\ (1) + 3\ PCl_5 \longrightarrow 5\ ClC(=O)-N=SCl_2\ (3) + 3\ PF_5$$

27 g of *(1)* is added slowly with ice cooling to 28 g of PCl_5. The mixture is then stirred for 12 h at 40 °C and for 10 h at 60 °C. A clear solution results which is worked up as described above. B.p. 32 °C/1.5 torr; m.p. −7 °C (great tendency to supercooling); yield 19 g (51 %); molecular weight 181 (cryoscopic in benzene; theor. 180.5). Compound *(3)* is a yellow liquid. The IR spectrum shows bands at 2300 (w), 1740 (vs), 1255 (m), 1170 (vs), 947 (s), 755 (s), 670 (m), 540 (w), and 425 (s) cm^{-1}.

Tentative assignments for *(2)* and *(3)* are: vibrations at 1800 and 1740 ν(CO), 1240 and 1170 ν(N=S), 1120 ν(CF), 947 ν(CCl), and 440 and 425 cm^{-1} ν(SCl).

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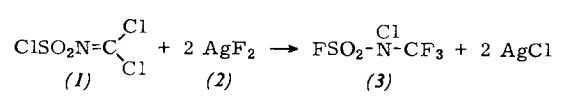
N-Chloro-*N*-(trifluoromethyl)-fluorosulfonamide [1]

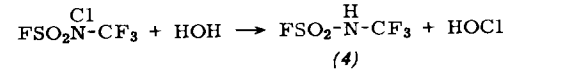
By *H. W. Roesky* [*]

N-(Dichloromethylene)chlorosulfonamide *(1)* [2] reacts with silver difluoride *(2)* to give *N*-chloro-*N*-(trifluoromethyl)-fluorosulfonamide *(3)* in 22% yield.



$$ClSO_2N=C(Cl)Cl\ (1) + 2\ AgF_2\ (2) \longrightarrow FSO_2-N(Cl)-CF_3\ (3) + 2\ AgCl$$

The compound *(3)* is a slightly yellow liquid having an unpleasant pungent odor. It liberates bromine from aqueous potassium bromide solution. The first step in the hydrolysis of *(3)* is the formation of hypochlorous acid.



$$FSO_2N(Cl)-CF_3 + HOH \longrightarrow FSO_2-N(H)-CF_3\ (4) + HOCl$$

N-Trifluoromethylfluorosulfonamide *(4)* could be isolated as the tetraphenylphosphonium salt [2].

The temperature-dependence of the vapor pressure of *(3)* between −20 and +15 °C gives the vapor pressure equation

$$\log p_{torr} = (-1503/T) + 7.31$$

The heat of vaporization of *(3)* is $\Delta H = 6850$ cal/mole and the Trouton constant is approximately 22.2 cal/deg. The extrapolated boiling point found from the vapor pressure curve is 33.9 °C, while the experimental value is 31–33 °C [3].

Elemental analysis verifies the composition of *(3)*. The mass spectrum shows fragments [4] at $m/e = 166$ (FSO_2NCF_3), 147 (FSO_2NCF_2 or SO_2NCF_3), and 83 (FSO_2 or NCF_3).

The ^{19}F–NMR spectrum of *(3)* gives a doublet at $\delta_F = 61.6$ ppm for the CF_3 group and a quartet at $\delta_F = -44.8$ ppm for the SO_2F group against CCl_3F as the external standard. The intensity ratio is 3:1. The coupling constant J_{FF} is 6.5 Hz. The following absorptions occur in the NaCl and KBr region of the IR spectrum (capillary film with AgCl plates): 1630 (w), 1595 (w), 1578 (w), 1480 vs), 1420 (w), 1280 (vs), 1250 (s), 1210 (vs), 1160 (vs), 1090 (w), 975 (vs), 930 (w), 810 (vs), 740 (w), 600 (vs), 565 (w), 525 (w), and 490 (w) cm^{-1} [5].

Procedure:

0.2 mole of *(1)* is added dropwise from a dropping funnel to an excess of silver difluoride in a two-neck flask, with stirring by a magnetic stirrer. The second neck of the flask carries a distillation head with a collecting flask followed by two condensation traps (cooled with acetone/Dry Ice). A yellow liquid collects in the receiver and in the first trap. NO_2 and SO_2F_2 are present as impurities. After the first trap has warmed to room temperature, the liquids are combined and fractionated in a packed column 30 cm long.

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[1] Part XII of Sulfur-Nitrogen Compounds. – Part XI: *H. W. Roesky*, Inorg. nucl. Chem. Letters, in press.

[2] *H. W. Roesky* and *U. Biermann*, Angew. Chem. *79*, 904 (1967); Angew. Chem. internat. Edit. *6*, 882 (1967).

[3] According to the analytical results, the ^{19}F–NMR and IR spectra, and the molecular weight, the 33–51 °C fraction had the same composition.

[4] The molecular ion was found only faintly at $m/e = 201$.

[5] w = weak, s = strong, vs = very strong.

Simple Synthesis of Oligomeric Phenyl-phosphines and -arsines

By *H. Schumann, A. Roth*, and *O. Stelzer* [*]

Oligomeric organo-phosphines and -arsines of defined composition have hardly been known hitherto. As well as tetra-organo-diphosphines and -diarsines and cyclic oligomers, only pentaphenyltriphosphane [1] has been described, though the possible formation of a tris(diphenylphosphino)arsine [2] has recently been mentioned. We have now found, in treatment of organostannylphosphines and organostannylarsines with phenylphosphorus chloride or phenylarsenic chloride, a simple process that makes readily accessible good yields of pure stable compounds with 2, 3, or 4 phosphorus or arsenic atoms linked to each other.

Tris(trimethylstannyl)-phosphine and -arsine in ethereal solution under an argon atmosphere react at room temperature with diphenylphosphorus chloride or diphenylarsenic chloride with elimination of trimethyl tin chloride and

formation of tris(diphenylphosphino)-phosphine *(1a)* and -arsine *(1b)* or tris(diphenylarsino)-phosphine *(1c)* and -arsine *(1d)*, respectively:

$$[(CH_3)_3Sn]_3R + 3\,(C_6H_5)_2XCl \rightarrow \underset{\displaystyle X(C_6H_5)_2}{\overset{\displaystyle (C_6H_5)_2X \quad X(C_6H_5)_2}{R}} + 3\,(CH_3)_3SnCl$$

(1)

	X	R	M.p. (°C)	Yield (%)
(a)	P	P	118–120	85
(b)	P	As	120–123	59
(c)	As	P	169–172	60
(d)	As	As	143–147	51

After being stirred for 6 h the ethereal solutions were evaporated in a vacuum, and the products were precipitated by addition of pentane. Trimethyltin chloride can be isolated in quantitative yield from the filtrate. The compounds *(1a)–(1d)*, obtained in pure form after repeated reprecipitation from ether/pentane, are extremely sensitive to oxygen and decompose with yellow coloration immediately on access to air; after decomposition of *(1a)*, triphenylphosphine, tetraphenyldiphosphine, and yellow phenylphosphine $(C_6H_5P)_n$ were isolated.

Analogously, reaction of diphenylphosphorus chloride or diphenylarsenic chloride with phenyl bis(trimethylstannyl)-phosphine or phenylbis(trimethylstannyl)arsine[3] afforded syntheses of the new compounds bis(diphenylarsino)phenylphosphine *(2a)*, bis(diphenylphosphino)phenylarsine *(2b)*, and bis(diphenylarsino)phenylarsine *(2c)*; reaction of diphenylphosphorus chloride with diphenyl(trimethylstannyl)-arsine gave (diphenylphosphino)diphenylarsine *(3)*:

$$[(CH_3)_3Sn]_2RC_6H_5 + 2\,(C_6H_5)_2XCl \rightarrow \underset{\displaystyle C_6H_5}{\overset{\displaystyle (C_6H_5)_2X \quad X(C_6H_5)_2}{R}} + 2\,(CH_3)_3SnCl$$

(2)

	X	R	M.p. (°C)	Yield (%)
(a)	As	P	155–158	90
(b)	P	As	125–129	66
(c)	As	As	185–190	65

$$(CH_3)_3Sn{-}As(C_6H_5)_2 + (C_6H_5)_2PCl \rightarrow (C_6H_5)_2P{-}As(C_6H_5)_2 + (CH_3)_3SnCl$$

(3), m.p. 115–117 °C, yield 71 %

The properties of compounds *(2a)–(2c)* and *(3)* are the same as those of three-fold substituted phosphines and arsines, but the sensitivity to oxygen decreases in the order $RX_3 \rightarrow RX_2 \rightarrow RX$, also with increasing substitution of the central atom R by phenyl groups.

In the pure state all the compounds are colorless crystalline substances that are found to dissolve without decomposition in diethyl ether, cyclohexane, and aromatic hydrocarbons. Their structures were proved by complete elemental analyses, cryoscopic determinations of molecular weight, and IR spectra[4]. In the IR spectra are found, not only the vibration bands of the phenyl nuclei dependent on the P and As substituents, but also the bands required by the C_{3v} symmetry $\nu_{as}RX_3$ and ν_sRX_3 at 486 and 427 cm^{-1} *(1a)*, 357 and 280 cm^{-1} *(1b)*, 311 and 274 cm^{-1} *(1c)*, and 285 and 262 cm^{-1} *(1d)*, the bands required by the C_{2v} symmetry $\nu_{as}RX_2$ and ν_sRX_2 at 354 and 282 cm^{-1} *(2a)*, 311 and 293 cm^{-1} *(2b)*, and 293 and 262 cm^{-1} *(2c)*, as well as the bands required for the C_s symmetry ν P–As at 353 cm^{-1} *(3)*.

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[1] *E. Wiberg, M. Van Ghemen,* and *G. Müller-Schiedmayer,* Angew. Chem. *75*, 814 (1963); Angew. Chem. internat. Edit. *2*, 646 (1963).

[2] *T. A. George* and *M. F. Lappert,* Chem. Commun. *1966*, 463.

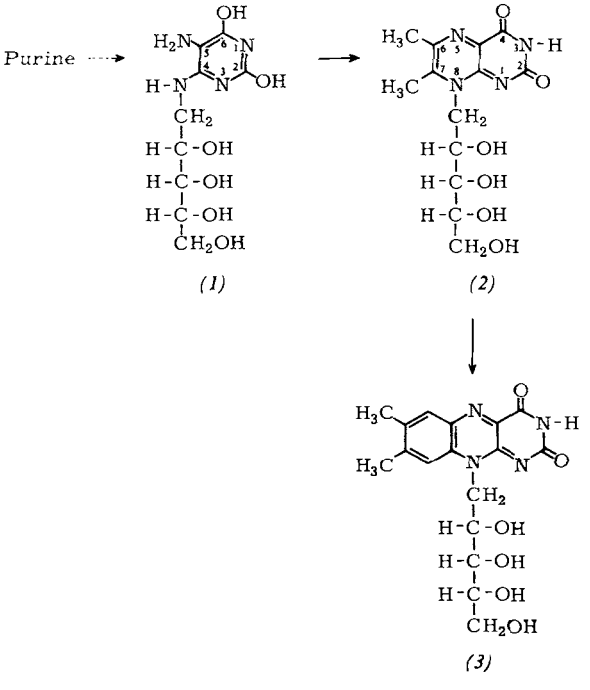
[3] *H. Schumann* and *A. Roth,* unpublished.

[4] Perkin-Elmer 221, in Nujol suspension; Beckman IR 11, in Nujol suspension between polyethylene.

Accumulation of 2,5-Diamino-6-hydroxy-4-ribityl-aminopyrimidine in a Riboflavin-deficient Mutant of *Saccharomyces cerevisiae*

By *A. Bacher* and *F. Lingens*[*]

The biosynthesis of riboflavin *(3)* leads from a purine compound[1] by way of several intermediates to 5-amino-2,6-dihydroxy-4-ribitylaminopyrimidine *(1)*[2] and then to 6,7-dimethyl-8-rityllumazine *(2)*[3]. 4,5-diaminopyrimidine compounds were expected to be precursors of *(1)*.



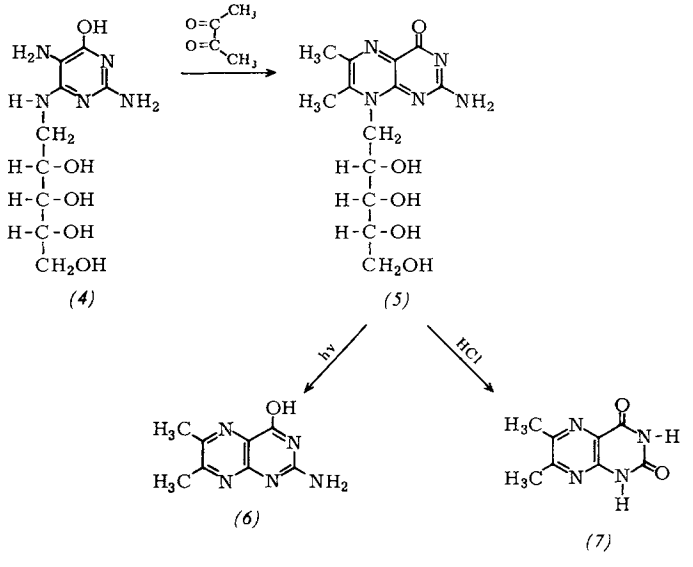
We have shown that a riboflavin-deficient mutant of *Saccharomyces cerevisiae*, HK 859[4], forms an intensely blue-green fluorescing compound on incubation in minimal medium supplemented with biacetyl. This product, which is not formed in absence of biacetyl, was isolated as follows: The yeast was grown in minimal medium[4] supplemented with yeast extract, peptone, and riboflavin, centrifuged off, and incubated with fresh minimal medium containing 0.8 ml biacetyl per liter. The cell-free medium was placed on a column of Magnesiumsilikat "Woelm". The column was washed with deionized water and eluted with acetone/4 N ammonia (2:1). The eluate was evaporated to dryness in a vacuum and placed on a column of Dowex 50 Wx 8 (NH_4^+ form). The column was washed with deionized water and

eluted with 0.1 N phosphate buffer (pH = 7). The green-fluorescing fractions were combined and once more adsorbed on Magnesiumsilikat "Woelm" (elution as described above). Further purification was by chromatography on a column of CM-Sephadex C-25 (Na^+ form, elution with distilled water). The green-fluorescing fractions were combined and lyophilized. All operations were conducted in dim light in a darkroom.

The yellow compound thus obtained decomposed in aqueous solution in sunlight with separation of colorless crystals, which were identified as 2-amino-4-hydroxy-6,7-dimethylpteridine *(6)* by comparative thin-layer chromatography with six different solvents. Hydrolysis of the accumulated substance in 6 N HCl at 115 °C (24 h) yielded 6,7-dimethyllumazine *(7)*, which was identified in the same way. The UV spectrum of the accumulated substance closely resembled that of 2-amino-4,8-dihydro-6,7,8-trimethyl-4-oxopteridine. Measurement of the optical rotatory dispersion and the mass spectrum revealed close similarity to 6,7-dimethyl-8-ribityllumazine *(2)*. We thus assign to the accumulated compound the structure 2-amino-4,8-dihydro-6,7-dimethyl-4-oxo-8-ribitylpteridine *(5)*. Compound *(5)* was synthesized[5] and proved identical with the accumulated compound in UV and IR spectra and in R_F values in four different solvents.

These results lead us to the conclusion that the mutant investigated originally accumulates 2,5-diamino-6-hydroxy-4-ribitylaminopyrimidine *(4)*.

We assume that *(4)* or a phosphoric ester of *(4)* is an intermediate in riboflavin biosynthesis and is converted by enzymatic deamination into the 5-amino-2,6-dihydroxy-4-ribitylaminopyrimidine *(1)* previously detected[2]. We further assume that riboflavin is formed from a guanine compound rather than from a xanthine compound as supposed hitherto[6].



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[1] *G. W. E. Plaut*, Ann. Rev. Biochem. *30*, 409 (1961).

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[4] *O. Oltmanns* and *F. Lingens*, Z. Naturforsch. *22b*, 751 (1967).

[5] *J. Davoll* and *D. D. Evans*, J. chem. Soc. (London) *1960*, 5041.

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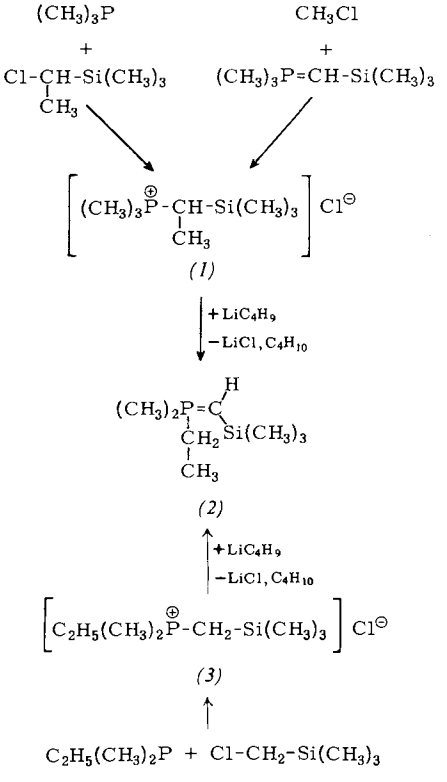
Silyl Shift in Phosphorus Ylides

By *H. Schmidbaur* and *W. Tronich* [*]

The ylide function in trialkylalkylidenephosphoranes is stabilized by silyl residues and destabilized by alkyl residues[1]. While examining the combined effects of silyl and alkyl ligands on an ylide C atom in alkylidenephosphoranes, we discovered a new type of 1,3-silyl shift.

1-(Trimethylsilyl)ethyltrimethylphosphonium chloride *(1)* can be obtained from trimethylphosphine and 1-chloroethyltrimethylsilane under mild conditions (8 days, < 50 °C). The same product is obtainable in quantitative yield from trimethyl(trimethylsilylmethylene)phosphorane[1] and methyl chloride (1 day, −30 °C). Volatile impurities are removed in a vacuum to leave colorless crystals of *(1)*, decomp. 180–185 °C.

Deprotonation of this phosphonium salt *(1)* with *n*-butyllithium at 20 °C in suspension in diethyl ether/*n*-hexane, followed by filtration to remove the precipitated LiCl and distillation under vacuum, surprisingly leads to ethyldimethyl(trimethylsilylmethylene)phosphorane *(2)*, b.p. 83–84 °C/14 torr, m.p. −32 to −30 °C, 65% yield. The structure of *(2)* is established by the ^1H-NMR spectrum[1] and by independent synthesis from ethyldimethylphosphine and chloromethyltrimethylsilane. The structures of *(1)* and *(3)* were also verified by NMR spectroscopy.



The formation of *(2)* from *(1)* on deprotonation with *n*-C_4H_9Li is interpreted as a silyl transfer from an ethyl group attached to phosphorus onto one of the methyl groups at the phosphorus, and corresponds to an exchange of a proton and a trimethylsilyl cation. Experiments with homologous compounds have shown that the silyl shift is a general phenomenon.

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[1] *H. Schmidbaur* and *W. Tronich*, Chem. Ber. *100*, 1032 (1966); *101*, 595, 604 (1968); Angew. Chem. *79*, 412 (1967); Angew. Chem. internat. Edit. *6*, 448 (1967).

Stereospecific *cis* Addition of Dichloroketene to *cis*- and *trans*-Cyclooctenes

By *R. Montaigne* and *L. Ghosez* [*]

The reaction of dichloroketene with olefins and dienes yields readily 1:1 cycloadducts [1], mechanistic alternatives being a synchronous or a two-step dipolar process. We now describe the stereochemistry of the cycloaddition.

Dichloroketene (liberated *in situ* from dichloroacetyl chloride and triethylamine at room temperature) reacts smoothly with *cis*-cyclooctene to yield the compound *cis*-10,10-dichlorobicyclo[6.2.0]decan-9-one *(1a)* (yield 50 %; b.p. 91 °C/0.4 torr; n_D^{25} = 1.5128) and with *trans*-cyclooctene to form the *trans*-isomer *(1b)* (yield *ca.* 100 %; b.p. 79.5 °C/0.2 torr; n_D^{25} = 1.5077). Intercontamination is estimated, gas chromatographically, to be lower than 4 % [2].

Both adducts show a strong absorption band at 1805 cm^{-1} indicative of an α,α-dichlorocyclobutanone. The structural assignments are supported by the ^1H–NMR spectra (60 MHz; CCl_4; TMS as internal standard):

(1a) τ = 6.4 (1H); 7.07 (1H); 7.75–8.25 (4H); 8.25–8.82 (8H)

(1b) τ = 6.63 (1H); 7.39 (1H); 7.62–9.1 (12H).

Dechlorination of *(1a)* and *(1b)* with tributyltin hydride in refluxing cyclohexane containing catalytic amounts of azobisisobutyronitrile yields respectively the parent ketones: *cis-(2a)* (yield 56 %; b.p. 51–52 °C/0.2 torr; n_D^{25} = 1.4859; $\nu_{C=O}$ = 1772 cm^{-1}) and *trans-(2b)* (yield 77 %; b.p. 59–61 °C/0.3 torr; n_D^{25} = 1.4821; $\nu_{C=O}$ = 1772 cm^{-1}).

The configurations of *(1a)*, *(1b)*, *(2a)*, and *(2b)* can be deduced from the comparison of their IR spectra in the 1500 to 1400 cm^{-1} region with those of *cis*- and *trans*-cyclooctenes and their carbene-adducts: the *cis* compounds show two main bands in this region whereas the *trans* configurations show only one [3].

	νCH_2 (cm^{-1})		
	cis		*trans*
Cyclooctene	1469	1444	1452
9,9-Dichlorobicyclo[6.1.0]nonane	1470	1450	1445
Bicyclo[6.1.0]nonane	1472	1445	1458
10,10-Dichlorobicyclo[6.2.0]decan-9-one	1465	1448	1450
Bicyclo[6.2.0]decan-9-one	1463	1447	1452

The addition of dichloroketene onto olefins is thus a *cis* stereospecific cycloaddition [4]. Furthermore, as we obtained the same results using either pentane or acetonitrile as solvent, the stereochemical course of the reaction is entirely independent of the dielectric constant of the reaction medium. The experimental evidence cited above leads to the following conclusions:

1. The reaction makes available a two-step method of synthesis of cyclobutanones having the same configuration as the olefins from which they are derived.

2. A rotating intermediate being excluded, the addition appears to occur in a single step. This indicates that the selection rules for concerted cycloaddition reactions [5] cannot be applied as such to the cycloaddition of ketenes.

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[1] *H. C. Stevens, D. A. Reich, D. R. Brandt, K. R. Fountain* and *E. J. Gaughan*, J. Amer. chem. Soc. *87*, 5257 (1965); *L. Ghosez, R. Montaigne* and *P. Mollet*, Tetrahedron Letters *1966*, 135; *R. Montaigne*, Dissertation, University of Louvain 1968.

[2] The small amount of isomerisation occurs during the work-up procedure. Direct dehalogenation of the crude reaction mixtures with $(C_4H_9)_3SnH$ leads to *(2a)* or *(2b)* with less than 1 % intercontamination.

[3] *P. Laroche*, Dissertation, University of Louvain, 1965.

[4] Diphenyl- and dimethylketenes have been shown to add stereospecifically to enol ethers: *R. Huisgen, L. Feiler*, and *G. Binsch*, Angew. Chem. *76*, 892 (1964); Angew. Chem. internat. Edit. *3*, 753 (1964); *J. C. Martin, V. W. Goodlett*, and *R. D. Burpitt*, J. org. Chemistry *30*, 4309 (1965).

[5] *R. Hoffmann* and *R. B. Woodward*, J. Amer. chem. Soc. *87*, 2046 (1965).

The Absolute Configuration of Chlorophyll [1]

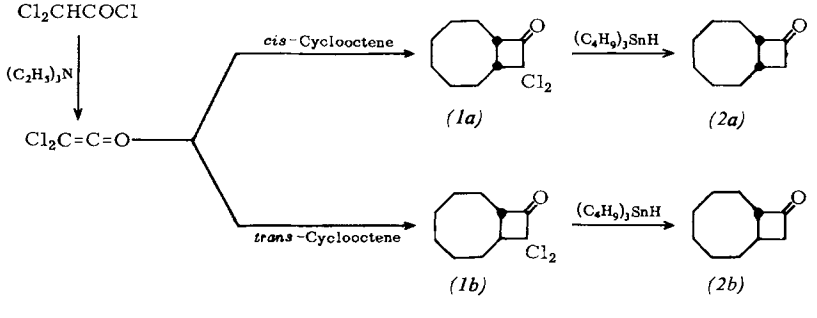
By *H. Brockmann jr.* [*]

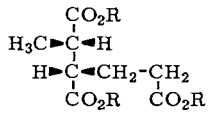
Tri-*p*-bromophenacyl (+)-*threo*-dihydrohematinate *(1)* [3], m.p. 108.5–109 °C, was obtained by *Fleming* [2] from (−)-α-santonin, and thus has the absolute configuration(2*S*,3*S*) [2]. Tri-*p*-bromophenacyl (−)-*threo*-dihydrohematinate *(2)* is formed from crystalline (+)-*threo*-dihydrohematinic acid *(3)*, which was first prepared by *Fleming* [2] by hydrolysis of synthetic dextrorotatory *threo*-dihydrohematinimide *(4)*, ($[\alpha]_D^{20}$ = +67 °). (+)-*(4)* consequently has the absolute configuration (2*R*,3*R*).

A levorotatory oily *threo*-dihydrohematinimide ($[\alpha]_D^{20}$ = −46 ° in methanol), which did not give a crystalline product on hydrolysis, but whose crystalline benzylamine salt gave an IR spectrum identical with that of the benzylamine salt of the racemic imide, and which gave no melting point depression with this salt, was obtained by *Ficken et al.* [4] and earlier by *H. Fischer* [5] by oxidative degradation of pyropheophorbide-*a*, a derivative of chlorophyll-*a*. Comparison of the rotation values of dihydrohematinimides prepared by different routes indicated that chlorophyll-*a* has the absolute configuration (7*S*,8*S*) [2].

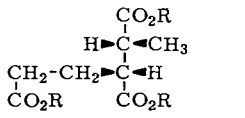
The degradation product from (−)-α-santonin had not yet been directly compared with a degradation product of chlorophyll.

Repetition of the oxidative degradation of methylpheophorbide-*a* with chromium trioxide in sulfuric acid [5], hydrolysis of the acidic degradation products with hydrochloric acid, and esterification with *p*-bromophenacyl bromide, followed by chromatography on silica gel with chloroform gave a moderate yield of crystalline dextrorotatory tri-*p*-bromophenacyl *threo*-dihydrohematinate, m.p. 109 °C, $[\alpha]_D^{20}$ = +2.6 ±0.3 °, $[\alpha]_{436}^{20}$ = +9.5 ± 0.4 °, *c* = 1.1 in chloroform. This product gave no melting point depression with *(1)* from

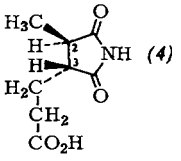




(1), R = $CH_2COC_6H_4$-p-Br



(2), R = $CH_2COC_6H_4$-p-Br
(3), R = H



(4)

(−)-α-santonin[6], and had the same R_f value in the thin layer chromatogram (silica gel HF_{254}, chloroform) as *(1)*, *(2)*[6], and the racemic ester. A simultaneously crystallized mixture of *(1)* from chlorophyll-*a* and *(2)* [from *(4)*] melts at 119 °C, and the melting point is not depressed by the addition of racemic ester.

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[1] Part XVI of Further Findings on Chlorophyll and Hemin. – Part XV: *H. H. Inhoffen* and *W. Nolte*, Tetrahedron Letters *1967*, 2185.

[2] *I. Fleming*, Nature (London) *216*, 151 (1967).

[3] The designations *threo* and *erythro* are preferable to *trans* and *cis* [4] in the case of open-chain compounds.

[4] *G. E. Ficken*, *R. B. Johns*, and *R. P. Linstead*, J. chem. Soc. (London) *1956*, 2272.

[5] *H. Fischer* and *H. Wenderoth*, Liebigs Ann. Chem. *537*, 170 (1939); *545*, 140 (1940).

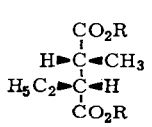
[6] I am grateful to Dr. *I. Fleming*, Cambridge (England), for authentic samples of *(1)* and *(2)* and for information about his rotation values, which agree with the value found by me.

The Absolute Configuration of Bacteriochlorophyll[1]

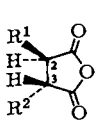
By *H. Brockmann jr.*[*]

Racemic *threo*-3-ethyl-2-methylsuccinic acid *(1)* was first resolved by *Berner* and *Leonardsen*[2]. The configuration of (+)-*(3)* was related to that of (+)-*(4)* and (+)-*(5)* by comparison of the optical rotations of acids, esters, and cyclic anhydrides at the sodium D line[2]. The absolute configuration of (+)-2,3-dimethylsuccinic anhydride *(4)* was very reliably[3] deduced by the application of the Kirkwood rule[4] on the basis of the known absolute configuration of (2*R*)-(+)-methylsuccinic anhydride *(6)*[3], which was established by X-ray diffraction[5]. Thus (+)-*threo*-3-ethyl-2-methylsuccinic acid is supposed to have the absolute configuration (2*R*,3*R*).

Like *Berner* and *Leonardsen*[2], we resolved racemic *(1)* into the enantiomers with strychnine, and prepared the di-*p*-bromophenacyl ester *(2)* (m.p. 115 °C, $[\alpha]_D^{20} = -49.4 \pm 3°$, $c = 1.3$ in chloroform) in good yield (86%) from the dextrorotatory acid *(1)*.



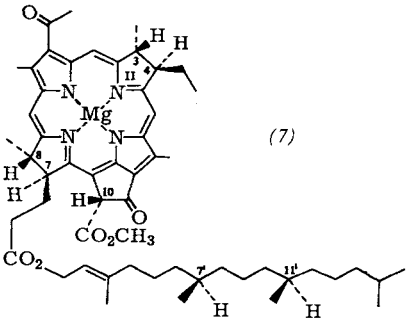
(1), R = H
(2), R = $CH_2COC_6H_4$-p-Br



(3), R^1 = CH_3, R^2 = C_2H_5
(4), R^1 = R^2 = CH_3
(5), R^1 = R^2 = C_2H_5
(6), R^1 = CH_3, R^2 = H

Levorotatory ester *(2)* (m.p. 112–113 °C, $[\alpha]_D^{24} = -37°$) was obtained by *Golden et al.*[6] by the oxidative degradation of a bacteriochlorophyll derivative, whose configuration in ring II must therefore be (3*R*,4*R*).

Bacteriochlorophyll *(7)* has already been converted by *Fischer*[7] into a derivative of chlorophyll-*a*[8], and so[9] has the same absolute configuration as chlorophyll-*a* at C-7 and C-8, which was recently recognized by *Fleming* as (7*S*,8*S*)[1,10]. If the 10-methoxycarbonyl group is assumed to occupy the energetically more favorable *trans* position with respect to the 7-propionic acid side chain, as has been found for derivatives of chlorophyll-*a*[11] and -*b*[12], then formula *(7)* represents the constitution and the absolute configuration at all the carbon atoms of bacteriochlorophyll[13].



(7)

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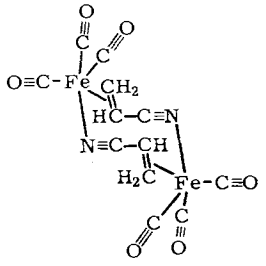
Acrylonitrile as a Hard and Soft Base in Di-μ-acrylonitrilebis(tricarbonyliron)

By *M. L. Ziegler*[*]

Three complexes having the compositions σ-$Fe(CO)_4AN$ *(2)*, π-$Fe(CO)_4AN$ *(3)*[1], and σ,π-$[Fe(CO)_3AN]_2$ *(1)*[2] have been isolated from the system $Fe(CO)_5$/acrylonitrile (AN). In

(2), the acrylonitrile molecule is bound *via* the nitrogen atom, and the trigonal bipyramid of the $Fe(CO)_5$ is axially substituted. In *(3)*, the olefinic double bond is coordinated, and the bipyramid is equatorially substituted.

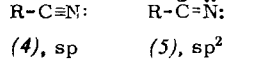
According to the HSAB concept [3], acrylonitrile is both a soft and a hard base, depending on whether the molecule reacts *via* the olefinic double bond or *via* the free electron pair on the nitrogen. It should therefore be possible to distinguish between a hard and a soft "position" in $Fe(CO)_5$, since hard ligands always substitute in the axial position [2]. X-ray structural analysis of *(1)* has shown that acrylonitrile is coordinated both as a hard and as a soft base in this complex. *(1)* contains



a ring system in which both of the iron atoms and both of the acrylonitrile molecules take part.

Each of the iron atoms is coordinated to one of the acrylonitrile molecules *via* the nitrogen atom and to the other *via* the olefinic double bond. The configuration at the iron atoms is a compromise between a trigonal bipyramid and a tetragonal pyramid. If the configuration is regarded as a distorted trigonal bipyramid, the olefinic double bonds have replaced an equatorial CO group and the nitrogen atoms an axial CO group, as must be expected from *(2)* and *(3)*.

According to the existing results, the $C\equiv N \rightarrow Fe$ linkage is not linear. This is understandable if the nitrogen is assumed to be sp^2 hybridized. In free nitriles, the resonance hybrids



(4), sp *(5)*, sp^2

(4) and *(5)* are present in roughly the same amounts [4], so that sp^2 hybridization may be assumed in *(1)*.

The compound *(1)* crystallizes in the triclinic system with the space group $C_i^1-P1_1^-$, with one molecule in the unit cell. The lattice constants are $a = 6.40$ Å, $b = 9.57$ Å, $c = 6.51$ Å, $\alpha = 93.0°$, $\beta = 106.6°$ $\gamma = 105.4°$. The structure was determined by three-dimensional Patterson and Fourier syntheses. The provisional *R* value is 20 %.

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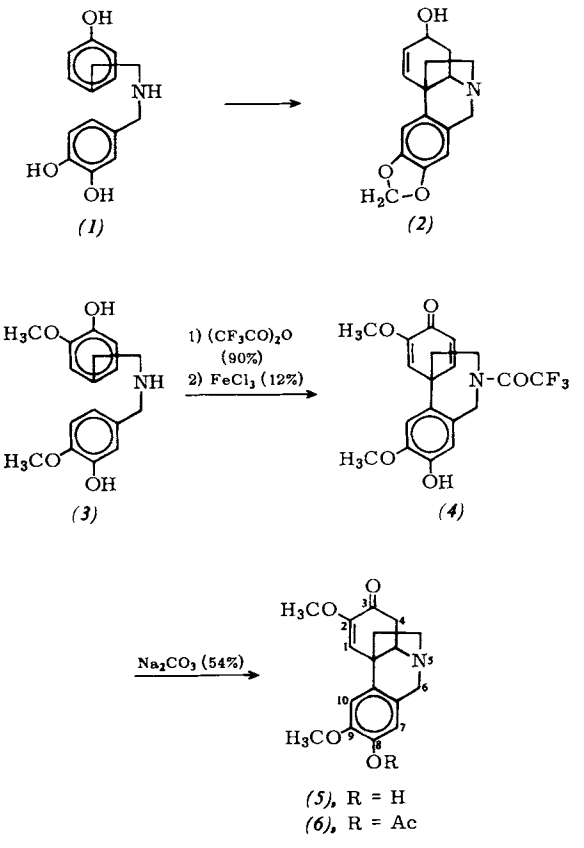
Model Reaction for the Biosynthesis of the Crinin Alkaloids [1]

By *B. Franck* and *H. J. Lubs* [*]

Crinin *(2)* and about thirty similar alkaloids from Amaryllidaceae are formed in the plant cell by oxidative condensation of norbelladin *(1)*, according to a hypothesis advanced by *Barton* [2] and verified by isotope experiments [3]. On the basis of this biosynthetic path, we found the ring system *(5)* of the crinin alkaloids particularly easy to prepare from a norbelladin derivative *(3)*.



Methoxy-*O*-methylnorbelladin *(3)* [4] was *N*-trifluoroacetylated and then oxidized for 48 hours at 20 °C in the two-phase system $CHCl_3$/1N $FeCl_3$ (1:1). Chromatography of the reaction mixture (ethyl acetate/benzene, 1:1, on silica gel G) gave the dienone *(4)* in 12 % yield. This underwent a second intramolecular condensation on hydrolysis with $CHCl_3$/2 N Na_2CO_3 (20 °C) to give the amine *(5)* $C_{17}H_{19}NO_4$, m.p. 232–234 °C (dec.), which takes up 1 mole of H_2 on hydrogenation with H_2/Pd in CH_3OH. The structure *(6)* is verified for the monoacetate $C_{19}H_{21}NO_5$, m.p. 210 °C, by the following spectroscopic data: IR spectrum in KBr: 1760 (ester), 1695, 1625 cm^{-1} (enone); NMR spectrum in $CDCl_3$ (TMS = 0): $\delta = 2.30$ ($COCH_3$), 3.75, 3.88 (2 OCH_3), 6.47, 6.75, and 6.98 (H on C-1, 7, 10); mass spectrum at 70 eV: $m/e = 343$ (91 %, $M^{\oplus}$), 301 (base peak, $M-CH_2=C=O$), 286 (301 − CH_3), 272 (301 − CHO), 258 (286 − CO), 227 (258 − CH_3).

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Slow Inversion at Pyramidal Nitrogen: Isolation of Diastereomeric 7-Chloro-7-azabicyclo-[4.1.0]heptanes at Room Temperature

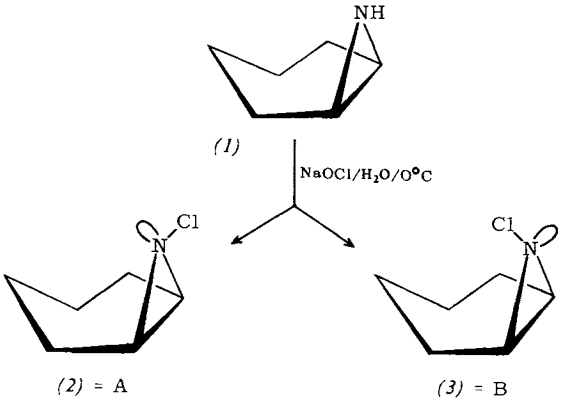
By *Dorothee Felix* and *A. Eschenmoser*[*]

The question of the existence of stereoisomerism at room temperature due to slow inversion at pyramidal nitrogen is a classical problem of stereochemistry[1]. On the basis of simple steric strain arguments it had been suggested[2] many years ago that this type of stereoisomerism might be found most likely in highly strained ethylene imine derivatives. Recent NMR studies on aziridine[3], oxaziridine[4] and diaziridene[5] derivatives support this suggestion, especially for the last case[6]. Today, an additional working hypothesis in the search for noninverting amines is based on the argument[7] that a higher σ-electronegativity of the ligands at nitrogen should be associated with a higher s-character of the nonbonding lone-pair orbital at nitrogen, and thus – *ceteris paribus* – with a higher inversion barrier. In fact, the amines known to invert most slowly among the acyclic series[8] are derivatives of hydroxylamine[9], and the barriers of oxaziridines and diaziridines[4,5] are higher than those of corresponding aziridines. On the other hand, repulsion between the nonbonding electron pairs of nitrogen and the adjacent hetero atom (conjugative destabilization) might primarily be responsible for the enhancement of the barriers in these systems[9,3e]; however, the relative importance of these inductive and conjugative factors has not yet been evaluated experimentally. Parallel with investigations on the structural requirements of high inversion varriers[10] we came upon the aziridine system named in the title; the diastereoisoisomerism exhibited by this system at room temperature presents a drastic illustration of the influence of electronegative ligands on the inversion barrier of amines.

N-chlorination[11] of 7-azabicyclo[4.1.0]heptane *(1)*[12] with sodium hypochlorite in water at 0 °C affords about 90 % of a product, the thin layer chromatographic analysis (silica gel/benzene-ethyl acetate/iodine) of which showed the presence of a stable major component A and a slow-moving labile component B. A clean separation of the two components could be achieved by column chromatography on silica gel (pentane/diethyl ether) at *ca.* 10 °C (yield ratio A:B *ca.* 4:1); rapid distillation at room temperature (0.05 torr) yielded the analytically (combustion analysis) pure liquids. Whereas samples of the component A isolated in such a manner are thin-layer chromatographically and NMR-spectroscopically homogeneous, samples of the labile component B contain small amounts (NMR: *ca.* 5 %) of component A. Compound A can be distilled unchanged at higher temperatures (b.p. 57–58 °C/11 torr) whereas component B is converted wholly, or partly, depending on the duration of heating, into component A. Both compounds release a molar equivalent of iodine from an acetic acid solution of potassium iodide and, on reduction with sodium hydrogen sulfite (in aqueous methanol/0 °C/10 min), revert to 7-azabicyclo[4.1.0]heptane *(1)* (yields 87 and 72 % resp.).

On the basis of their mode of formation, the thermal conversion of B into A, the re-reduction of B and A to *(1)*, as well as the analytical and spectroscopic data reproduced in the Table and Figures 1 and 2, we conclude that compounds A and B are the diastereoisomers *(2)* and *(3)* of 7-chlorobicyclo[4.1.0]heptane. We assume that the presumably more strained *endo*-configuration *(3)* belongs[13] to the labile, more dense, more highly refracting isomer B. In the NMR spectrum of this isomer the multiplet signals that are ascribed to the two bridgehead hydrogens occur at 2.1 ppm, *i.e.*, approximately 0.2 ppm[14] upfield from the corresponding multiplet in the spectrum of isomer A (cf. Fig. 1).

In the spectra of mixtures of isomers A and B these multiplets can be integrated separately; this affords a simple means of following the course of the conversion B → A with time. In benzene solution (*ca.* 6 wt.-% of B) at 29.5 °C the epimerization clearly follows the first order rate law with a rate constant $k = 4.3 \times 10^{-5}$ sec^{-1} (halflife 4.5 h). Under these conditions the conversion is complete within about a day, *i.e.*, it leads to the NMR-spectroscopically homogeneous isomer A. The completeness of this conversion can also be observed from the change in the IR spectrum with time; the two isomers can be clearly differentiated by the position and intensity of a band at 600 cm^{-1} that is ascribed to the (N–Cl)-stretching vibration[14] (cf. Fig. 2).



	Isomer A	Isomer B
n_D^{21} d_4^{23}	1.4954 1.103	1.5105 1.146
λ_{max}(nm) [ε] in isooctane	257 [330]	260 [420]
m/e	133 ($M^+/^{37}Cl$/1.5 %), 131 ($M^+/^{35}Cl$/0.9 %), 96 (45 %), 82 (25 %), 81 (11 %), 79 (17 %), 77 (26 %), 69 (67 %), 68 (43 %), 67 (23 %), 56 (28 %), 55 (23 %), 54 (21 %), 43 (17 %), 42 (71 %), 41 (100 %)	133 ($M^+/^{37}Cl$/1 %), 131 ($M^+/^{35}Cl$/1 %), 96 (60 %), 82 (19 %), 81 (10 %), 79 (17 %), 77 (25 %), 69 (88 %), 68 (52 %), 67 (27 %), 56 (12 %), 55 (28 %), 54 (25 %), 43 (19 %), 42 (100 %), 41 (35 %)

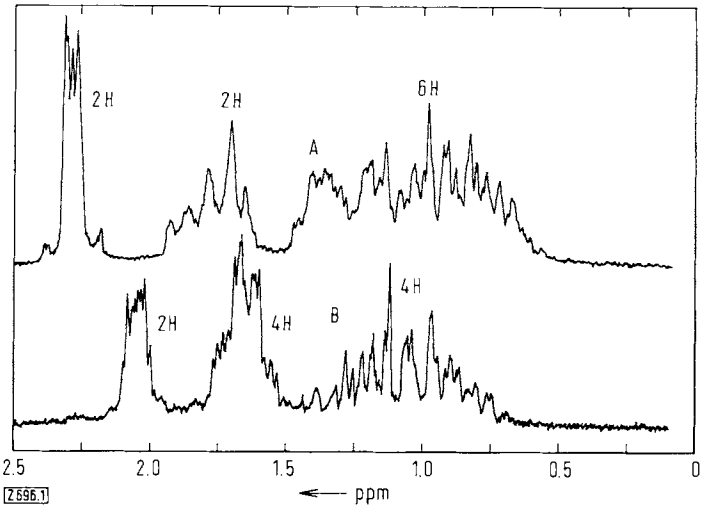


Fig. 1. NMR-Spectra of A and B, Varian HA–100, in deuteriobenzene, 20 °C.

So far as we know the above example is the first case of a "voluntary"[1b] nitrogen-inversion stereoisomerism at room temperature that has been demonstrated by isolation[**]. It appears to result from a favorable accumulation of factors that would be expected to raise the nitrogen inversion barrier, *i.e.*, (i) the increased ring strain of the three-membered ring in the planar inversion transition state relative to the pyramidal

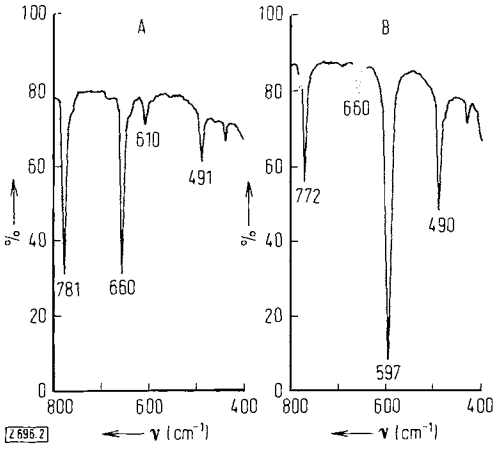


Fig. 2. IR-Spectra of A and B, liquid, KBr-cell.

ground state, (ii) the greater s-character of the lone-pair nitrogen orbital in the three-membered ring (possibly enhanced by the inductive influence of the chlorine) relative to a normal amine, and (iii) the conjugative destabilization of the planar inversion transition state (relative to the pyramidal ground state) resulting from the proximity of the formally non-bonding electron pairs of the nitrogen and chlorine. The type of structure displayed by the aziridines [15] that are electronegatively substituted on the nitrogen obviously affords an especially suitable model system for the experimental study of the influence of these factors on the inversion at nitrogen. Experiments in this direction are being carried out with investigations of other properties of the diastereomeric pair A/B and the kinetic determination of the inversion-activation parameters [16].

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[14] The AB-doublets of the methylene protons of 1-chloro-2-2-dimethylaziridine appear at 1.57 and 1.77 ppm (deuteriobenzene, room temperature). In the IR-spectrum this chloroaziridine derivative shows an intense band at 600 cm^{-1} which can be ascribed to the (N–Cl)-stretching vibration (unpublished observation of *J. Schreiber*, ETH). With regard to the position of the (N–Cl)-stretching vibration in the spectrum cf. *e.g. G. E. Moore* and *R. M. Badger*, J. Amer. chem. Soc. *74*, 6076 (1952).

[**] Note added in proof: Obviously not! – cf. *S. J. Brois*, J. Amer. chem. Soc. *90*, 508 (1968); compare also *J. M. Lehn* and *J. Wagner*, Chem. Commun. *1968*, 148 for NMR-studies on *N*-chloro- and *N*-bromoaziridines, and *M. Raban*, Chem. Commun. *1967*, 1017 for the inversion barrier of *N,N*-dibenzyltrichloromethane sulfenamide.

[15] Cf. the account given in Ref. [3e] concerning the NMR-spectrum of the unsubstituted *N*-chloroaziridine.

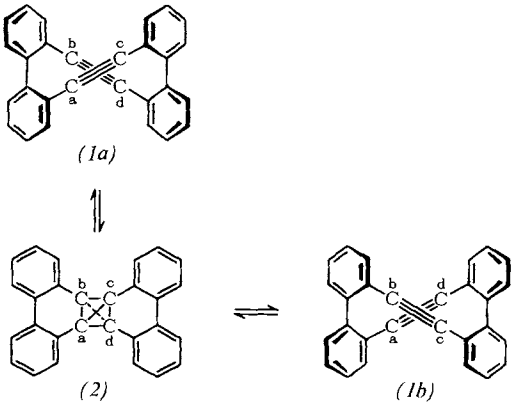
[16] This work was supported by Firma Firmenich et Cie., Geneva. We thank Frl. *I. Buhrow* for experimental assistance.

Synthesis of 9,10,19,20-Tetradehydrotetrabenzo-[*acgi*]cyclododecene

By *H. A. Staab* and *E. Wehinger* [*]

9,10,19,20-Tetradehydrotetrabenzo[*acgi*]cyclododecene *(1)*, whose fixed crossed triple bonds had attracted our attention [1], was obtained by metalation of bi(2-bromophenyl)-acetylene with *n*-butyllithium at −40 °C and subsequent cyclization of the metalated species with anhydrous copper(II) chloride. Compound *(1)* (m.p. 221–222 °C, from ligroin 60–70 °C) was isolated by thin layer chromatography (silica gel HF_{254}; ligroin, 60–70 °C/benzene 1:1) of the reaction product. The mass-spectrometrically determined molecular weight (M^+ at *m/e* 352) and hydrogenation (Pd/C, benzene) to 9,10,19,20 - tetrahydrotetrabenzo[*acgi*]cyclododecane [2] provide proof of structure. The UV absorption of *(1)* at remarkably short wavelengths [λ_{max} = 240 nm (ε = 72600); 222 nm (73700)] is explained as a result of twisting of the aromatic rings.

Consideration of models shows that *(1)* has a completely rigid carbon skeleton in which the four carbon atoms of the two triple bonds occupy the apexes of a distorted tetrahedron. With regular valence angles, the triple bonds, whose effective radii are assumed to be 1.6 Å [3], would have to approach each other to within 2 Å. Nevertheless, *(1)* exists unequivocally as a diacetylene and not as the tetrahedrane *(2)* since the most intense Raman absorption is ν′(C≡C) at 2220 cm^{-1} [4]. However, regarding the prevailing stereochemical conditions, we would not rule out the possibility of thermal or photochemical valence isomerization of *(1)* to the tetrahedrane *(2)*. Because of the chirality of the mole-



cule, the formation of *(2)* as an intermediate should involve a racemization as well as a novel rearrangement of the carbon skeleton *(1a)* ⇌ *(1b)*. Experiments to settle this question are in progress.

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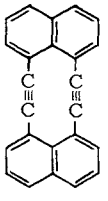
[4] We thank Dr. *B. Schrader*, Institut für Spektrochemie Dortmund, for recording the Raman spectrum.

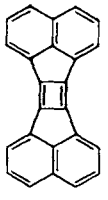
Attempted Preparation of 7,8,15,16-Tetradehydrodinaphtho[1,8-*ab*; 1,8-*fg*]cyclodecene

By *H. A. Staab*, *A. Nissen*, and *J. Ipaktschi* [*]

In connection with investigations of intramolecular interactions between triple bonds[1,2], our interest became centered on 7,8,15,16-tetradehydrodinaphtho[1,8-*ab*; 1,8-*fg*]-cyclodecene *(1)*, whose triple bonds should be even more rigidly fixed in a parallel arrangement than those of 1,8-diethynylnaphthalenes[1]. This should particularly favor overlapping of the in-plane π electrons, which in the extreme case would lead to a cyclobutadiene system *(2)* with rehybridized σ bonds.

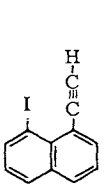


(1)



(2)

1-Ethynyl-8-iodonaphthalene *(3)*, m.p. 75–76 °C, was obtained from 8-iodo-1-naphthoyl chloride[3] *via* 1-acetyl-8-iodonaphthalene and 1-(1-chlorovinyl)-8-iodonaphthalene. However, coupling of the copper compound of *(3)* in pyridine (8 h, 115 °C) yielded not *(1)*, but a compound (yield 50 %) containing two more hydrogen atoms that was identified as zethrene *(4)*[4].



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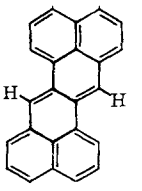

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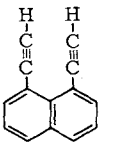
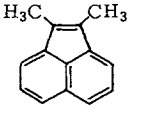


(5)

It appears that compound *(4)* is formed from *(1)*, which is not stable under the conditions of reaction, for the presence of compound *(4)* was also established during an attempt to prepare *(1)* by coupling of the dicopper compound of 1,8-diethynylnaphthalene *(5)* with 1,8-diiodonaphthalene. Compound *(5)*, m.p. 75 °C, was obtained in very good yield from 1,8 - divinylnaphthalene[5] *via* the tetrabromide (m.p. 127–129 °C) after dehydrobromination with potassium *tert*-butoxide in tetrahydrofuran.

The reactions of compound *(5)* also evidence special intramolecular interactions between the spatially proximate triple bonds. Thus hydrogenation with Lindlar catalyst gives predominately (50 % yield) 1,2-dimethylacenaphthylene *(6)*. Evidence for the intermediacy of 1,2-dimethyleneacenaphthene *(7)* was obtained when *(7)* was trapped during hydrogenation of *(5)* (Lindlar catalyst, tetrahydrofuran) in the presence of maleic anhydride as the 1:1 adduct (m.p. 191–195 °C, 30 % yield[6].



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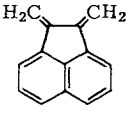

(7)

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German version: Angew. Chem. *80*, 241 (1968)

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[1] *J. Ipaktschi* and *H. A. Staab*, Tetrahedron Letters *1967*, 4403.

[2] *H. A. Staab*, *H. Mack*, and *E. Wehinger*, Tetrahedron Letters, in press; *H. A. Staab* and *E. Wehinger*, Angew. Chem. *80*, 240 (1968); Angew. Chem. internat. Edit. *7*, 225 (1968).

[3] *H. Goldstein* and *P. Francey*, Helv. chim. Acta *15*, 1362 (1932).

[4] *E. Clar*, *K. F. Lang*, and *H. Schulz-Kiesow*, Chem. Ber. *88*, 1520 (1955); we thank Professor *Clar*, Glasgow, for an authentic sample of compound *(4)*.

[5] *J. K. Stille* and *R. T. Foster*, J. org. Chemistry *28*, 2703 (1963).

[6] *R. H. Mitchell* and *F. Sondheimer*, who recently also reported the synthesis of *(5)* [Tetrahedron *24*, 1397 (1968)], obtained 1,8-diethylnaphthalene and 1,8-diethyltetralin on hydrogenation of *(5)* with platinum catalyst in acetic ester.

Ninth Lyons-Tübingen Chemical Meeting

The Ninth Lyons-Tübingen Chemical Meeting took place on September 27–29, 1967, at Tübingen on the invitation of the Tübingen Academic Chemical Staff. Three plenary lectures and twenty-five short papers were read.

Extracts from the lectures and papers:

The Structure of Some Fluorides, Oxides, and Oxide Fluorides: the $RbNiCrF_6$ Type

By *D. Babel* (Lecturer), *G. Pausewang*, and *W. Viebahn*[*]

Among the oxide systems there are compounds AM_2O_6 that crystallize in the perovskite lattice with only half the A cation sites occupied, *e.g.*, $CaNb_2O_6 = Ca_{0.5}NbO_3$. An analogous structure was at first expected for corresponding fluorides $A^IM^{II}M^{III}F_6$ where A^I = large alkali ions, M^{II} and M^{III} = small ions, in particular of the first transition series, since many of the components required, *e.g.*, $KNiF_3 + CrF_3$, are already known to crystallize with the perovskite lattice or with closely related structures.

A number of new compounds $A^IM^{II}M^{III}F_6$ were prepared, where A^I = K, Rb, or Cs, M^{II} = Mg, Ni, Cu, Co, Fe, or Mn, and M^{III} = Al, Ga, Cr, Fe, or V, by heating mixtures of the binary fluorides $AHF_2 + MF_2 + M'F_3$ in stoichiometric amounts under an inert atmosphere. However, X-ray structure analysis of the crystalline powders showed that these were not perovskites but belonged to a hitherto unknown face-centered cubic structure type ($RbNiCrF_6$ type).

Further, numerous oxides $A^IM^{V'}M^{VI}O_6$ with A^I = K, Rb, or Cs, as well as oxide fluorides have this structure, whose relations to the perovskite type on the one hand and to the pyrochlore type on the other were illustrated.

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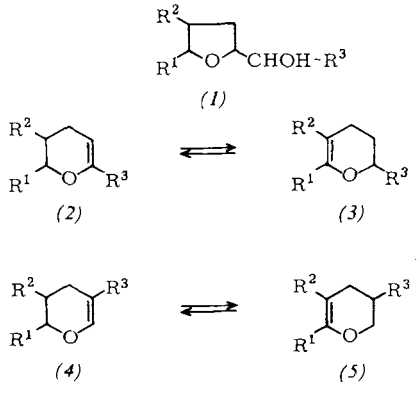
Catalytic Elimination and Isomerization Reactions of *O*-Heterocycles

By *G. Descotes*[*]

The mechanism and stereochemistry of ring-expansion of α-alkylfurfuryl alcohols *(1)* are determined by the number, position, and steric relations of the substituents. The cation



(with the positive charge on a carbon atom) that is adsorbed on aluminum oxide as intermediate usually undergoes heterolysis of the C–O bond. However, for conformations that are only slightly hindered sterically and thus favor *trans*-elimination, cleavage of C–C occurs. On heterolysis of *threo-(1)* ($R^1 = R^2 = H$; $R^3 \neq H$) the latter applies exclusively and leads to dihydropyrans *(2)* and *(3)*, as well as *(4)* and *(5)*.

The isomerizations *(2)* ⇄ *(3)* and *(4)* ⇄ *(5)* depend on complex intra- and inter-molecular migrations of hydride ions which are hindered if the substituents are bulky or are in *cis*-relation to the hydroxylated chain.

Analogous isomerizations are observed among tetrahydropyrans.

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A New Method for Estimating Thermodynamic Properties of Crystalline Substances: Alkali Halides and Hydrides (NaCl System)

By *J. Bousquet, J. Cl. David* (Lecturer), *M. Diot*, and *A. Guillon*[*]

The dependence of the following thermodynamic parameters (referred to the standard state) on molar volumes was studied: lattice energy, enthalpy of formation, entropy of formation (1. elements in the ideal monoatomic gas state; 2. alkali elements in the standard state, halogens in the gas state), and free energy of formation. Linear functions of the logarithm of the molar volume resulted; the lines representing them are, in general, characteristic of each cation.

For the alkali hydrides, which crystallize in the NaCl system, the representative points lie distinctly off these lines and it is assumed that the hydrides occur as trimers $M^+(M_2H_3)^-$. With such assumptions it is possible to supplement and interpret the experimentally observed thermodynamic results. Agreement with previously estimated analogous values is very good.

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Some Properties of 3-Phenoxyacrolein

By *R. Gelin* (Lecturer) and *D. Makula*[*]

3-Phenoxyacrolein is a stable starting material for preparation of malonaldehyde:

$$C_6N_5O\text{–}CH{=}CH\text{–}CHO \xrightarrow{H_2O} [HOCH{=}CH\text{–}CHO \rightleftharpoons OHC\text{–}CH_2\text{–}CHO] + C_6H_5OH$$

Hydrochlorides of the corresponding imino enamines are obtained quantitatively on reaction with hydrochlorides of primary aromatic amines:

$$[Ar\overset{\oplus}{N}H{=}CH\text{–}CH{=}CH\text{–}NHAr]Cl^{\ominus}$$

With alcohols and a catalyst diacetals of malonaldehyde (1,1,3,3-tetraalkoxypropanes) are obtained.

Other nucleophilic reagents (organomagnesium compounds, secondary amines, and Na derivatives of compounds with active methylene groups) react with addition-elimination. With organomagnesium compounds α,β-unsaturated aldehydes result; Na derivatives of compounds with active methylene groups afford quantitative yields of dienolates:

$[XYC{=}CH{-}CH{=}CHO^{\ominus}]\ Na^{\oplus}$

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Microcalorimetric Investigation of Heterogeneous Catalytic Reactions

By *P. C. Gravelle* [*]

In a catalytic reaction at least one reactant is adsorbed on the surface of the catalyst. The adsorbed species takes part in surface reactions, and the final step in the reaction cycle is desorption of the reaction product. All the partial processes deliver or take up energy and can thus be followed directly by calorimetry.

An apparatus was described for measurement of the heat of adsorption of small quantities of gas. The curve showing the dependence of the differential heats of adsorption on the degree of occupation of the surface at a given temperature are characteristic of the adsorbed gas on the one hand and of the solid adsorbent on the other. Calorimetry discloses the change of surface activity of a catalyst with respect to a gas on variation, particularly, of the temperature of adsorption and of the surface structure. The same applies to chemisorption processes occurring on the surface. The calorimetric results are refined by thermochemical cyclic processes, and reaction mechanisms and kinetic conclusions are derived from them.

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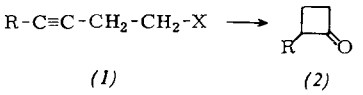
Conversion of Acetylene Compounds into Small-Ring Compounds

By *M. Hanack* (Lecturer), *I. Herterich*, *V. Vött*, and *H. Ehrhardt* [*]

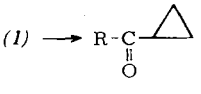
The C–C triple bond shows an unexpected readiness to take part in carbonium ion reactions, and this makes possible novel types of synthesis of small-ring compounds.

If acetylene derivatives of structure *(1)* (R = CH_3, C_2H_5, or i-C_3H_7; X = *m*-$OSO_2C_6H_4NO_2$) are solvolyzed in media of high ionizing power (*e.g.* formic or trifluoroacetic acid), they are converted completely into 2-alkylcyclobutanones *(2)*.



(1) *(2)*

The direction of rearrangement can be controlled by changing the reaction conditions: if acetylenes *(1)* are solvolyzed with addition of catalytic amounts of Hg(II) salts, then alkyl cyclopropyl ketones *(3)* are the preponderant products isolated.



(3)

Cyclization is not the only result of solvolysis of *(1)* when R = H; the cyclobutanones are then accompanied by esters of analogous structure.

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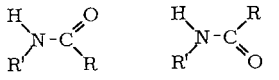
cis-trans-Isomerism of *N*-Monosubstituted Amides

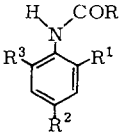
By *H. Kessler* [*]

N-Monosubstituted amides exist mainly in the *trans*-form (b) [1]. The *cis*-form (a) takes part in the equilibrium only to the extent of < 1 % (the activation energy of the equilibration (a) ⇌ (b) amounts to *ca.* 15–23 kcal/mole). But with formamides alone (R = H) (a) is preferred.



cis *trans*

(a) *(b)*



(1)

R = H, CH_3, C_2H_5, i-C_3H_7, *tert*-C_5H_9
R^1, R^2, R^3 = CH_3, C_2H_5, i-C_3H_7 or *tert*-C_4H_9

The position of the equilibrium and the height of the energy barrier (a) ⇌ (b) have been studied by NMR spectrometry for nuclear-substituted anilides *(1)*. In contrast to the case with acetanilide (R = CH_3; R^1 = R^2 = R^3 = H) appreciable amounts of (a) are found in *ortho*-substituted acetanilides [2]; the proportion of (a) increases with the size of the *ortho*-substituent [for 2,4,6-tri-*tert*-butylacetanilide the equilibrium mixture contains (a):(b) = 45:55].

Simultaneously, the free activation enthalpy of establishment of equilibrium increases with increasing steric hindrance. For the tri-*tert*-butylacetanilide it amounts to 24 kcal/mole, sufficing to enable (a) and (b) to be isolated in quantity by thin-layer chromatography at 0 °C, and thus constituting the first separation of *cis*- and *trans*-forms of a *N*-monosubstituted amide.

Increase in the size of the group R (from H to *tert*-C_4H_9) decreases the proportion of (a).

The effects observed are explained by twisting of the benzene ring relative to the plane of the amide bond by means of the *ortho*-substituents. The steric effect of the phenyl ring is reduced in the twisted form.

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[1] *L. A. La Planche* and *M. T. Rogers*, J. Amer. chem. Soc. *86*, 337 (1964).

[2] *H. Kessler* and *A. Rieker*, Liebigs Ann. Chem. *708*, 57 (1967).

Polarimetric Study of Simple and Mixed Metal-Amino Acid Complexes

By *M. R. Pâris* (Lecturer) and *M. Petit-Ramel* [*]

The optical rotation is changed when an optically active ligand is coordinated to a metal ion. The specific rotation of a species is an additive property (in the same way as, for example, absorption). The pH-dependence of the optical

rotation permits determination of the stability constants and the specific rotation of each of the complexes that are successively formed. For this purpose the pH values and the rotations of solutions ($HClO_4/NaClO_4$ at constant ionic strength 0.5) containing originally the metal ion and the complex-forming agent are measured simultaneously during progressive neutralization with NaOH. For determination of the stability constants and specific rotations the graphical method of *Fronaeus-Yatsimirskii*, plus the analytical method of least squares, were applied, this being their first use in polarimetry. Studies to date have been concerned with simple complexes of Cu, Zn, Cd, and Ni with D-alanine, D-valine, and L-proline, and mixed complexes of Cu with these amino acids and with glycine, the last named complex showing no rotation.

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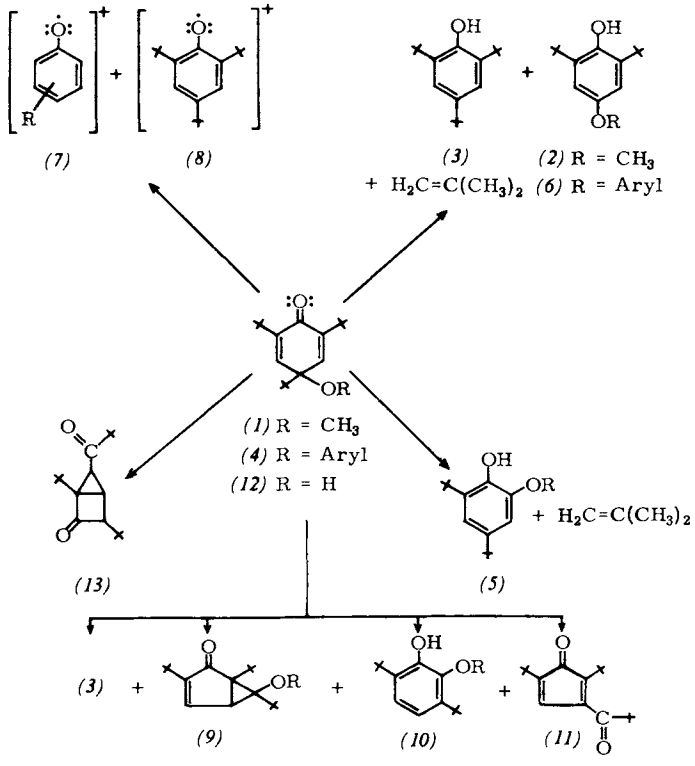
Specific Fragmentation of Cyclohexadienones

By *A. Rieker*[*]

Aliphatic ethers of *para*-quinol *(1)* decompose on pyrolysis, on acid fission, or in the mass spectrometer into isobutene, 2,4,6-tri-*tert*-butylphenol *(3)*, and the *p*-hydroxyphenyl ether *(2)* as main products. Aryl ethers of type *(4)*, however, are cleaved by pyrolysis into *o*-hydroxydiphenyl ethers *(5)* and isobutene, on acid fission into *(5)* or *(6)* according to the conditions, and in the mass spectrometer into the radical components *(7)* and *(8)*.



Photolysis of *para*-quinol derivatives proceeds quite differently: thus compounds *(3)*, *(9)*, *(10)*, and *(11)* are formed from *(1)* in ether (254 nm), whereas irradiation of *(12)* affords two stereoisomeric bicyclo[2.1.0]pentan-2-one derivatives having, probably, the structure *(13)*.

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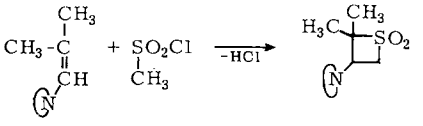
Formation of Sulfenes from Aliphatic Sulfonyl Chlorides and Trialkylamines

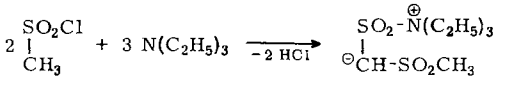
By *K. Rieth*[*]

S,S-Dioxides of thioaldehydes are formed as intermediates on reaction of tertiary bases with primary sulfonyl chlorides. They can be detected indirectly by trapping with suitable cycloaddition reagents (olefins with strongly polar double bonds, such as enamines and ketene acetals). Derivatives of thietane *S,S*-dioxide result.



The reactions are preferentially carried out in ether at room temperature. Cycloaddition of thioketone *S,S*-dioxides from secondary sulfonyl chlorides does not occur under these conditions, but it takes place smoothly in acetonitrile at −40 °C.

Mesylsulfene is formed from methanesulfonyl chloride and triethylamine under these conditions, and is detected as the triethylamine adduct.



The steric course of the cycloaddition of mesylsulfene to *cis*- and *trans*-1-butoxy-1-butene can be recognized from the ^1H–NMR spectra.

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Ternary Oxides of Rutile Structure: Systems containing WO_2, MoO_2, VO_2, or TiO_2

By *W. Rüdorff* (Lecturer) and *H. Kornelson*[*]

The dioxides VO_2, MoO_2, and WO_2 crystallize in a monoclinic deformed rutile structure. In this structure the M–M pair has a remarkably short separation (Mo–Mo = 2.50 Å) in the direction of the *c*-axis. These dioxides have only a small, temperature-independent paramagnetism (TIP), which indicates direct metal-metal bonding. The authors have studied whether

a) the monoclinic structure is retained on formation of mixed crystals among themselves or with TiO_2,

b) M–M bonds still occur in the mixed crystals, and

c) electron transfer (change of valence) occurs between the cations.

There is a complete series of mixed crystals having monoclinic structure in the series MoO_2–WO_2. The TIP is retained, *i.e.*, Mo–Mo, W–W, and Mo–W pairs occur.

TiO_2 and WO_2 form a tetragonal rutile phase $(Ti_xW_{1-x})O_2$ with $1 > x > 0.42$, the magnetic behavior indicating that the W atoms still occur mainly in pairs.

In the system VO_2–WO_2, however, $x = 0.95$ to about 0.33 for the tetragonal rutile phase $(V_xW_{1-x})O_2$, but at $x < 0.33$ the structure passes continously into the WO_2 structure. At the composition $(V_{0.67}W_{0.33})O_2$ $(= V_2WO_6)$ the substance has the trirutile structure with V^{III} and W^{VI}; at the same time the conductivity reaches a minimum. This compound is antiferromagnetic, like the trirutiles Cr_2WO_6, $(VCr)WO_6$, $(FeV)WO_6$, and Cr_2TeO_6. At the transition trirutile-rutile

which occurs by inclusion of VO_2 or TiO_2 into $(V^{III}_{0.67}W^{VI}_{0.33})O_2$, the paramagnetism increases greatly since the magnetically active M^{3+} ions no longer occupy neighboring sites.

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Galvanic Metal—Non-metal Elements

By *J. P. Soulier, D. Bouquet,* and *J. Gauthier* (Lecturer) [*]

The reaction

Metal + Non-metal → Salt $\qquad \Delta H < 0$

in galvanic elements was studied for many combinations of elements by means of suitable electrolytes. The EMF is independent of the concentration and to a certain extent also of the nature of the electrolyte; it depends only on the solubility product of the resulting difficultly soluble salt. EMF measurements thus permit exact determination of solubility products.

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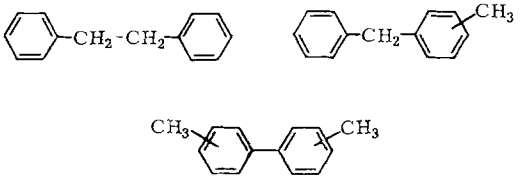
Organic Syntheses in the Plasma of High Voltage Discharges

By *H. Suhr* [*]

When vapors of organic compounds are led at pressures of a few torr through the plasma of cold discharges, various processes can take place. The molecular ions that are primarily formed may recombine, decompose into smaller fragments, or undergo chemical reactions with neighboring neutral molecules. At 25–50 V/cm and pressures of 1–10 torr reaction with neutral molecules predominates. The behavior, in the glow discharge, of a great number of different types of substance with molecular weights of 50 to 150 has been studied: most of the compounds give mixtures in which dimerization products (formed from molecular ions and neutral molecules) predominate. From the proportions of the isomers formed from, *e.g.*, toluene, information about the lifetime of the molecular ions and about their reactive



behavior can be obtained. If vapors of different compounds are fed together through the discharge tube, the proportions in which the products are formed gives information about the selectivity of the molecular ions.

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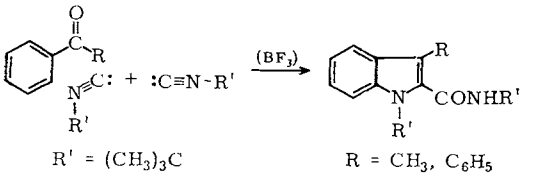
A New Synthesis of Indole Derivatives

By *B. Zeeh* [*]

Ketones are activated by Lewis acids such as BF_3 (the polarity of the carbonyl group is greatly increased) and can then react with nucleophilic reagents. If the nucleophile is an isocyanide, a series of unexpected reactions is observed, in which always two molecules of isocyanide react with one of ketone. When an aromatic ring is present, indole derivatives are formed.

tert-Butyl amides of 2-indolecarboxylic acids are formed from aromatic ketones, such as acetophenone or benzophenone, and *tert*-butyl isocyanide:



$R' = (CH_3)_3C$ $\qquad$ $R = CH_3, C_6H_5$

If, however, the aromatic substituent is in the isocyanide component (*e.g.*, phenyl isocyanide), cycloaliphatic ketones afford 2-indoleninecarboxanilides [1]. [VB 128 IE]

German version: Angew. Chem. *80*, 199 (1968)

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[1] *B. Zeeh*, Angew. Chem. *79*, 415 (1967); Angew. Chem. internat. Edit. *6*, 453 (1967).

Quantum-mechanical Prediction of the Existence and Properties of the Unknown Molecule BeH_2

By *W. Kutzelnigg* and *R. Ahlrichs* [*]

Quantitative predictions of the properties of unknown molecules by "*ab initio* calculations" have so far been rarely possible because of the extraordinarily complicated quantum-mechanical equations to be solved. (By *ab initio* calculations we mean those in which only the number and kind of the nuclei and the number of electrons are put in, and in which, for instance, the equilibrium geometry of the molecule comes out of the calculation.)

Almost all *ab initio* calculations are based on the "independent particle model". This means that one orbital (one one-electron wave function) is associated with each electron and that the interaction between the electrons is calculated as the electrostatic repulsion between the electron clouds that correspond to the orbitals. Since, however, the electrons are not smeared charge distributions, and only a probability distribution of all the electrons has any physical meaning, this description in which the "electron correlation" is neglected cannot be quite correct. However, it permits certain properties, such as dipole moments, equilibrium distances and angles, and force constants, to be obtained surprisingly well. The independent particle model is, however, quite insufficient to permit calculation of bond energies and electron excitation energies.

A method developed by the authors [1] for calculation of a major part of the electron correlation – the "electron pair correlation" – now makes *ab initio* calculation of bond energies possible. The procedure has been applied with success to some known small molecules and then to the unknown molecule BeH_2.

The BeH_2 molecule is linear and symmetrical in the ground state. The equilibirum Be–H separation (1.35 ± 0.01 Å) is almost the same as in the known [2] BeH molecule (1.343 Å); valence force constants are also similar [f_r = 2.23 (BeH_2) and 2.26 (BeH) mdyn/Å]. The Be atom is in almost the same valence state in the two molecules. In accord therewith the dissociation energy for separation of one H atom from BeH_2 (consideration being given to zero point vibrations) at 89 ± 6 kcal/mole is distinctly greater than that for separation of the second H atom (53 ± 6 kcal/mole) because bonding of

a further H atom to BeH requires no additional "promotion energy".

The calculated limits of error in our results arise mainly because the "interpair correlation energy", although small, is not negligible and so far can only be estimated rather than calculated.

BeH_2(gas) is exothermic with respect to BeH + $^1/_2$ H_2 or Be(gas) + H_2, but endothermic (by 38 ± 6 kcal/mole) with respect to Be(solid) + H_2 or (by 48 ± 6 kcal/mole) with respect to the known[3,4] solid BeH_2 which, however, apparently does not consist of BeH_2 molecules but is high-polymeric. The BeH_2 molecule cannot be obtained by heating solid BeH_2 since at the temperature at which this decomposes into the elements[3] (about 400 °K) the BeH_2 equilibrium pressure amounts to only $10^{-18\pm3}$ atm. However, reaction of metallic Be and H_2 ($p \geq 1$ atm) at temperatures between 1000 and 1500 °K should afford BeH_2 molecules in measurable concentration.

Lecture at Göttingen (Germany) on December 14, 1967 [VB 110 IE]
German version: Angew. Chem. 80, 245 (1968)

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[4] *G. D. Barbaras et al.*, J. Amer. chem. Soc. *73*, 4585 (1951).

Behavior of Molecules in High Electric Fields and at Surfaces

By *J. H. Block*[*]

In extremely high electric fields (> 10^7 V/cm) molecules are so strongly polarized that an electron can tunnel out, whereby an ion arises. This process of field ionization is utilized in studying the behavior of molecules in high electric fields by means of mass spectrometry.

These high fields can be established only on surfaces, for instance in the field ion microscope of *E. W. Müller*. Field-ion mass spectrometry can thus be used for studying certain surface reactions.

The energies induced in molecules at field strengths of 10^6 to 10^7 V/cm cause a perceptible change in the chemical behavior of, particularly polar, substances. For instance, association reactions of dipolar molecules become field-dependent. This dependence can be demonstrated by field pulse methods. For this purpose an electric field (< 10^7 V/cm) is first created so as to produce a desired species, which is then ionized by a pulse of short duration and analyzed directly in the mass spectrometer. It can thus be shown that the HCOOH molecule, whose polar monomer is associated to the nonpolar dimeric form, becomes stabilized in the monomeric form in high electric fields.

Field pulse methods, coupled with direct mass spectrometric analysis of the resulting ions, also makes it possible to study surface reactions kinetically. By varying the pulse frequency from 1 sec to 10^{-5} sec, products of surface reactions can be analyzed that have been formed within very short times. This procedure provides a very direct method of investigating heterogeneous catalysis, interpretation of the results being made difficult only by field-induced processes. The molecular ions produced by field ionization are of particular interest. Owing to their very low excitation, they show peculiar chemical behavior most impressively.

Lecture at Hannover (Germany) on November 9, 1967 [VB 112 IE]
German version: Angew. Chem. 80, 243 (1968)

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New Developments in the Crystal Chemistry of Multicomponent Oxides

By *E. Kordes*[*]

An astonishing tolerance for isomorphous replacement of cations, even if of different valence, is often observed, not only with complicated, but also with simple lattices. As long ago as 1935 formation of a continuous series of mixed crystals was established for MgO, $LiFeO_2$, and Li_2TiO_3[1] (all three with NaCl structure), and more recently of MgO or NiO and $LiFeO_2$ (all with NaCl structure) with the rhombohedral $LiCrO_2$ (deformed NaCl structure with ordered cationic distribution[2]), and also between MgO and $LiVO_2$ (isotypic with $LiCrO_2$). Cubic compounds Li_3NbO_4 and Li_3TaO_4, isotypic with MgO, are also known. These two mixed oxides give further continuous series of mixed crystals with MgO, Li_2TiO_3, and $LiFeO_2$; these are thus cases of coupled isomorphous replacement of $(Li^+)_9(M^{5+})_3$ by $(Mg^{2+})_{12}$ or $(Li^+)_8(Ti^{4+})_4$ or $(Li^+)_6(Fe^{3+})_6$.

Stable homogeneous mixed crystals with the composition

$$Li_{10}MgFe^{III}Ti^{IV}M^{V}M'^{VI}O_{15}$$

(M = Nb on Ta; M' = W or Mo)

and NaCl structure have also been prepared.

The oxidic spinel lattice shows a similar tolerance for cation replacement. The alkali spinel $LiAl_5O_8$ can be derived from the very similar spinel $Mg_2Al_4O_8$ by the replacement 2 $Mg^{2+} \rightarrow Li^+Al^{3+}$; a corresponding derivation applies to the analogous spinel $LiFe_5O_8$. Surprisingly, $LiFe_5O_8$ gives a continuous series of mixed crystals with the rhombohedral $LiCrO_2$ or $Li_4Cr_4O_8$ (deformed NaCl structure) that is not isotypic with it: an excess of cations is accommodated in the spinel lattice of the $LiFe_5O_8$.

Cu^I ions can also be accommodated in spinels. $LiFe_5O_8$ and $CuFe_5O_8$, for instance, give a continuous series of mixed crystals. 20 mole-% of Li^+ in $LiIn^{III}Cr^{III}_4O_8$ can be replaced by Cu^+.

Cu_2O also forms compounds with the oxides of the lighter trivalent rare-earth metals; for instance, new mixed oxides $CuLaO_2$, $CuPrO_2$, $CuNdO_2$, $CuSmO_2$, and $CuEuO_2$ have been obtained that are isotypic with one another and crystallize with the rhomobedral $NaHF_2$ lattice.

Lecture at Bonn (Germany) on November 7, 1967 [VB 113 IE]
German version: Angew. Chem. 80, 243 (1968)

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[1] *E. Kordes*, Z. Kristallogr. Mineralog. Petrogr., Part A, *92*, 139 (1935).

[2] *W. Rüdorff*, Z. Naturforsch. *9b*, 614 (1954).

New Results in the Chemistry of Complex Compounds of Metals in Lower Oxidation States

By *H. Behrens*[*]

Oxidation by iodine of $Na_2[Cr_2(CO)_{10}]$, which is isoelectronic with $Mn_2(CO)_{10}$, leads stepwise to $[Cr(CO)_5I]^-$, $Cr_2(CO)_{10}I$, and $Cr(CO)_5I$[1,2]. The binuclear anionic complex $[Cr_2(CO)_{10}I]^-$, which is not accessible by this route, is formed when the binuclear neutral complex is reduced with sodium amalgam in THF[3]. The IR spectra of $(OC)_5Cr-I-Cr(CO)_5$ and $[(OC)_5Cr-I-Cr(CO)_5]^-$ indicate a double octahedral arrangement of the ligands with I as common apex and linear Cr–I–Cr linkage[4]. The ionic Cr^I complex $[Cr(CO)_2(NH_3)_4]I$, in which the CO groups are *trans* to one another, can be obtained from $Cr(CO)_5I$ and liquid NH_3. $Cr(CO)_5I$ generally reacts with other uni- or bidentate N or P ligands by oxidation to elemental iodine and reduction to penta- or tetra-carbonylchromium(0) compounds[5].

In the series $Cr(CO)_5X$, $[Cr(CO)_5X]^-$, $Cr_2(CO)_{10}X$, and $[Cr_2(CO)_{10}X]^-$ (X = CN, SCN, or OCN)[3,6,7] the pseudohalogen of the binuclear complexes is in the bridge position, as is iodine in the iodine derivatives. Like $[Cr(CO)_5NCS]^-$, $Cr(CO)_5NCS$ is an isothiocyanate compound with a Cr–N bond[4].

M^0 compounds can be synthesized from cyanometalates(0)[8] as well as from pure dicyclopentadienyl complexes(π-$C_5H_5)_2M$ (M = V, Cr, Fe, Co, or Ni) and mixed cyclopentadienylmetal-carbon monoxide complexes[9,10]. Particular mention may be made of the preparation of the trigonal-bipyramidal $Fe(CO)_2$tripy from $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ and 2,2′:6′,2″-terpyridyl (tripy)[11].

Whereas $Co_2(CO)_8$ disproportionates with Lewis bases to Co^{II} and Co^{I-}, the compounds

$[Co^{I}(bipy)_3]\,[Co^{-I}(CO)_4]$ and $[Co^{I}(phen)_3]\,[Co^{-I}(CO)_4]$ [12]

are formed on treatment of $(C_6H_8)_2Co_2(CO)_4$ (C_6H_8 = 1,3-cyclohexadiene) with 2,2′-bipyridyl (bipy) or 1,10-phenanthroline (phen), respectively.

However, the norbornadiene in $(nor\text{-}C_7H_8)_2Co_2(CO)_4$ can be replaced according to the equation:

$$(nor\text{-}C_7H_8)_2Co_2(CO)_4 + 2\,L \rightarrow Co_2(CO)_4L_2 + 2\,nor\text{-}C_7H_8$$

(L = bipy, phen, or $[(C_6H_5)_2PCH_2]_2$)

these being the first cobalt carbonyl derivatives to be obtained in which four CO groups are replaced by N or P ligands[12]; they have the same structure as $Co_2(CO)_8$.

The compounds $Co_2(CO)_4L_2$ are oxidized by I_2 to the covalent pentacoordinated $ICo(CO)_2L$, but are reduced by sodium to the salt-like tetracoordinated $Na[Co(CO)_2L]$[12].

Lecture at Erlangen (Germany) on November 17, 1967, and at Tübingen (Germany) on December 7, 1967 [VB 114 IE]
German version: Angew. Chem. *80*, 244 (1968)

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[1] *H. Behrens* and *H. Zizlsperger*, Z. Naturforsch. *16b*, 349 (1961).
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Valence Force Constants of Various Phosphorus Compounds

By *J. Goubeau*[*]

The author's method of calculating "force constants" was described. By examining systematically selected examples from various transition series of the type PX_3–PX_2Y–PXY_2–PY_3 and similar series with quadri- and quinque-valent phosphorus the important bases for changes of force constants (differences of up to nearly 200 %) were established as:

1. differences in hybridization,
2. differences in electronegativity of the components,
3. multiple bonding ($d\pi$–$p\pi$), and
4. polar valence contributions.

The force constants increase markedly with increasing s-contribution to the σ-bonds, in phosphorus chemistry as in other combinations of elements. Force constants of certain phosphorus compounds become larger with increase in electronegativity of the other components when other bonding conditions are unchanged (hydrogen bonds are understandably an exception). In both these cases the maximum change in the force constants is of the order of 30–40 %.

The greatest changes are due to contributions from multiple bonds: as an example, the PS force constants in tetraligated SPXYZ were discussed; the bond order varies between 2.0 and 1.3 according to the electronegativity of the ligands. The influence of polar contributions to the bonding, which weaken the force constants, was explained for the cases of some fluorine, chlorine, and cyanide derivatives of phosphorus; with these examples the effect of variation in force constant on the reactivity of the compounds could be demonstrated.

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German version: Angew. Chem. *80*, 246 (1968)

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Mechanism of Eliminations over Solid Catalysts

By *H. Noller*[*]

Static and dynamic studies have been carried out, particularly by the microcatalytic method, with C_2 to C_4 alkanes between 100 and 400 °C. The catalysts were salts and oxides; metals are ineffective. Alkaline-earth salts have much greater activity than alkali salts, doubtless because of their higher cationic charge. The activity of cations with the same charge increases with decreasing radius. The activity of the anions approximately parallels their basicity.

Reactivity decreases in the substituent series Cl, Br, OH, NH_2, C_6H_5. Methyl and, in particular, phenyl substitution on C_α increases the reactivity appreciably. Methyl substitution on C_β is without influence, but this does not apply to phenyl substitution. Deuterium introduced on C_α remains in the molecule (indicating β-elimination), although not always on C_α. The secondary kinetic isotope effect, if present at all, is < 5 %.

Reactions are always of the first order. It is impossible to decide kinetically between E1 and E2 mechanisms, but this can be done by considering the distribution of primary products. On alkaline-earth salts the primary products from 1-halogenobutanes (X = Cl or Br) are the same as from 2-halogenobutanes; 2-butenes always largely preponderate (Saytzeff rule), and among these in the lower temperature region often the (thermodynamically less stable) *cis*-2-butene. This indicates an E1 mechanism that operates through the same 2-butyl cation. Lithium salts are highly selective; with 2-halogenobutanes they give primarily *cis*-2-butene, and with 1-halogenobutanes they yield primarily 1-butene.

The stereoselectivity of the catalysts follows from the *cis*/*trans* proportions of the 2-halogeno-2-butenes that are formed from the *meso*- and DL-forms of 2,3-dihalogenobutanes. The series of catalysts with decreasing selectivity KBO_2, K_2CO_3, K_3PO_4, K_2SO_4, $BaCO_3$, $Ca(BO_2)_2$, $Ba_3(PO_4)_2$, $CaCl_2$ covers the whole range of almost complete stereoselectivity (KBO_2: *cis*/*trans* from *meso* = 97:3, from DL 9:91, at 250 °C), *i.e.*, *trans*-elimination, to vanishing stereoselectivity ($CaCl_2$: *cis*/*trans* from *meso* = *cis*/*trans* from DL = 17:83, at 200 °C),

i.e., pure carbonium ion mechanism. Interpretation is provided by the relative strengths of the interaction between cation and halogen on the one hand and between anion and H on the other. If the two interactions are comparable in strength, the E2 mechanism is found to operate; if interaction between cation and halogen is the stronger, the E1 mechanism is observed.

Stereoselectivity decreases with rise in temperature.

Lecture at Köln (Germany) on November 24, 1967 [VB 116 IE]
German version: Angew. Chem. *80*, 242 (1968)

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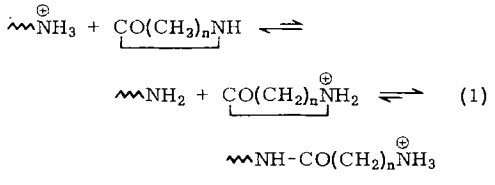
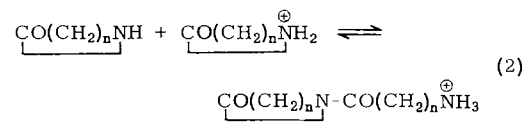
Cationic Polymerization of Lactams

By *M. Rothe* [*]

Polymerization of lactams by Brønsted acids (protic acids, ammonium salts, H_2O) and by Lewis acids[1,2] can be assigned similar types of mechanism in which the active end of the chain is always an ammonium ion[3]. Chain growth can occur after proton exchange with lactams; the lactam cation that is formed acylates the amino group thus freed.



Differences in the course of polymerization with different initiators can be ascribed to the mechanism of the corresponding starting reactions as well as to side reactions brought about by the different end groups formed [(a) carboxyl, (b) *N*-acyllactam, (c) amidine groups[4]]; such end groups can contribute to different types of chain growth (a, b) or lead to chain termination (c). Also of importance are ring size and substitution of the lactam: 5- and 6-membered lactams give only short-chain oligomers; *N*-methylcaprolactam does not react, but *N*-methylaminocaproic acid forms the lactam quantitatively with cationic initiators; 8- and higher-membered lactams, on the contrary, give polymers almost quantitatively because termination with amidine formation, which must lead to rings of medium size, does not occur. Polymerization with protic acids (halogen hydrides, various phosphorus and sulfonic acids, picric acid, CF_3COOH) occurs with acylation of the lactam by the corresponding lactam salt to form the *N*-(ω-aminoacyl)lactam salt.



This and the next higher oligomers were detected, as previously with caprolactam[1], during polymerization of the other lactams mentioned by IR spectroscopy and by electrophoresis with help of the hydroxamic acid reaction. Model reactions with oligomers confirm the mechanism assigned. Acyllactams react with ammonium groups with fission of lactam[5] (chain growth on the C-terminal end); this is indicated by a decrease in the acyllactam content of the polymer during polymerization, as determined titrimetrically and by IR spectroscopy.

The amidine formation was demonstrated chromatographically in the oligomer region, which is easier to study, for $H_2N(CH_2)_5CO-[NH(CH_2)_5CO]_2-NHCH_2C_6H_5 \cdot HCl$; at temperatures above 190 °C, this compound cyclizes partially at the terminal NH_2 group with loss of water.

Lewis acids (BF_3, P_2O_5) and lactams give adducts that acylate monomers in accord with eq. (2). However, polymerization occurs only in presence of cocatalysts (H_2O), the $H[BF_3OH]$ formed acting as protic acid.

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[1] *M. Rothe, G. Reinisch, W. Jaeger*, and *I. Schopov*, Makromolekulare Chem. *54*, 183 (1962); *M. Rothe, H. Boenisch*, and *D. Essig ibid. 91*, 24 (1966).

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Thermokinetic Measurements

By *F. Becker* [*]

The principle of thermokinetic measurements is to follow the progress of a chemical reaction by means of its evolution of heat. Apart from the fact that it gives heats of reaction as well as velocity constants, the method has the advantage that the output dQ_R/dt can be recorded as a function of the heat of the reaction Q_R as the reaction proceeds; and the rate laws are thus evaluated directly in their simple differential form. For a reaction of the first order the function $dQ_R/dt = f(Q_R)$ is a straight line with the slope k_1; its intercept with the abscissa represents the heat of reaction for complete conversion. For a reaction of the second order with equal initial concentrations, recording the function $[dQ_R/dt]^{1/2} = f(Q_R)$ gives a straight line that can be evaluated equally simply.

Two methods were used for experimental realization of this measuring principle. The first is isothermal calorimetry with controlled Peltier cooling, in which the cooling current from a semiconductor Peltier battery in thermal contact with the reaction vessel is controlled so as to provide a cooling output equivalent at each moment to the heat output of the reaction, whereby the initial temperature of the calorimeter is unchanged. The measuring signal is then a voltage proportional to the cooling current i_k, which is recorded by a two-coordinate pen as function of the integral $\int i_k \, dt$ provided by an electronic integrator. The second method is "quasi-isothermal" heat flow calorimetry, in which the temperature difference ΔT between the calorimeter and the thermostat liquid, which is proportional to the heat flow dQ/dt, is used as measuring signal and a function analogous to $dQ/dt = f(Q)$ is recorded, again by means of an electronic integrator and, when required, a root function generator. Sufficient heat flow is provided so that ΔT remains < 0.05 deg, whereupon the temperature-dependence of the rate constants can be neglected. A theoretical study was made of the conditions under which the relation of heat flow dQ/dt to total heat removed Q has the same mathematical form as the thermokinetic rate law $dQ_R/dt = f(Q_R)$.

Examples of reactions were provided to show that these methods enable rate constants to be determined within ± 1 % and reaction enthalpies within ± 2 %, 25 ml of 0.02–0.04 molar solutions of reactants and reaction times of 5–10 min sufficing for this purpose.

Lecture at Bonn (Germany) on November 28, 1967 [VB 120 IE]
German version: Angew. Chem. *80*, 242 (1968)

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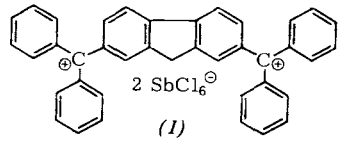
Studies with Stable Carbonium Ions

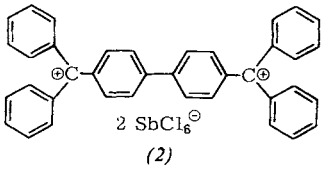
By *H. Volz* [*]

According to HMO calculations the cyclopentadienyl cation in the ground state should have an open molecular shell and triplet character. If the Jahn-Teller effect intervenes, the character of the open molecular shell is retained but the ground state should show singlet character. ESR studies of pentaphenylcyclopentadienyl hexachloroantimonate [1] indicate that the molecule has singlet character in the ground state. An open molecular shell is also obtained by HMO calculation for the indenyl and the fluorenyl cations [2], whose thermodynamic stabilities are accordingly appreciably less than those of the isoelectronic diarylmethyl and triarylmethyl cations, as is shown by study of the chloride ionization equilibria. On account of its electronic instability the fluorenyl cation itself cannot be isolated, even at −70 °C; but the 9-chlorofluorenyl cation can be obtained; the reason for this is probably on the one hand the electron-donating effect of the chlorine [3], and on the other the fact that chlorine in the 9-position is not removed as Cl^+ whereas in the fluorenyl cation the H in the 9-position can be easily removed as H^+.

The acceptor strength of carbonium ions should be raised by introduction of a second or third positive charge into the molecule, owing to mutual action of the positive centers. HMO calculations and chloride ionization experiments show, however, that the acceptor strength of the dication *(1)* is about the same as that of the triphenylmethyl cation.



(1)



(2)

X-Ray structure analysis [5] of single crystals [4] of the dication *(2)* show that the two positive centers (sp^2-hybridized) lie in the same plane as the four aryl carbon atoms attached to them. The two hexachloroantimonate anions are regular octahedrons and the shortest distance between one of the positively charged C atoms and a Cl atom of the $SbCl_6$ amounts to 3.5 Å.

Lecture at Düsseldorf (Germany) on December 4, 1967 [VB 119 IE]
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[1] *H. Volz*, Tetrahedron Letters *1964*, 1899.

[2] *H. Volz*, Tetrahedron Letters *1963*, 1965.

[3] *H. Volz* and *W. D. Mayer*, Tetrahedron Letters *1966*, 5249.

[4] Prepared by Dr. *M. J. Volz de Lecea*.

[5] *J. S. McKechnie*, and *I. C. Paul*, J. Amer. chem. Soc. *89*, 5482 (1967).

Transformation Processes in Fiber Keratins

By *G. Ebert* [*]

A differential calorimeter operating on the principle of differential thermal analysis has been used to study order-disorder transitions in fiber keratin which is gradually heated in water or concentrated electrolyte solutions, attention being paid to the position of the transition temperature, the sharpness of the transition, and the heat of transformation. Also the contraction of the fiber under the conditions of heating used was measured and correlated with the caloric effects.

The influence of cystine bridges on these processes was determined by stepwise reduction of the cystine content (reduction with sodium mercaptoacetate and blocking or elimination of SH groups by $C_2H_4Br_2$ or CH_3I); the transformation temperature and the half-width of the peak are altered only when the cystine content has been reduced to below 25 % of its original value; thus the major portion of the cystine present contributes little to the thermal stability of the ordered region. This is in agreement with the fact that most of the cystine is contained in the amorphous matrix. The cooperative character of the transformation process decreases very rapidly only after degradation of the last of the cystine bridges to be attacked, these bridges being responsible for stabilization of the ordered region and possibly linking the chains. Sulfide cross-links (introduced by treating partially reduced keratin with 1,2-dibromoethane) shift the process to higher temperatures. The same is true within limits for alkali-treated keratin of increased lanthionine content.

In concentrated LiBr solutions (3.5 to 12 molar) an exothermic process is observed which is shifted to higher temperature linearly with rising concentration. The assumption that this is connected with sorption of electrolytes on the keratin fiber, this sorption being hindered below certain temperatures, was confirmed titrimetrically and by conductivity measurements. Causes of the hindrance are to be sought (i) in the structure of highly concentrated electrolytes and (ii) in hindrance of diffusion through cuticula and through cross-linkages in the fiber stock.

The contraction and the exothermic process are linked in such a way that contraction occurs only after the peak has reached its maximum. Essential for the contractive effect are: (i) a not too large cation, which apparently is sorbed onto the polar groups, increases the hydrophilicity of this region, and weakens the stabilizing hydrogen bridges; and (ii) a large, singly charged anion, which is probably sorbed near the hydrophobic groups, disturbs the structure of the water in the neighborhood, and thus makes easier the cleavage of the hydrophobic linkages.

Lecture at Marburg (Germany) on December 15, 1967 [VB 122 IE]
German version: Angew. Chem. *80*, 246 (1968)

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Study of Surface Reactions by Diffraction of Low-energy Electrons

By *G. Ertl* [*]

The method of diffraction of slow electrons (LEED) was used in the classical experiment of *Davisson* and *Germer* for demonstration of the wave nature of electrons, but only recently has it been developed into a useable tool for study of processes occurring on clean surfaces.

If a monochromatic beam of electrons with energies between *ca.* 20 and 300 eV impinges perpendicularly on a single-crystal surface, then because of the slight penetration only diffraction on the uppermost layers of atoms occurs. Thus, after post-acceleration of the elastically scattered electrons, diffraction spots can be seen on a fluorescent screen and from their positions the unit cell of the surface structure can be derived. Exact determination of the structure is unfortunately not yet possible because the nature of the scattering process is not yet completely understood.

Adsorption of gases on clean surfaces often leads to appearance of additional, new spots in the diffraction picture, showing that the adsorption layer is an ordered two-dimen-

sional superstructure. In favorable cases plausible structural models can be given; the adsorption of ethylene on a (110) surface of copper may be cited as an example. Covering of a surface can extend in various ways: for instance, by formation of several different two-dimensional phases with different degrees of coverage, which in the transition area can exist next to one another as large islands (O_2 on (110)-Cu); or with a more or less continuous increase in the (microscopic) degree of coverage and continuous change in position of the diffraction spots (O_2 on (110)-Pd). The successive action of different types of particle can in certain circumstances lead to expulsion or to formation of ordered mixed phases (C + O_2 + (100)-Cu). Decomposition reactions can be followed by means of changes in the diffraction picture (C_2H_4 on (110)-Ni). Quantitative kinetic information can be obtained by measuring the intensity of a specific diffraction spot (reaction $O_{ad} + CO_2 \rightarrow CO_{2,g}$ on (110)- and (100)-Cu).

Lecture at Hannover (Germany) on November 16, 1967 [VB 123 IE]
German version: Angew. Chem. *80*, 244 (1968)

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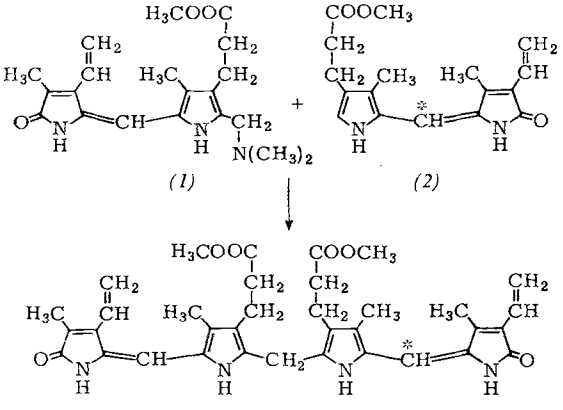
Syntheses in the Pyrrolone and Pyrrole Series[**]

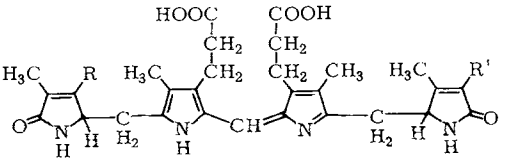
By *H. Plieninger*[*]

The decisive step in a new high-yielding synthesis of bilirubin is the linking of a Mannich base of type *(1)* with an oxodipyrromethene of type *(2)* by the action of acetylenedicarboxylic ester[1] (the formation of bilirubin dimethyl ester is shown schematically below). The reaction is suitable as a general synthesis of unsymmetrical biladienes, *e.g.*, mesobilirubin.



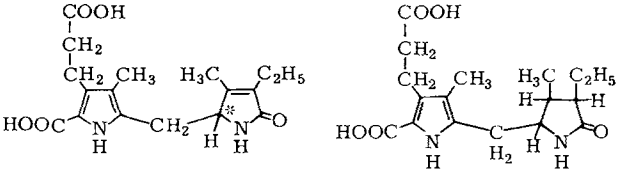
(1) *(2)*

Radioactive bilirubin is easily obtained by using a compound *(2)* labeled by ^{14}C on the methine bridge (asterisk). The linkage of *(1)* to *(2)* is proved because the specific activity in the bilirubin dimethyl ester agrees with that of the component *(2)*; this proof was necessary because it was found that under the same conditions *(1)* can dimerize without addition of *(2)*.



(3), R = $-CH=CH_2$, R' = $-C_2H_5$
(4), R = $-C_2H_5$, R' = $-CH=CH_2$

Further, the synthesis of two vinyl-substituted urobilins *(3)* and *(4)* was described. Compounds of this type are excreted in optically active form in feces after administration of antibiotics.



(5) *(6)*

We have achieved the first resolution of pyrrolone derivatives of type *(5)* and the corresponding pyrrolidone derivatives *(6)*. The compounds are to be used for synthesis of optically active urobilins and stercobilins.

Lecture at München (Germany) on November 14, 1967 [VB 127 IE]
German version: Angew. Chem. *80*, 242 (1968)

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Organisch-chemisches Institut der Universität
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[**] The experimental work was carried out by Mr. *F. El-Barkawi*, Dr. *U. Lerch*, and Messrs. *R. Steinsträsser*, *U. Oswalt*, *J. Ruppert*, and *A. Tapia*.

SELECTED ABSTRACTS

$As_4(NCH_3)_6$ has an adamantane structure. The structure proposed by *H. Nöth et al.* for the compound which they had synthesized was confirmed by *J. Weiss* and *W. Eisenhuth* by a Weissenberg photograph, three-dimensional Patterson synthesis, and three-dimensional Fourier syntheses. An *R* value of 0.153 was obtained. The compound crystallizes monoclinically in the space group C_{2h}^5–$P2_1/n$ with lattice constants a = 7.523 Å, b = 16.696 Å, c = 11.907 Å, β = 93.1°. The unit cell contains four molecules. The four arsenic atoms form a tetrahedron (mean distance 3.271 ± 0.007 Å; edge length of the tetrahedron) and the six nitrogen atoms form an octahedron (edge length 4.110 ± 0.01 Å). Both are completely regular, whereas the six carbon atoms of the CH_3 groups occupy the corners of a highly distorted octahedron. The mean length of the arsenic-nitrogen bond, 1.867 Å, is in good agreement with the calculated value of 1.87 Å. / Z. anorg. allg. Chem. *350*, 9 (1967) / –Sch.

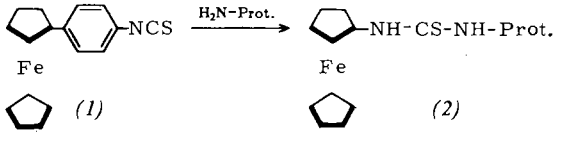
[Rd 762 IE]

Acid-base titrations on powdered quartz and also powdered vitreous silica (Vitreosil) and flint glass (particle sizes 20–10, 10–4, 4–2, and 2 µm; titration in deionized water with 0.1 N NaOH and HCl at 20–22 °C within 10–15 min) led *S. S. Jørgensen* and *A. T. Jensen* to the following conclusions. For quartz (approximately 2.6 acid groups per 100 Å^2) and for vitreous silica the acid-base properties are determined almost entirely by the outer surface, *i.e.* the protolysis capacity (equivalents of acid or base used per 100 g of powder over a defined pH range) increases linearly with specific surface area. The titration curves (pH 3–11) are S-shaped and can be divided into three regions (pH 3–5, 5–9, 9–11); the flatter end regions have the greater protolysis capacities (and thus greater buffer capacities) and show hysteresis effects. On washing the quartz with HCl (removal of the Fe, *ca.* 0.03 %), the protolysis capacity decreases in the acid region and increases in the alkaline region; on washing with HF (removal of the limited crystalline surface), the protolysis

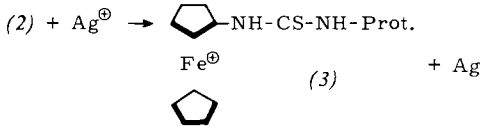
capacity shows an overall decrease. In 1 N NaCl solution the alkaline protolysis capacity is greater than in pure water, and the buffer range is at a lower pH value. The time and hysteresis effects are due to "latent" acidity (dissolution of the silica), though this is obscured by an instantaneous and reversible acidity. The protolysis capacity of flint glass lies completely above pH 4.5 and is about ten times greater than those of quartz and vitreous silica; however, it is not dependent on the specific surface area. In this case there must therefore exist protolytically active inner surfaces. / J. physic. Chem. *71*, 745 (1967) / –Jg. [Rd 785 IE]

The preparation of eleven labeled trinucleotides on a preparative scale is described by *G. Högenauer*. The radioactive trinucleotides, which were required for the investigation of codon-anticodon interactions, were obtained from *E. coli* and bakers' yeast that had been grown in nutrient media containing ^{32}P phosphate. The total RNA was hydrolyzed enzymatically (pancreatic extract), the oligonucleotide mixture was subjected to preliminary purification on a DEAE-cellulose column, and the trinucleotides were separated. Paper electrophoresis and chromatography in the other direction of the paper led to an extensive separation of the nucleotides, GGU, AAU, GGC, and AAC being obtained pure. If the RNA was hydrolyzed with ribonuclease T1, the preliminary purification was unnecessary. Electrophoresis und chromatography gave as final products pure ACG, CAG, AAG, CCG, UUG, UAG, and AUG. The trinucleotide components were identified by high-voltage electrophoresis of the fragments obtained on hydrolysis. / Mh. Chem. *98*, 494 (1967) / –DK. [Rd 754 IE]

Ferrocene-labeled proteins *(2)* have been prepared by *H. Franz* by way of the *p*-ferrocenylphenyl isothiocyanate *(1)* (m.p. 133–135 °C; IR: 2150 cm^{-1}) which he has synthesized.



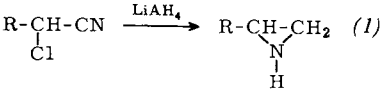
(1) *(2)*



(3)

It is thus possible to label proteins with heavy metals whilst avoiding disturbing complex association. Under the mild conditions of this reaction, the proteins largely retain their immunobiological properties. The author suggests that a further reaction of *(2)* with silver ions, giving *(3)* with separation of silver, could be used for electron-optical investigations. Compound *(1)* is obtained in a yield of 70 % by coupling ferrocene with diazotized *p*-nitraniline, reduction of the nitro compound to *p*-ferrocenylaniline, and further reaction with thiophosgene. / Naturwissenschaften *54*, 339 (1967); Z. Chem. *7*, 235 (1967) / –DK. [Rd 756 IE]

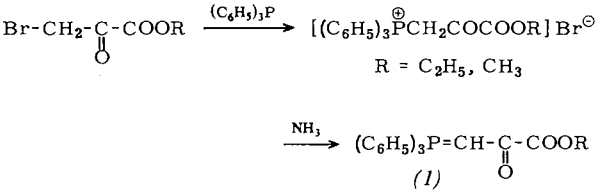
2-Monosubstituted aziridines can be obtained, according to *K. Ichimura* and *M. Ohta*, under very mild conditions in a new synthesis of general importance. The reduction of α-chloronitriles with $LiAlH_4$ at –5 to 0 °C proceeds *via* a reaction which is initially exothermic to give the corresponding aziridine *(1)* in good yield and without by-products.



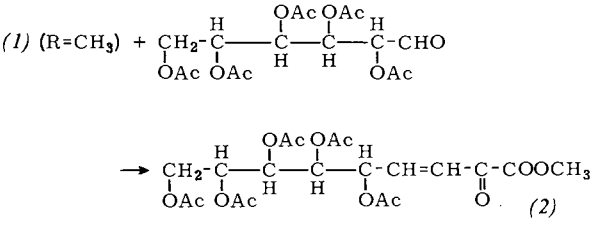
(1)

Thus, for example, 2-(*n*-propyl)aziridine is obtained from α-chloropentanenitrile in 82 % yield (R = n-C_3H_7; b.p. 114–118 °C). / Bull. chem. Soc. Japan *40*, 432 (1967) / –DK. [Rd 757 IE]

(Triphenylphosphoranylidene)pyruvic acid esters *(1)* were prepared for the first time by *Yu. A. Zhdanov* and *L. A. Uzlova* by the reaction of α-bromopyruvic esters with triphenylphosphine and NH_3 (m.p. 169–171 °C).



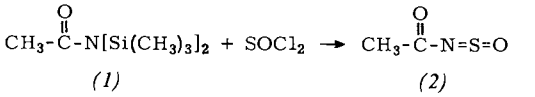
(1)



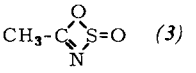
(2)

Wittig reaction of *(1)* (R = CH_3) with D-galactose pentaacetate gave the methyl ester of pentaacetyl-3,4-didehydro-3,4-dideoxy-D-galactononulonic acid *(2)* (m.p. 141–143 °C) in 52 % yield. The reaction thus gave a carbohydrate with an additional three carbon atoms, and thereby provides a means for the preparation of higher sugars and their derivatives, for example those found in lipids, gangliosides, *etc.* / Žh. obšč. Chim. *36*, 1211 (1966); Engl. translation: J. general Chem. USSR *36*, 1225 (1966) / –DK. [Rd 759 IE]

***N*-Thionylacetamide** *(2)*, attempts to prepare which from acetamide and $SOCl_2$ or by "transthionylation" had previously only given acetonitrile and SO_2, was obtained by *O. J. Scherer* and *R. Schmitt* in 70 % yield by the reaction of *N*-(bistrimethylsilyl)acetamide *(1)* with $SOCl_2$. Compound *(2)*, which is the first representative of a new group of compounds of thionylcarboxamides, is a yellow liquid (b.p. 36–37 °C/11 torr) that is insoluble in petroleum ether, readily soluble in ether, CCl_4, $CHCl_3$, and CH_2Cl_2, and reacts explosively with H_2O and alcohols. The possibility of a four-membered ring structure *(3)* was excluded on the



(1) *(2)*



(3)

basis of the IR band at 1740 cm^{-1} (C=O). / Z. Naturforsch. *22b*, 224 (1967) / –DK. [Rd 760 IE]

Novel manganese(II) complexes with the coordination number 8 were obtained by *K. C. Dash* and *D. V. R. Rao* by the reaction of dihalobispyridinemanganese(II) complexes with thiourea in methanol.

$$[Mn{\cdot}py_2{\cdot}X_2] + 4\ NH_2{-}CS{-}NH_2 \rightarrow [Mn{\cdot}py_2{\cdot}(NH_2{-}CS{-}NH_2)_4{\cdot}X_2]$$

(1)

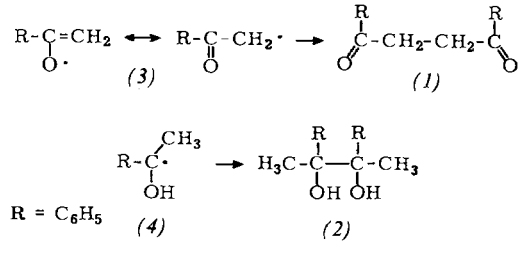
(1a): X = Cl, m.p. 177 °C, white platelets that are soluble in alcohol, nitrobenzene, and acetone. The compound is a weak electrolyte in acetone, and in the solid form it is paramagnetic (χ = 17770, μ_{eff} = 6.6 B.M.). *(1b)*: X = Br, m.p. 167 °C, white platelets with the same properties as *(1a)*, (χ = 15655, μ_{eff} = 6.1 B.M.). / Z. anorg. allg. Chem. *350*, 207 (1967) / –Sch.

[Rd 765 IE]

The mechanism of tRNA degradation by polynucleotide phosphorylases was studied by *M. N. Thang*, *W. Guschlbauer*, *H. G. Zachau*, and *M. Grunberg-Manago*. The enzyme cleaves the ribopolynucleotides by phosphorolysis, thus liberating 5′-nucleoside diphosphates. If ^{32}P phosphate is introduced, the diphosphates are labeled in the β-position. Phosphorolysis of tRNA is complete only above 45 °C, since at this point the chains are denatured, but not at, for example, 42 °C. At temperatures below 45 °C intact tRNA molecules remain, which are only very slowly decomposed. The degradation takes place as follows: (1) addition of the enzyme to the 3′-OH end; (2) step-by-step movement of the enzyme along the nucleotide chain with liberation of nucleoside diphosphates; (3) regions with secondary structure (base pairing) are only attacked very slowly; and (4) the enzyme does not separate from the substrate until it reaches the 5′-OH end. Polynucleotide phosphorylase is well known for its reverse reaction; it provided the first means of synthesizing polyribonucleotides and thereby the means for the beginning of the elucidation of the genetic code. / J. molecular Biol. *26*, 403 (1967) / –Hö.

[Rd 772 IE]

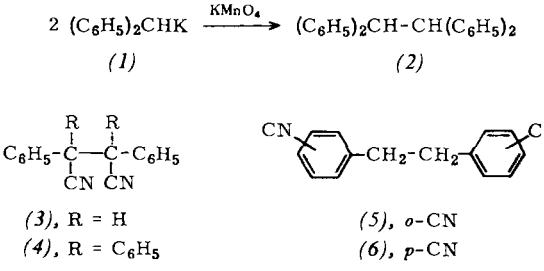
A new photochemical reaction of acetophenone is described by *H.-D. Becker*. When liquid acetophenone is irradiated with UV light in the presence of catalytic amounts of phenol (Hg high-pressure lamp, Pyrex filter), 1,2-dibenzoylethane *(1)* is formed in 86 % yield (calculated on the acetophenone reacted) together with a mixture of stereoisomeric acetophenone pinacols *(2)*. Methyl-substituted acetophenones react in the same way; the phenol may be replaced by certain substituted phenols, though these are less effective. It is assumed that the acetophenone undergoes a photochemical enolization catalyzed by phenol, and that the resulting product undergoes disproportionation to give a phenoxy *(3)* and a semipinacol



radical *(4)*, which then dimerize to give the reaction products *(1)* and *(2)*. / J. org. Chemistry *32*, 2140 (1967) / –Ma.

[Rd 777 IE]

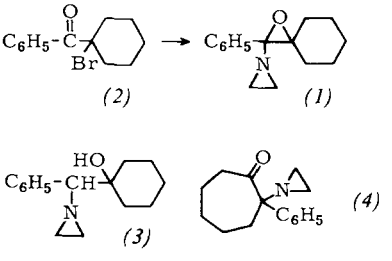
The oxidative dimerization of carbanions is described by *E. M. Kaiser*. The carbanions were prepared by means of alkali metal amides, and were dimerized rapidly and smoothly with oxidizing agents in liquid NH_3, the only impurity being the starting material. Solid $KMnO_4$ reacts with diphenylmethylsodium to give 1,1,2,2-tetraphenylethane *(2)* in 42 % yield, and with the potassium compound *(1)* to give *(2)* in 69 % yield; lower yields are obtained with $CuBr_2$, $K_2Cr_2O_7$, $KClO_4$, or air. The reaction is not limited to hydrocarbons; the potassium salts of phenylacetonitrile and diphenylacetonitrile react with $KMnO_4$ to give the dimers *(3)* and *(4)* in 67 and 77 % yields, and the potassium salts of *o*- and *p*-



tolunitrile give *(5)* and *(6)* in yields of 50 and 47 %. / J. Amer. chem. Soc. *89*, 3659 (1967) / –Ma.

[Rd 778 IE]

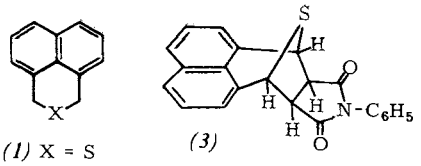
Epoxyamines are a new class of organic compounds. The first stable representative of this class, 2-(1-aziridinyl)-2-phenyl-1-oxaspiro[2.5]octane *(1)*, was synthesized by *C. L. Stevens* and *P. M. Pillai* by the action of the lithium salt of ethylenimine on α-bromocyclohexyl phenyl ketone *(2)* in ether at room temperature (b.p. 90–95 °C/0.001 torr; m.p. 20–22 °C; yield 70–75 %). Acid hydrolysis of *(1)* gave α-hydroxycyclohexyl phenyl ketone, reduction with $NaBH_4$ gave 1-[α-(1-aziridinyl)-benzyl]cyclohexanol *(3)*, and catalytic hydrogenation gave 1-(α-*N*-ethylaminobenzyl)cyclohexanol. When *(1)* was heated in boiling *o*-dichlorobenzene under nitrogen, ring expansion occurred with the formation of 2-(1-aziridinyl)-2-phenyl-



cycloheptanone *(4)*. / J. Amer. chem. Soc. *89*, 3084 (1967) / –Ma.

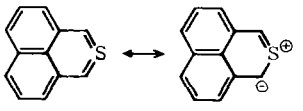
[Rd 779 IE]

Reactive aromatic heterocycles containing tetravalent sulfur have been identified by *R. H. Schlessinger* and *I. S. Ponticello*, and also by *M. P. Cava*, *N. M. Pollack*, and *D. A. Repella*. 1,8-bis(hydroxymethyl)naphthalene reacted with P_2S_5 in CS_2 to give the sulfide *(1)* (85 %, m.p. 102 °C), which was then oxidized with $NaIO_4$ to give the sulfoxide *(2)* (m.p. 230 °C; decomp.). Compound *(2)* reacted with *N*-phenylmaleimide in acetic anhydride to give the Diels-Alder adduct *(3)*. The mass spectrum of *(3)* contained a peak at *m/e* = 184, which was assigned to the retrodiene product naphtho[1,8-*c*,*d*]thiapyran *(4)*. Acenaphtho[5,6-*c*,*d*]thiapyran *(5)* was detected in an analogous reaction starting from 5,6-bis(hydroxymethyl)-acenaphthene. The trapping of *(4)* by dienophiles offers a simple method for the preparation of pleiadene derivatives.

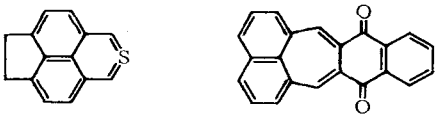


(1) X = S
(2) X = SO

(3)



(4)

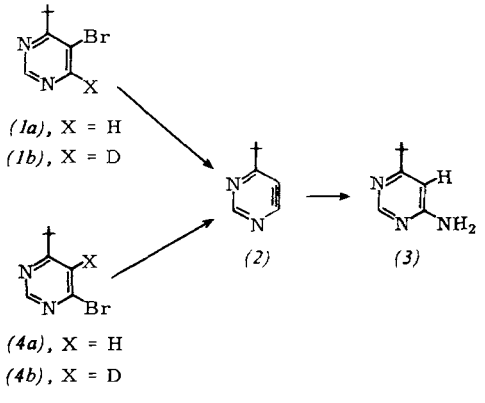


(5) (6)

For example, if the starting materials were *(2)* and 1,4-naphthoquinone, it was possible to prepare the unusually stable benzo[*l*]pleiadene-8,13-quinone *(6)* in the form of brown needles of m.p. 247–248 °C. / J. Amer. chem. Soc. *89*, 3640, 3641 (1967) / –Ma. [Rd 780 IE]

Mono-Na acetonitrile and homologous compounds, which are assumed to be the intermediates in many condensation reactions of nitriles with α-H atoms and in alkylation reactions of such nitriles, are reported by *C. Krüger* to be obtainable by the reaction of Na bis(trimethylsilyl)amide with acetonitrile or similar nitriles in ether at –40 to –60 °C (to avoid self-condensation of the nitrile). $NaCH_2CN$ adds only to polar double bonds (CO, CN); however, it also acts as a carbene precursor, particularly in the presence of cyanide acceptors. For example, after heating the compound in cyclohexene it is possible to demonstrate (by gas chromatography) the presence of norcarane (2 %). / J. organometallic Chem. *9*, 125 (1967) / –Ma. [Rd 781 IE]

The existence of the heteroaryne 6-*tert*-butyl-4,5-didehydropyrimidine *(2)* has been established by *H. C. van der Plas, P. Smit,* and *A. Koudijs.* Reaction of *(1a)* with KNH_2/NH_3 at –33 °C affords 6-amino-4-*tert*-butylpyrimidine *(3)* in 14 % yield. Under the same conditions, the isomer *(4a)* gives *(3)* in quantitative yield.



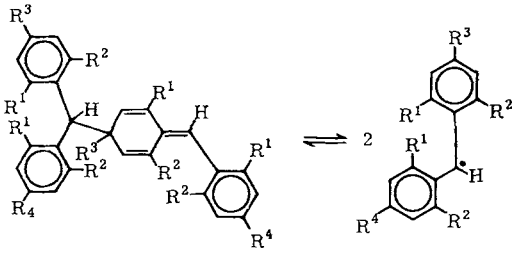
(1a), X = H
(1b), X = D

(2) (3)

(4a), X = H
(4b), X = D

The results of experiments conducted with the deuterated compounds *(1b)* and *(4b)* ruled out other possible reaction courses, such as attack by the amide ion at the electron-depleted 6-position of *(1a)* and subsequent hydride shift, or addition/elimination reaction of *(4a) via* a resonance-stabilized anion. The reactions yielded compound *(3)* only, and not [5-D]-6-amino-4-*tert*-butylpyrimidine. / Tetrahedron Letters *1968*, 9 / –Kr. [Rd 830 IE]

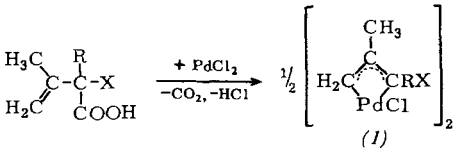
Formation of methylenecyclohexadiene derivatives on dimerization of di- and triarylmethyl radicals has been established by *H. Lankamp, W. Th. Nauta,* and *C. Maclean.* On the basis of chemical properties and spectra, the authors deduce that there are two kinds of radical dimers: ethane derivatives, which only decompose slowly, if at all, into radicals (*e.g.* di-, (unsubstituted) tetra-, and pentaphenylethanes, as well as all tetraphenylethanes bearing a moderate number of *o*-alkyl groups). On the other hand, dimers that are in equilibrium with the free radicals in solution have a methylenecyclohexadiene structure. Examples:



	R^1	R^2	R^3	R^4	M.p. (°C)
(1)	CH_3	CH_3	H	H	120
(2)	CH_3	CH_3	H	CH_3	115
(3)	CH_3	CH_3	CH_3	CH_3	137
(4)	$(CH_3)_3C$	H	H	H	–

In solution, *(1)*, *(2)*, and *(4)* dissociate to approximately the same extent. Compound *(3)* is completely dissociated in solution; it can only be prepared from dimesitylmethanol with V^{2+} or Cr^{2+} in acetone/H_2SO_4 at low temperature. The UV and NMR spectra of *(1)* through *(4)* are in agreement with the structures assigned. For purposes of comparison, the ethane derivatives *(1a)* and *(3a)* corresponding to *(1)* and *(3)*, respectively, were prepared from the diarylmethanol with an excess of V^{2+} or Cr^{2+} at room temperature (yield 10–20 %). *(1a)*, m.p. 227–228 °C, and *(3a)*, m.p. 230–231 °C, rearrange to form the radical-containing equilibrium mixture or the radicals corresponding to *(3)* if they are heated for a short time at 220–240 °C and then quenched. *Gomberg*'s "hexaphenylethane" apparently also exists in the form of a methylenecyclohexadiene derivative. / Tetrahedron Letters *1968*, 249 / –Kr. [Rd 831 IE]

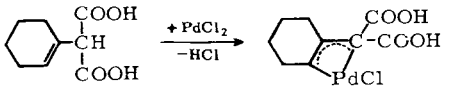
A new method for the preparation of π-allylpalladium chloride complexes *(1)*, which carry a carboxyl, an ester, an acid amide, or a nitrile group on C-1 and a CH_3 group on C-2, is reported by *R. Hüttel* and *H. Schmid.* The complexes are formed on reaction of unsaturated derivatives of malonic acid with $PdCl_2$ under mild conditions.



(1)

Examples: *(1a)*, R = CH_3, X = COOH, yield 97 % (as compared to a yield of 13 % when prepared from trimethylacrylic acid and a yield of 3 % of a mixture of isomers when prepared from isopropenylpropionic acid); *(1b)*, R = CH_3,

X = CN, yield 78 %; and *(1c)*, R = C_2H_5, X = $COOC_2H_5$, yield 70 %. In order to investigate the competition between proton loss and decarboxylation when the proton and the carboxyl group are both attached to the same C atom, 1-cyclohexenylmalonic acid was used as starting material in place of the unknown isopropenylmalonic acid. The formation of compound *(2)* proves that the highly activated α-

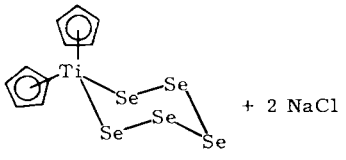


(2)

hydrogen atom is split off preferentially. / Chem. Ber. *101*, 252 (1968) / –Kr. [Rd 832 IE]

Di-π-cyclopentadienyltitanium(IV)pentaselenide *(1)* has been prepared by *H. Köpf, B. Block*, and *M. Schmidt*. They made use of the following reaction in aqueous acetone:

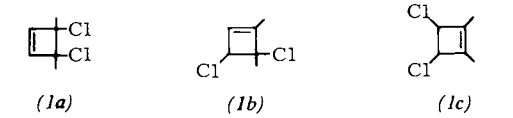
$(\pi\text{-}C_5H_5)_2TiCl_2 + Na_2Se_5 \longrightarrow$



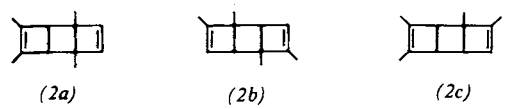
(1)

Compound *(1)*, dark violet crystals of m.p. 211 °C, is insoluble in water, difficultly soluble in ether or benzene, and moderately soluble in H_2S or dimethyldisulfide. *(1)* is stable in air. Its ^1H–NMR spectrum is temperature dependent: when recorded at room temperature, the spectrum contains two signals of equal intensity, irrespective of which solvent is used; as the temperature increases these signals (measured in dimethyldisulfide) broaden reversibly and finally coalesce. Above 100 °C, compound *(1)* reacts irreversibly with the solvent. The temperature dependence of the spectrum is interpreted as inversion of the six-membered ring, whose conformation is fixed. The ^1H–NMR spectrum of the known analogous pentasulfide, red-violet needles of m.p. 201–202 °C, shows the same temperature dependence. / Chem. Ber. *101*, 272 (1968) / –Kr. [Rd 833 IE]

"Dimers of 1,2-dimethylcyclobutadiene" *(2a)—(2c)* have been obtained by *R. Criegee, W. Eberius*, and *H.-A. Brune* on dechlorination of a mixture of the dichlorides *(1a)–(1c)* that is formed by addition of HCl to dimethylenecyclobutene. On dechlorination with lithium- or sodium amalgam, the compounds *(2a)–(2c)* were always formed in the molar



(1a) *(1b)* *(1c)*



(2a) *(2b)* *(2c)*

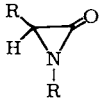
(3a) *(3b)*

ratio 1:1.4:5.4, irrespective of the molar ratio of the isomers *(1)*. Their pyrolysis to tetramethylcyclooctatetraenes served as proof of structure. In *(2c)* the rings are *syn*-fused, as the ozonization shows. The formation of *(2a)–(2c)* can be interpreted as a Diels-Alder synthesis from two molecules of 1,2-dimethylcyclobutadiene: *(2a)* and *(2b)* could be formed from one molecule each of *(3a)* and *(3b)*, and *(2c)* from two molecules of *(3a)* or *(3b)*. It is assumed that *(3a)* and *(3b)* are tautomers. / Chem. Ber. *101*, 94 (1968) / –Kr. [Rd 834 IE]

An unusually stable α-lactam that is derived from adamantane has been prepared by *E. R. Talaty, A. E. Dupuy jr.*, and *A. E. Cancienne jr.* 1-Adamantylacetyl chloride forms the bromine derivative *(1)* which yields the bromoamide *(2)* on reaction with 1-aminoadamantane (2 mole). Reaction of *(2)* with potassium *tert*-butoxide in ether at 0 °C affords the α-lactam *(3)*, m.p. 180 °C, 72 % yield. Compound *(3)* sublimes at

$R\text{-}CH_2\text{-}COCl \longrightarrow R\text{-}CHBr\text{-}COCl$ *(1)*

$\longrightarrow R\text{-}CHBr\text{-}CONH\text{-}R \longrightarrow$ *(2)*

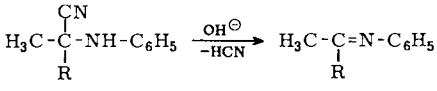


(3) R = 1-Adamantyl

105–110 °C/0.025 torr, and does not decompose in boiling xylene; decomposition in boiling methanol is not complete until a period of 30 h has passed. / J. heterocyclic Chem. *4*, 657 (1967) / –Ma. [Rd 835 IE]

Ketanils and ketimines may be prepared *via* α-cyanamines *(1)*, according to *J. S. Walia, L. Heindl, H. Lader*, and *P. S. Walia*. The compounds *(1)* are formed in excellent yields on reaction of ketones with aniline and $CN^{\ominus}$ ions in the presence of acetic acid. Reaction of *(1)* with methanolic KOH at room temperature affords ketaniles *(2)*. The reaction presumably proceeds by way of the base-catalyzed elimination of HCN from *(1)*. Examples:

R	Yield of *(1)* (%)	Yield of *(2)* (%)
Phenyl	87	94
p-Chlorophenyl	98	99
2-Thiophenyl	82	95
2-Pyridyl	89	72
Styryl	97	80



(1) *(2)*

/ Chem. and Ind. *1968*, 155 / –Ma. [Rd 836 IE]

The molecular structure of gaseous disulfane has been determined by *M. Winnewisser* and *J. Haase*, who combined the results obtained from electron diffraction experiments and microwave spectrometry. The electron diffraction data obtained by the sector microphotometer method indicated

the interatomic distances d(S–S) = 2.055 ± 0.001 Å and d(S–H) = 1.352 ± 0.010 Å and the angle (HSS) = 91° 57′ ± 30′. The H–H distance, and thus the dihedral angle between the two half molecules, could not be determined by electron diffraction because of the low scattering power of the H atom; for this reason the dihedral angle was established by microwave spectroscopy. For the molecule in question, it was possible to determine only differences in the rotation constants from which a value of 90°37′ ± 3′ can be calculated for the dihedral angle. / Z. Naturforsch. *23a*, 56 (1968) / –Hz.
[Rd 837 IE]

The use of tetrakis(triphenylphosphine)platinum(0) as initiator for radical polymerizations has been suggested by *C. H. Bamford, G. C. Eastmond,* and *K. Hargreaves.* It is used in combination with a suitable halogen compound (*e.g.* CCl_4). Since the activation energy for the initiation of the polymerization of methyl methacrylate amounts to only 11.2 kcal/mole, the combination is effective at temperatures between below room temperature and 80 °C. The unusually low frequency factor is assumed to result from steric hindrance to the formation of a transition complex with the monomer or the solvent. No inhibition occurs at high halogen concentrations. / Trans. Faraday Soc. *64*, 175 (1968) / –Hz.
[Rd 838 IE]

The absorption spectra of liquids in the millimeter range have been measured by *J. E. Chamberlain, H. A. Gebbie, G. W. F. Pardoe,* and *M. Davies* by means of Fourier transformation of interferograms. If an indium antimonide detector that is cooled by liquid helium is used, the long-wave limit of interferometry can be extended to 5 mm. The range of application of the method thus overlaps with that of microwave spectroscopy. The authors consider that the advantage of their method lies in the fact that broad absorption bands – such as are encountered with dielectric liquids in this spectral region – can be recorded better than with microwaves, since the tuning of microwaves over a wide range is very difficult. The spectra of water and of chlorobenzene as obtained by the new method are given as examples. / Chem. Physics Letters *1*, 523 (1968) / –Hz.
[Rd 839 IE]

The oxidation of phenylhydroxylamine by OH radicals in dilute (approx. 5×10^{-4} M) solutions saturated with N_2O, has been followed by pulse radiolysis by *A. Wigger, A. Henglein,* and *K.-D. Asmus.* The following reactions and data are deduced from the dime-dependence of the absorption spectra (0 to 20 μsec after the pulse):

$$C_6H_5NHOH + OH \rightarrow C_6H_5NHOH(OH) \quad (a)$$
$$\lambda_{max} = 440, 350, 270\ \mu m$$

($k = 1.2\times10^{10}$ to 1.5×10^{10} l·mole^{-1}·sec^{-1}, independent of pH between 3.7 and 11.5).

$$C_6H_5NHOH + e_{aq} \rightarrow C_6H_5NHOH(e_{aq}) \quad (b)$$

($k = 1.4\times10^{9}$ to 1.8×10^{9} l·mole^{-1}·sec^{-1}, *i.e.* slower than expected for a diffusion-controlled reaction).

$$C_6H_5NHOH(OH) \rightarrow C_6H_5NOH + H_2O \quad (c)$$
$$\lambda_{max} = 450, 270\ \mu m$$

($k = 1.8\times10^{5}$ sec^{-1}; $\tau_{1/2} \approx 5$ μsec at pH 4.5 to 7, ≈ 1 μsec at pH = 2 and 10)

$$C_6H_5NOH \rightarrow C_6H_5NO^- + H^+ \quad (d)$$
$$\lambda_{max} = 450, 290\ \mu m$$

($pK_a = 11.7$)

$$2\ C_6H_5NOH \rightarrow C_6H_5NO + C_6H_5NHOH \quad (e)$$
$$\lambda_{max} = 330\ \mu m$$

($k_{max} = 4\times10^{7}$ l·mole^{-1}·sec^{-1} at pH = 11.5).

/ Ber. Bunsenges. physik. Chem. *71*, 513 (1967) / –Jg.
[Rd 813 IE]

BOOK REVIEWS

Massenspektrometrische Strukturanalyse organischer Verbindungen. Eine Einführung. (Mass Spectrometric Structural Analysis of Organic Compounds. An Introduction). By *G. Spiteller.* Verlag Chemie GmbH., Weinheim/Bergstr. 1966. 1st Edit., xii, 355 pp., 91 illustrations, 2 tables, DM 44.–.

Now that this work has been published, we have at our disposal a German-language book that presents the principles of this modern physical technique which, during the last decade, has achieved immeasurable importance for structural analysis of organic molecules; the book also enables the reader to use the method practically. Combinations with gas chromatography, thin-layer chromatography, and pyrolysis, together with the insights thereby obtained into fragmentation processes, have converted mass spectrometry into a specialist area with great possibilities for interpretations over a wide section of chemistry as a whole. The appearance of a monograph of this kind is thus particularly welcome.

The first section treats briefly the physical principles and details of apparatus. It is to be welcomed that attention is paid to practical directions for addition of samples, relative quantities, purity of samples, evaluation of spectral quantities, *etc.* This is of great value because, in the reviewer's experience, the difficulties of the beginner start with reading the graph that emerges from the mass spectrometer.

In the second section the mechanisms of ion formation and degradative reactions of organic molecules in the mass spectrometer are explained in great detail.

In the third section there follow descriptions and explanations of the mass spectra of the most important classes of chemical compounds. Here it has proved valuable to divide substances into aliphatic hydrocarbons and those with substituents of class 1 and 2, aromatic types of compounds, heterocyclic compounds, and aliphatic compounds containing several functional groups. Numerous examples are given, by means of which the key fragments typical of a class of compounds are clearly set out.

The fourth section contains mass spectra of natural products. Typical decomposition reactions are presented by means of characteristic examples and with references to the literature.

The fifth and final section is devoted to an introduction into the evaluation of mass spectra of substances of unknown composition. It contains very helpful and useful tables showing the neutral fragments split off in the first stage of decomposition and also the key fragment ions. Experimental details are also given for chemical reactions on the micro scale which are particularly useful since they permit pre-

paration of those derivatives that are most suited to mass spectrometric work.

The author's great experience in mass spectrometric structural analysis is evident from the many valuable and practical directions. The book provides an excellent foundation for chemists who have to deal with mass spectrometry of organic compounds. *K. Heyns* [NB 662 IE]

Grundlagen der Synthese von Zwischenprodukten und Farbstoffen (Principles of the Synthesis of Intermediates and Dyestuffs). By *N. N. Woroshzow*, Translated into German by *E. Baumann* and *F. Bahr*. Akademie-Verlag, Berlin 1966, 1059 pp., 26 illustrations and 12 charts, DM 135.–.

After an interval of several decades a major work has appeared in which the principles of the synthetic methods of interest in dyestuff chemistry are discussed in detail. The present book contains a wealth of material collected from the literature and critically surveyed. An introductory chapter, treating in particular the principles of aromatic electrophilic and nucleophilic substitution, is followed by 14 chapters concerned with sulfonation, nitrosation, introduction of halogen, introduction of amino groups, replacement of the sulfo group by a hydroxyl group, replacement of halogen by other substituents, interconversion of amino and hydroxy compounds, diazotization, acylation, oxidation, and sulfuration, reduction of compounds containing nitrogen-free functional groups, condensations, and rearrangements.

The individual chapters treat the synthetic principles in general first, then the mechanistic principles, and finally the preparative and sometimes the technical operations, as well as special cases. Every chapter is characterized by an extraordinarily large number of references to the old and new literature; the many references to Russian papers are sure to be of particular importance to readers in the Western hemisphere. One can point, for instance, to the discussion of the kinetics of alkali melts (p. 351) where it is shown that the experimental proof, usually attributed to *J. F. Bunnett*, for the two-stage mechanism of nucleophilic aromatic substitution by means of *Bodenstein*'s equation for the stationary state, was given as early as 1938 by *Woroshzow jun.* for alkali melts of aromatic sulfonic acids.

On the other hand, a remarkable feature of this book is that sections presented in a very modern way are often placed next to problems that are discussed in the manner of the 1920's. In spite of this limitation, *Woroshzow*'s book is a mine of knowledge, not only for the dyestuff chemist, but also for all chemists who are interested in the principles of aromatic chemistry. It shows again how many interesting basic problems advanced by the technical development of dyes during the past hundred years still await detailed investigation. *H. Zollinger* [NB 660 IE]

Zuckerchemie. Eine Einführung (Sugar Chemistry. An Introduction). By *G. Henseke*. Akademie-Verlag, Berlin 1966. 1st Edit., 167 pp., 3 tables, 3 charts, DM 25.–.

This little book follows a mainly conventional pattern. The author has succeeded in collecting a very large amount of the wide area of carbohydrate chemistry in a small space; the book consequently bears some resemblance to a dictionary. Corresponding to their importance, the significant classes of compound and the fundamental reactions are discussed, their arrangement being easy to follow. In this respect the book fulfils its purpose and provides a rapid survey for all who are interested and particularly for readers who are not chemists. The numerous formulas are clear and have been prepared with great care; however, most of them are drawn with the sugar chain vertical, whereas in recent years presentation by means of ring formulas and, whenever possible, by stereochemical formulas has been preferred because these lead to a better understanding of the actual molecular shapes and the course of reactions. It is only in the latter way that the reader can readily appreciate how considerations of mechanisms developed in the past decade and modern methods of measurement apply also to carbohydrate chemistry. The relation of reaction mechanism to stereochemistry, questions of conformational analysis, and the importance of NMR spectroscopy for determination of structure could well have been more strongly emphasized. *H. Paulsen* [NB 663 IE]

Kunststofftechnisches Wörterbuch (Plastics dictionary), Vol. III, French-German. By *A. M. Wittfoht*. Carl Hanser Verlag, München 1966. 1st Edit., xvi, 768 pp., plastic cover, DM 124.–.

The previously published Volume 4 (German-French) has been warmly recommended because of the very good compilation and excellent explanation of individual words, often supported by most useful drawings and diagrams.

The same can be said about the present volume. As such, the dictionary is exemplary in arrangement and typography, and hence very lucid as well as convenient to use. The fields of application of plastics dealt with in Volume 4, *e.g.* adhesives, reinforced plastics and foams, have been expanded to include the latest developments. Novel chemical processing and processing machinery, *e.g.* winding techniques and heat insulation by ablation, have been added. The inclusion of units and standards employed in plastics testing is welcome. A further feature is the inclusion of size-reduction machinery, winding techniques, glass fibers, coating, dryers, welding and a section on "plastic pipes" in the illustrated section previously comprising shaping, presses, molds, processing and mixers.

A very high standard has been achieved through the collaboration of numerous German and French specialists, particularly *Max Windsor*, whose name appears as co-editor. The book has become the standard work in the plastics field for technologists, businessmen, and translators alike, and can be warmly recommended to all interested in this field. *O. Horn* [NB 653 IE]

Zur Viskosimetrie (Viscometry). By *L. Ubbelohde*. Completely revised by *G. H. Gottner* and *W. Weber*. S. Hirzel Verlag, Stuttgart 1965. 7th Edit., xii, 75 pp., 15 illustrations and 19 tables, DM 18.60.

The seventh edition of this standard work, which has been thoroughly revised, differs from the previous editions in introduction of the standard value 1.002 cP for the viscosity of water at 20 °C.

The book is divided into three parts: a general part, a theoretical part, and tables for conversions and calculations. A pleasing feature is the concise and clear exposition, which strives towards a general presentation of the problems of viscometry and yet remains close to everyday practice.

The book has won for itself a wide readership among research and industrial workers, although in this edition specialization on the requirements of the petroleum industry has been avoided. *K. F. Elgert* [NB 681 IE]

Handbuch der mikrochemischen Methoden (Handbook of Microchemical Methods). Edited by *F. Hecht* and *M. K. Zacherl*. Vol. 4: Elektronenstrahl-Mikroanalyse (Electron Beam Microanalysis). By *H. Malissa*. Springer-Verlag, Vienna-New York 1966. 1st Edit., viii, 154 pp., 79 illustrations, linen DM 49.–/Subs. price DM 39.60.

In this volume of the Handbook, theory, technique, and uses of electron beam microanalysis are described in detail. The main section includes X-ray emission analysis with ex-

citation of the X-radiation by a focused electron beam. Other techniques such as those involving electron and X-ray absorption, electron scattering, and X-ray and electron diffraction are treated more briefly because of their lesser analytical importance. Electron microscopy is omitted.

The presentation is illustrated by means of many examples that are taken from the literature or from the authors' own researches. An exhaustive list of references is added to each of the five chapters; in particular, the last chapter, which concerns actual examples from research, has a literature appendix containing 238 references, arranged according to subjects. In view of the wide range of material considered, and the fact that it is partly new, it is not surprising that a few errors occur, *e.g.* the explanation and numerical values for resolving power on p. 61 and some formulas and dimensions in section b on pp. 83–89. An author index and a (regrettably too short) subject index are attached. The book will be a valuable help to all engaged in electron and X-ray microanalysis. *H. Massmann* [NB 678 IE]

[1] Cf. Angew. Chem. *75*, 239 (1964).

Kernmagnetische Resonanz (Nuclear Magnetic Resonance). By *H. Sillescu*. Springer-Verlag, Berlin-Heidelberg-New York 1966. 1st Edit., viii, 136 pp., illustrations, DM 32.–.

Nuclear magnetic resonance spectra, particularly high-resolution spectra of organic liquids, present the chemist with clear relations to the parameters of a given molecule; the former assumption that theoretical calculations would be fruitful in this field has indeed proved accurate during recent years. However, for a thorough understanding the chemist needs knowledge of sections of theoretical physics that had to be sought out tediously from textbooks written for physicists. In this area the present book fills a gap for German-speaking chemists, in that the classical relations are briefly summarized and applied to the operator formalism of quantum mechanics, thence are derived the consequences that apply to nuclear resonance spectroscopy, and indeed in a breadth and with a detail that do not use a phrase such as "a short calculation shows that" to fob off the chemist who is not always very proficient in mathematics.

The theory of broad line nuclear resonance spectroscopy, as well as that of high-resolution techniques, are treated very thoroughly, but the double resonance methods that are so important for the organic chemist are barely mentioned. Chapters on quadrupole coupling and relaxation phenomena complete the physical section. However, the mathematical appendix is likely to be too brief for the chemist who has had only the minimum of training. In spite of its didactically precise construction the book requires concentrated reading by the beginner; for the expert it will be a welcome revision. The production is good, but in the interest of a lower price it could have been more economical.

E. G. Hoffmann [NB 667 IE]

Reaktionen an und in Festen Stoffen (Reactions on and in Solid Substances). By *K. Hauffe*. Anorganische und Allgemeine Chemie in Einzeldarstellungen (Inorganic and General Chemistry), Volume II. Springer-Verlag, Berlin-Heidelberg-New York 1966. 2nd revised Edit., xii, 968 pp., 525 illustrations, DM 148.–.

The first edition of this book was reviewed in this Journal [*] over ten years ago. Since that time, "on and in", as this book is called in the laboratory, has proved a reliable guide to research in the field of solid-state reactions, and what was said then still applies today. The work rests on two foundations: disorder theory and diffusion theory. Great progress has meanwhile been made in both areas, also in their relation to solid-state chemistry, and not least through two symposia, severally in Amsterdam and Munich. It is thus not surprising that the author has wished to modernize his book; but it is surprising that he has found the time and strength for such an undertaking; the shear increase in size from 700 to 1000 pages shows how much had to be done. However, the increased range and the increased documentation promotes the book from the ground state of a textbook for students into the conductivity band of a handbook for the active research worker.

The general layout of the book has not changed. After a general chapter on defect phenomena, defects in ionic and covalent crystals are treated as special cases, and boundary-layer phenomena receive particular emphasis. Then follows the extensive chapter on diffusion, and thus the ground is prepared for discussion of special groups of phenomena: oxidation (scaling), formation of higher ionic compounds (additions), reduction, and roasting. A final chapter briefly collects together what has not yet been discussed in the book: ceramics and metal ceramics, photography, catalyst carriers, passivity, deformability, crystal growth, epitaxy.

Treatment of this very varied material is brought up to date in the present edition. The means by which this was done are as follows. The theoretical part of the chapter on diffusion has been completely revised by *C. Seyfert*, a former collaborator of the author and now in Karlsruhe; it now provides solutions for the most varied geometries and boundary conditions. Except for a number of additions, the atomistic part of this chapter has undergone little change. The electrochemistry of ionic crystals has been included at appropriate places in the text; progress since the first edition makes it now possible to obtain some information about defects and carrier activities from potential measurements on solid-state cells.

New results on the interaction of gases with semiconductors are discussed in the hope that these phenomena will become more important to catalysis and to the reduction of ores, though progress in these directions is not yet remarkable. Much new material has been added concerning oxidation of metals and reduction of ores.

This book thus bears witness to steady progress in solid-state chemistry with the help of solid-state physics, but progress is not marked by spectacular breakthroughs. An impression, admittedly a fleeting one, was formed by the reviewer that the first edition, conceived originally as a whole, has not absorbed the newer experimental material quite homogeneously, but that the latter has been treated more in the form of abstracts and thus creates a kind of disturbance. This was probably unavoidable and will certainly not stop "on and in" from being, in the future as hitherto, a faithful and indispensible aid for all solid-state chemists.

G.-M. Schwab [NB 676 IE]

[*] Cf. Angew. Chem. *68*, 631 (1956).

Der Stoffwechsel im Zentralnervensystem (Metabolism in the Central Nervous System). By *N. Seiler*. Verlag Georg Thieme, Stuttgart 1966. xi, 139 pp., 23 illustrations, 11 tables, paperback, DM 24.–.

This volume in the monograph series "Biochemie und Klinik" (Biochemistry and the Clinic) gives a welcome survey of present views on basic dynamic biochemistry, exemplified for the central nervous system in physiological and pathological states. General metabolic processes, as they occur in other organs, are first described as an essential preliminary for understanding of special functions, and then the peculiarities of the central nervous system are set out. In this way the metabolic problems such as anoxia, narcosis, and mental illnesses which are so typical for the brain are explained. The author describes in particular detail the metabolic disturbances that so often lead to mental illness.

Although the most recent knowledge is not considered in all the chapters, a particular merit of this book is the consistently brief presentation of the most important results in this field, a presentation that is based on an underlying knowledge of the literature. The book provides a worthwhile foundation for all who may be occupied with the special questions of the functions of nerves or brain. Further, the text is everywhere so richly provided with references that it eases the way to further information for those interested in greater detail.

H. Wiegandt [NB 661 IE]

Die Entwicklung der Chemie in der neueren Zeit (The Development of Chemistry in Modern Times) by *H. Kopp*. Geschichte der Wissenschaften in Deutschland, Band X (History of Science in Germany, Vol. 10). Johnson Reprint Corp., New York. Georg Olms Verlagsbuchhandlung, Hildesheim 1966. Reprographic reprint of the 1873 Munich edition. xx, 854 pp., DM 118.–.

The Development of Chemistry constitutes Volume 10 of the "Geschichte der Wissenschaften in Deutschland – Neuere Zeit" (History of Science in Germany – Modern Times), issued by the Historical Commission of the Royal Academy of Sciences in Munich under the patronage of Maximilian II, King of Bavaria. Other volumes included *Karmarsch*, "The History of Technology" (Vol. 11, 1872) and *Hirsch*, "The History of Medicine" (Vol. 22, 1893). This series, to which the reprint unfortunately makes no reference, was a continuation of a similarly conceived encyclopedia entitled "A history of arts and sciences from the Renaissance to the end of the 18th century", including contributions by *J. F. Gmelin* on chemistry (1797–1799), *Poppe* on technology (1807–1811), and *Haeser* on medicine (1846–1860). These form the subject of an earlier review[1].

The present work, entitled "Development" by the author in order to "eliminate the possibility of confusion with my earlier [1843–47] 'History of Chemistry' " is interesting for two reasons. Shortly after the proclamation of the Empire in 1871, which put an end to the multiple-state system in Germany, *i.e.* in a strongly national, even emphatically nationalistic epoch, *Kopp* wrote in a preface "chemistry belongs ... to those branches of knowledge which neither in regard to the subject matter, nor in the treatment, nor in the form in which the results obtained are expressed, can be property of a particular nation". For this reason "the historian must consider himself as having no particular home, and as a citizen of no particular country". In complying with this premise, *Kopp* did not write a history which put the development of chemistry in Germany in the foreground, but one in which the individual national contributions were given a status according to their importance. On the other hand, *Kopp*'s "Development", which records the results up to around 1858, is to a large extent a contemporary account of the origins of the "knowledge now becoming important". Although the author did not himself set out to present this, he had to report on its origin. Thus, only about the first 200 pages of the book lead the reader from the chemical knowledge of antiquity to the general acceptance of the antiphlogiston system of Lavoisier. The major part of the book is taken up by discussion concerning the development of the theoretical aspects of chemistry, above all progress in organic chemistry up to about the time of *Laurent*, *Gerhardt*, and *Kolbe*; *Kekulé*'s treatise "On the constitution and the metamorphoses of chemical compounds" [1858] forms the conclusion, because "these reflections belong to the chemistry of the present ... and should not form the subject of a historical essay".

Both *Kopp*'s "History" and "Development" are standard works in the history of chemistry; a reprint of the latter is therefore very welcome. *W. Ruske* [NB 654 IE]

[1] *W. Ruske*, Angew. Chem. *79*, 587 (1967); Angew. Chem. internat. Edit. *6*, 578 (1967).

Actions Chimiques et Biologiques des Radiations. (Chemical and Biological Action of Radiation.) Edited by *M. Haissinsky* with contributions by *E. J. Hart*, *C. Ferradini*, *T. J. Hardwick*, and *A. Chapiro*. 10th series. Masson & Cie. Editeurs, Paris 1966. 1st Edit., 324 pp., 78 figures, 49 tables, F 120.–.

This new volume in the series, which is intended as an exchange of information between radiochemists and radiobiologists, again contains four authoritative reviews of the latest developments in certain fields of radiochemistry.

The first article is on the hydrated electrons formed on radiolysis of water (*E. J. Hart*, English, 88 pp., 150 references). A short introduction on their discovery is followed by a description of the experimental methods that are used for their production and detection. The physical properties and the structure of the hydrated electrons are then described, as are their reactions with free radicals and with stable inorganic and organic substances. The rate constants of the reactions discussed are tabulated in a 12-page appendix. It would have done no harm to mention in connection with the discovery of hydrated electrons that they were first observed and identified in irradiated frozen aqueous systems in a German radiochemical laboratory.

The content of the second article, "Reaction Rates of Free Radicals in the Radiolysis of Water" (*C. Ferradini*, French, 35 pp., 120 references), follows on from that of the first. It deals with the rates of the reactions of the other radicals OH, H, HO_2, and $O^{\ominus}$, formed by the action of radiation on water, with one another and with other inorganic and organic substances (13 pages of tables giving rate constants).

In the next article, "Radiolysis of Liquid Hydrocarbons" (*T. J. Hardwick*, English, 61 pp., 120 references), an attempt is made in the introduction to explain the processes that precede the actual chemical reactions when ionizing radiation passes through a liquid system. This is followed by an outline of the radiolysis of saturated and unsaturated aliphatic compounds and of aromatic compounds, in which reaction mechanisms and yields are given and discussed.

The last contribution is devoted to the interesting but as yet unexplained "Radiation-Induced Polymerization in the Solid Phase" (*A. Chapiro*, French, 125 pp., 230 references). The author confines his discussion to the polymerization of vinyl derivatives, a few heterocyclic compounds, and aldehydes and nitriles. Discussion of the kinetics of the reactions is deliberately avoided, but an attempt is made to apply the general principles of radiochemistry to the reactions.

Since the coverage of the latest literature is very comprehensive, these very readable articles should provide valuable information for all chemists and biologists working in related fields. *U. Schindewolf* [NB 684 IE]

Polyolefins. Structure and Properties. By *H. von Boenig*. Elsevier Publishing Company, Amsterdam-London-New York 1966. 1st. Edit., ix, 319 pp., 80 illustrations, 117 tables, Dfl. 47.50.

As can be seen from the subtitle, the author has set himself the aim of accounting for the properties of the olefins on the basis of their molecular structure, which immediately determines their crystalline, supermolecular structure (single crystals, spherolithic aggregates) which in turn plays an important role in the industrial applications of these compounds. The choice and subdivision of the material, which is presented in a condensed form, corresponds to this aim.

A short consideration of the historical development in the first chapter is followed by a treatment of the structure of the polyolefins in the Chapter 2. The latter deals with the steric regularity, the helix conformation, and the connected problem of crystallization from solution and from the melt.

In the third chapter the author considers in detail the dependence of some properties on the density; a topic which permits far-reaching conclusions to be drawn regarding the molec-

ular structure and also gives some indication of the tensile strength, stiffness, hardness, and modulus of elasticity. Polyethylenes are therefore expediently classified as being of low, medium, or high density.

In the remaining five chapters the connections are investigated which exist between the structure of polyolefins and their physical, chemical, electrical, and thermal properties and their behavior on being processed. The last chapter is particularly important for people interested in the technology of plastics. Great emphasis is placed upon the relation between structure and rheology, the melt flow index being stressed as a suitable parameter. When the molecular weight distribution, which determines *inter alia* the shrinkability and distortion tendency, is taken into account, the melt flow index proves a good numerical indication of the workability, as well as of the shock and breaking behavior of formed objects. The progress which has been made in the extrusion of polymers is alluded to and phenonema such as melt fracture are discussed.

Boenig's book should appeal to both researchers and technologists. The fruitfulness of the cooperation of these two groups of workers is evidenced by the spectacular advances made in the field of polyolefins during the last decade. The book may well make an important contribution to this continuing development.

The book is comprehensibly written, comprehensively subdivided, richly furnished with illustrations and tables, and contains a wealth of references to the original literature.

H. Weber [NB 624 IE]

Electrophilic Additions to Unsaturated Systems. By *P. B. D. de la Mare* and *R. Bolton*. Reaction Mechanisms in Organic Chemistry, Monograph 4. Edited by *C. Eaborn* and *E. D. Hughes*. Elsevier Publishing Company, Amsterdam-London-New York 1966. 1st Edit., x, 284 pp., numerous schemes and tables, Dfl. 40.00.

The present monograph, which is the fourth in the series "Reaction Mechanisms in Organic Chemistry", deals with electrophilic additions to unsaturated systems. One of the authors, Professor *de la Mare*, has himself made numerous experimental contributions in this field.

The book is divided into 13 chapters. A short introduction and a chapter on the chemistry of carbonium ions are followed by a discussion of the principal electrophilic additions. These include hydration, the addition of weak acids, of mineral acids, and of halogens, epoxidation, and the addition of sulfenyl halides and of compounds containing electrophilic nitrogen, phosphorus, or arsenic. The final chapter deals with electrophilic additions to acetylenes, allenes, conjugated dienes, and to other systems such as C=O, C=N, S=O, and N=N double bonds.

The content of the book, which is built up on a purely theoretical basis, is extremely rich; the literature is covered up to the end of 1964.

No procedures are given for the execution of electrophilic additions, nor are any to be expected in view of the very concise presentation.

The book is very well written, and as a valuable contribution to theoretical organic chemistry it makes an excellent companion to the volumes published earlier.

F. Asinger [NB 583 IE]

Introduction to Practical High Resolution Nuclear Magnetic Resonance Spectroscopy. By *D. Chapman* and *P. D. Magnus*. Academic Press Inc., London-New York 1966. 1st Edit., ix, 112 pp., 30 illustrations, numerous tables, 25 s/$ 4.25.

This book is intended to provide a first introduction to nuclear magnetic resonance spectroscopy and its potentialities for students and for chemists engaged in structure determinations of organic molecules; its particular aim is to introduce them to carrying out these studies in practice. For this reason the authors intentionally desist from any form of theoretical derivation.

The fundamental ideas such as chemical shift and spin-spin coupling are introduced in a few words and are clearly explained by means of examples. Reference is made to detailed monographs for deeper study. The section on experimental technique is somewhat more expansive. The use of ^{19}F, ^{31}P, ^{14}N, and ^{13}C nuclear resonance in organic structural analysis, and five well chosen examples, close the first part.

The second part consists of 37 very clearly arranged tables of τ values and coupling constants from recent literature.

This book can be recommended as a brief introduction into the methods and experimental technique, and into the analysis of spectra, for chemists who wish to use nuclear resonance spectroscopy for determination of structure.

H. Friebolin [NB 665 IE]

Advances in Alicyclic Chemistry. Edited by *H. Hart* and *G. J. Karabatsos*. Academic Press Inc., London-New York 1966. 1st Edit., x, 395 pp., numerous illustrations and tables, bound $ 16.50.

This book is the first volume of a new series in which it is intended regularly to report the most recent results in the chemistry of alicyclic compounds. The reviewer agrees with the editors that the explosive growth of the original literature justifies a further new series.

The editors have been successful in obtaining for this volume competent authors who in their own papers have contributed important material to the fields which they treat here. Considered as a whole, the book provides a balanced and in parts highly critical survey.

J. Meinwald and *Y. C. Meinwald* report on bicyclo[*n*.1.1]-alkanes and related tricyclic systems. It would be welcomed by the reviewer if the nomenclature rules for bicyclic and tricyclic bridged compounds given by the authors in their introduction were generally adopted. The main discussion of the bicyclic compounds is devoted to the bicyclo[2.1.1]hexane and the bicyclo[1.1.1]pentane system, their syntheses and reactions, and rearrangements of their derivatives. A special section is devoted to consideration of highly strained tricyclic compounds (tricyclopentane, -hexane, and -octane).

The chemistry of cyclopropenes is surveyed by *G.L.Closs*. He discusses in detail, not only the synthetic possibilities for cyclopropene and its derivatives, but also their reactions, the spectral properties, and the bonding. The peculiar "aromatic" properties of the cyclopropenyl cations and of the cyclopropenones are treated in depth.

A detailed chapter (*A. J. Waring*) is devoted to cyclohexadienones. The author brings together the extensive and widely scattered material with great care. Of the 121 pages of this chapter, 53 pages are reserved for the varied ways of forming cyclohexadienones; other parts describe their transformations and reactions. A special section is reserved for the photochemistry of cyclohexadienones.

In the next chapter *K. F. Koch* surveys the photochemical rearrangements of monocyclic tropolones and benzotropolones, and of colchicine and isocolchicine. The structures of the "lumi"-products are discussed in detail with reference to their UV, IR, and NMR spectra.

In spite of two previous reviews of "reactions at a bridgehead" [1], the chapter by *R. C. Fort* and *P. v. R. Schleyer* on the same theme contains much new experimental material that has become available only during the last five years. Besides containing a theoretical section, this chapter collects

[1] *D. E. Applequist* and *J. D. Roberts*, Chem. Reviews, *54*, 1065 (1954); *U. Schöllkopf*, Angew. Chem. *72*, 147 (1960).

together the reactions of bridgehead carbenium ions, carbanions, and free radicals.

One can only hope that the same high level will be maintained in the further volumes planned for this series. The editors and authors will then have given us a good "Advances" series. *M. Hanack* [NB 668 IE]

High Resolution Nuclear Magnetic Resonance Spectroscopy. By *J. W. Emsley, J. Feeney,* and *L. H. Sutcliffe.* Pergamon Press, Oxford 1965 and 1966. 1st Edit., 2 volumes, xxiii, 1154 pp., numerous illustrations and tables, linen 105 s.

The two volumes of this work begin with a detailed description of the physical principles underlying NMR techniques, which is followed by two chapters (together 79 pp.) on the calculation of chemical shifts and coupling constants in accord with various theories. The individual parts of a spectrometer are described for the experimentalist, as are the practical methods of preparing the sample, of standardization, and of the actual measurement; information on these subjects had previously to be searched out from different sources and supplemented by personal experience. The chapter on spectral analysis, *i.e.* on determination of δ- and J-values from measured spectra occupies 200 pages, which constitute almost a third of volume 1. The theory is used to develop expressions needed for the analysis of all the important spin systems and gives indications for their evaluation. Spectroscopic effects of chemical equilibria and fast reactions are placed in a special chapter.

The whole of volume 2 is devoted to special applications of the method to chemical problems, the voluminous material being arranged according to the atomic nuclei under study (^{1}H 205 pp., ^{19}F 97 pp., other nuclei 139 pp.) and within each such section according to the chemical classes of compounds. Although the literature has not been completely covered up to 1963, this collection of material, with its many clear tables, is an imposing performance by the authors. It is a pity that two whole years passed before publication of this work! The appendix to the book must also be recognized as very useful; it contains, *inter alia*, the contributions of a benzene ring to the shielding of a neighboring proton (according to *Johnson* and *Bovey*) and *Tiers*' tables of τ values which were hitherto of limited availability.

The work reviews mainly the results and opinions in the original papers and generally refrains from new interpretations of the material reported. Evaluations, if made at all, are expressed in very restrained language; for instance one does not read "The authors' measurements are valueless" but, instead, "It is difficult to assess the theoretical significance of their measurements".

The opportunity to unify definitions, terms, and symbols has not been exploited; on the contrary, the usage, *e.g.* for chemical shift, for line width, or for mean lifetime, changes according to what was used in the paper being reviewed. Some equations in volume 1 (particularly on pages 481 to 491) contain errors which can mislead the user; and in these places the conscientious reader may need many hours to recognize errors as such.

Naturally it is not difficult, with a work of this range, to find items that have been incompletely or incorrectly described, particularly as this is a field of study that touches on a series of different scientific disciplines – from theoretical physics to the chemistry of natural products. Thus no author – and also no reviewer – will be able to master the whole of the material. All the greater, therefore, is it to the authors' credit that they have provided a comprehensive book. It is not conceived as an introduction to the method; but it can be recommended to every NMR spectroscopist for advanced, critical study. Further, these volumes are likely to be essential to everyone as a reference work; for this purpose they may be considered as a new edition of *Pople, Schneider,* and *Bernstein*'s standard work that appeared in 1959.

A. Mannschreck [NB 671 IE]

Indole Alkaloids. An Introduction to the Enamine Chemistry of Natural Products. By *W. I. Taylor.* Vol. XXVIII of the series: A Course in Organic Chemistry, Advanced Section. Pergamon Press, Oxford 1966. 1st Edit., 148 pp., numerous figures, paper back 25/–.

On 140 pocket-book pages, half of which are filled with structural formulae, an attempt is made to treat the chemistry of the indole alkaloids unconventionally deductively by emphasizing the reactions of the indole system and biogenetic considerations. This method, the fulfilment of which has become possible only as a result of the rich volume of data collected during the last 10 years (the principle is due to Sir *Robert Robinson*) assures the reader of continuity, while the individual facts do not appear overwhelming. In his search for (generally biogenetic) inter-relationships the author has not hesitated to formulate hypothetical intermediate stages and as yet undiscovered alkaloid variants. Occasionally more remote analogies are resorted to in order to explain the course of reactions (*e.g.* Lycorine-neostrychnine on p.79). By adhering to this method the author succeeds in including, although sometimes only briefly, a large number of preparative and physicochemical details.

As a result of its recent date of publication, and the concepts that are consequently involved, the book is somewhat more modern than other works on alkaloids. Numerous results of the last few years appear to have been summarized here for the first time. Entries such as picraline, echitamine, copsine, vindoline, vincamine, voacamine, schizozygine, burnamicine, and also skytanthine as a mevalonoid nonindole alkaloid, characterize part of the developments revealed by the author. In general, the biogenetic postulates are based on mevalonic acid, although at the time of writing the book no confirmatory labeling experiments had been carried out.

Although the book could be recommended as a summary, or to those who wish to gain a brief overall picture of the more recent classes of alkaloids, a certain degree of familiarity is taken for granted. Compared with the books by Bentley, Boit, or Manske-Holmes, it is not really suitable as an introduction. The formulas are well presented, misprints are rare, and the price is not unreasonable. *H.-J. Teuber* [NB 637 IE]

Treatise on Analytical Chemistry. Edited by *I. M. Kolthoff* and *P. J. Elving.* Part II, Vol. 4: Analytical Chemistry of Inorganic and Organic Compounds. Interscience Publishers, a Division of John Wiley and Sons, New York-London-Sydney 1966. Part II, Vol. 13: Analytical Chemistry of Inorganic and Organic Compounds. 1st Edit., xxi, 528 pp., 14 illustrations, 29 tables, bound 160 s.

Two very different volumes of *Kolthoff* and *Elving*'s Handbook of Analytical Chemistry are now available for review, Volume 4 of Part II of this work[*] deals with the analysis of the elements silver (*E. P. Przybylowicz* and *C. W. Zuehlke*), gold (*N. Herz*), calcium (*K. K. Turekian* and *E. Bolter*), strontium and barium (*K. K. Turekian* and *E. Bolter*), radon and radium (*J. Sedlet*), and aluminum (*G. H. Farrah* and *M. L. Moss*). This volume, like its predecessors, is written by experts in the analysis of the elements that they treat, and it is in line with the usual careful work that is known from previous volumes.

Volume 13 deals with the determination of functional groups in organic compounds. The two preceding volumes 11 and 12 dealt with methods of elemental analysis of organic compounds, *i.e.* the determination of carbon, hydrogen, nitrogen, phosphorus, oxygen, sulfur, the halogens, boron, silicon, *etc.* The present volume describes the analytical methods used for determining functional groups in organic compounds, *i.e.* typical structural features that can be used for characterization or for quantitative determination of organic compounds. Chemical and physical methods (IR, UV, Raman, NMR, and mass spectrometry, as well as chromatographic methods of

[*] Cf. Angew. Chem. 76, 739 (1963).

separation) are here treated side by side and frequently their values are compared. The individual authors have written their sections with excellent knowledge of their subjects; this volume in particular can be recommended as reference work for all concerned with structural analysis of organic compounds.

An introduction about functional groups is given by *J. Mitchell*. The section on determination of active hydrogen was contributed by *F.T. Weiss*, analysis of the C–CH_3 group by *K. G. Stone*. Analysis for carbonyl groups is treated by *J. G. Hanna* and *S. Siggia*, that of the carboxyl group by *S. Veibel*. The volume closes with two sections on phosphorus functional groups (*D. N. Bernhart*) and on functional groups containing bivalent sulfur, –SH, –S–, –S–S–, *etc.* (*J. H. Karchmer*).

It is hoped that the further volumes on the determination of functional groups will soon appear and that they will supplement the present volume at the same high level.

H. Kienitz [NB 682 IE]

Organic Photochemistry. Edited by *O. L. Chapman*. Marcel Dekker Inc., New York 1967. Vol. 1. 1st Edit., ix, 339 pp. numerous illustrations, $ 15.75.

The ever increasing number of original papers that appear each year in the field of organic photochemistry illustrate the present preparative and theoretical importance of this subject. The bewildering profusion of new photochemical reactions makes it difficult even for the investigator active in this area to keep informed about the many new facts. It is therefore to be welcomed that an attempt is being made to collect the many facts from original papers into the series entitled "Organic Photochemistry" and to arrange them in a critical manner. In accordance with this aim, the present volume is not a textbook, but is a collection of reviews intended in the first place for the chemist engaged in syntheses.

The titles of the seven contributions are: Photochemical Transformations of Cyclohexadienones and Related Compounds (*P. J. Kropp*); Photochemical Transformations of Small-ring Carbonyl Compounds (*A. Padwa*); Photo-Fries Reaction and Related Rearrangements (*V. I. Stenberg*); Photochemistry of Troponoid Compounds (*D. J. Pasto*); Photochemistry of Olefins (*G. J. Fonken*); The Photocyclization of Stilbenes (*F. R. Stermitz*); and Photocycloaddition Reactions (*O. L. Chapman* and *G. Lenz*).

The authors, who are all distinguished in their fields, have achieved a competent presentation of their material. The titles show, however, that the subject has been divided according to classes of compound as well as according to type of reaction. Thus some duplication has been inevitable. The rearrangement carvone $\xrightarrow{h\nu}$ carvonecamphor is shown in formulas no fewer than three times (pp. 82, 240, and 296), as also is the photocycloaddition of 2-cyclohexenone to isobutene (pp. 81, 240, and 299); the list of such examples could be considerably extended (*e.g.*, p. 79 → p. 294; p. 80 → p.180; p. 216 → p. 315).

With new scientific books at their present price, such duplications are not a welcome feature. It is to be hoped that, when continuing the series, the editors will coordinate the contributions of the various authors more carefully and thus ensure for the series the success that it deserves.

R. Steinmetz [NB 672 IE]

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The Reduction of Organic Compounds with Chromium(II) Salts

BY J. R. HANSON[*] AND E. PREMUZIC[**]

Chromium(II) salts can be used for a variety of reductions in organic chemistry; for example, alkyl halides and suitably substituted olefins may both be reduced to alkanes, and alkynes may be converted into trans-olefins. Several epoxyketones are reduced to α,β-unsaturated ketones or β-hydroxyketones, and a nitro steroid was found to give a hydroxy(hydroxyimino) compound. The reduction of alkyl halides is reported to proceed by a free-radical mechanism; the halogen atom that is set free forms a bridge between two chromium atoms.

1. Introduction

In 1916, *Traube* and *Passarge* reported[1] that an acidic aqueous solution of chromium(II) chloride in an inert atmosphere reduces maleic acid and fumaric acid to succinic acid. On treatment of a chromium(II) chloride solution with sodium hydroxide, a suspension of chromium(II) hydroxide was obtained, which reduced cinnamic acid to β-phenylpropionic acid. Nitrous oxide was quantitatively reduced by alkaline and acidic solutions of chromium(II) salts to ammonia. Nitrites, on the other hand, were not reduced. An oxime, benzaldoxime, was reduced under alkaline conditions at 100 °C to benzylamine.

During the 1920's, titanium(III), chromium(II), and vanadium(II) salts were shown to be efficient agents for the generation of free radicals. For example, *Conant* and *Sloan*[2] prepared free radicals from triphenylmethylpyrylium chloride and phenylxanthenol in the presence of acidic vanadium(II) chloride. Thus one-electron transfer to the carbonium ion derived from triphenylmethanol gives the triphenylmethyl radical.

$$(C_6H_5)_3C^+ + e \rightarrow (C_6H_5)_3C^\bullet$$

Dimeric products were often observed, for example, in the reduction of aromatic α,β-unsaturated ketones[3,4]. In 1930, *Hein*, *Farl*, and *Baer* reported[5] the action of chromium(II) halides on diethyl ether and established the existence of compounds of the type $CrX_2OC_2H_5$ (X = Cl, Br, or I) containing trivalent chromium.

$$2\ CrX_2 + 2\ C_2H_5OC_2H_5 \rightarrow 2\ CrX_2OC_2H_5 + C_4H_{10}$$

Similar compounds are formed with dioxane and benzyl ethyl ether. However, aromatic ethers such as phenetole and anisole are unreactive at room temperature. Aniline, pyridine, and piperidine produce diamino complexes of the type $CrX_2OC_2H_5(amine)_2$.

In 1934, *v. Braun* and *Rudolph* used chromium(II) chloride for reduction of carbonimidoyl chlorides to Schiff's bases[6]. Eleven years later, *Cole* and *Julian*[7]

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Ridgefield, Conn. 06877 (U.S.A.)

[1] *W. Traube* and *W. Passarge*, Ber. dtsch. chem. Ges. *49*, 1692 (1916).

[2] *J. B. Conant* and *A. W. Sloan*, J. Amer. chem. Soc. *45*, 2466 (1923); *J. B. Conant* and *A. W. Sloan*, *ibid. 47*, 472 (1925); *J. B. Conant* and *R. E. Lutz*, *ibid. 47*, 881 (1925); *J. B. Conant*, *L. F. Small*, and *B. S. Taylor*, *ibid. 47*, 1959 (1925); *J. B. Conant* and *H. B. Cutter*, *ibid. 48*, 1016 (1926).

[3] *W. Traube* and *W. Lange*, Ber. dtsch. chem. Ges. *58*, 2773 (1925).

[4] *K. Ziegler*, *F. A. Fries*, and *F. Salzer*, Liebigs Ann. Chem. *448*, 249 (1926).

[5] *F. Hein*, *H. Farl*, and *H. Baer*, Ber. dtsch. chem. Ges. *63*, 1418 (1930).

[6] *J. von Braun*, *W. Rudolph*, *H. Kooper*, and *W. Pinkernelle*, Ber. dtsch. chem. Ges. *67*, 269, 1735 (1934).

[7] *W. Cole*, *P. L. Julian*, *A. Magnani*, and *E. W. Meyer*, J. Amer. chem. Soc. *67*, 1728 (1945).

described the use of acidic chromium(II) chloride for the dehalogenation of 5,6-dibromo-3-keto steroids. *Royer* [8] used acidic chromium(II) sulfate to prepare 5,5-biacridyl from 5-chloroacridine. More recent applications of the reagent include its use in the reduction of epoxyketones [9]. A better knowledge of the inorganic chemistry of the system and, in particular, the importance of bridging complexes [10] has been reflected in a clearer understanding of the mechanism of the reduction [11–15].

Chromium(II) chloride and acetate are readily prepared by the zinc and hydrochloric acid reduction of chromium(III) chloride. The acetate is a relatively insoluble salt prepared by the addition of sodium acetate to chromium(II) chloride. Both may be handled quite easily at room temperature in a nitrogen or carbon dioxide atmosphere.

2. The Role of Bridging Ligands in Reductions by the Chromium(II) Ion

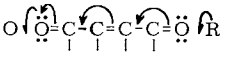
Chromium(II) salts react with a variety of ions of the type $[Co(NH_3)_5X]^{2+}$, which serve as the oxidizing agent *via* a quantitative transfer of X to the reducing agent [10]. For the system where X = Cl, the transfer takes place without an exchange with chloride ion in solution. This suggests that the activated complex for the electron transfer reaction has a configuration in which X is bonded simultaneously to Cr and Co to form a Co···X···Cr complex. There is further evidence [16] for this in the exchange reaction between Cr^{2+} and $CrCl^{2+}$. Such bridge-activated complexes are also formed by other ions and atoms, *viz.* Ti^{2+}, Ti^{3+}, Ti^{IV}, V^{2+}, V^{3+}, V^{IV}, V^{V}, and Cr^{2+}. The nature of the bridging group plays an important part in determining the rates of these exchange reactions. Thus in the Cr(II)/Cr(III) system, where the bridging group in the intermediate $(H_2O)_5Cr^{3+}\cdots X\cdots Cr^{2+}(OH_2)_5$ forms a part of the inner coordination shell of both ions, the rate decreases by a factor of 10^7 along the series $X = Br^- > N_3^- > Cl^- > OH^- > F^- > NCS^- > NCS^- > H_2O$ [17].

Organic anions can serve as bridging groups in oxidation-reduction reactions of this type. Again the nature of the coordination shell is important; for example, free oxalate is rapidly reduced to glycolate by chromium(II) perchlorate, whereas oxalate bound to Cr(III) is reduced very slowly by Cr(II) [18].

Sebera and *Taube* have conducted [19] a kinetic study of the reactions of the chromium(II) ion with complex ions of the type $[(NH_3)_5Co(III)L]^{2+}$, where L is an organic ligand such as succinate, succinate monomethyl ester, fumarate, fumarate monomethyl ester, or one of the three isomers of phthalic acid. The system is suitable for study since cobalt(III) complexes have an absorption band at 350 nm ($\varepsilon = 53-79$) which may be used to follow the course of this series of reactions. The net changes of the system are represented by

$$[(NH_3)_5CoL]^{2+} + Cr^{2+} + 5\ H^+ \rightarrow Co^{2+} + CrL^{2+} + 5\ NH_4^+$$

and a chromium(III) complex is formed. The mechanism involves attack by the chromium(II) ion at a carboxyl adjacent to Co(III), except in the case of fumarate, monomethyl fumarate, and terephthalic acid where there is conjugation between the free carboxyl group and that bearing the Co(III) center. The electron transfer reaction between solvated Cr^{2+} and $[(NH_3)_5CoL]^{2+}$ then takes place through an attack by the reducing species at the free carboxyl group [20]. An interesting mechanism of electron conduction by the conjugated systems was described by *Taube* and co-workers:



Many organic ligands, both aromatic and heterocyclic, can serve as bridging groups for electron transfer. In a further study, *Gould* and *Taube* [21] have shown that the rates of reduction also depend on the substituents on the ligand itself and the stability of the complex formed. Their experiments have also demonstrated the formation of free radicals during the course of these reductions and the influence that they exert on the rates of reaction. For example, in the reduction of pyridine-2- and -4-carboxylate ions the ligands are thought to facilitate the electron transfer by permitting delocalization of the reducing electron in the pyridine ring, with the formation of a radical-ion intermediate.

Other investigations [22] have revealed the formation of 2,5-dihydroxy-*p*-benzoquinone complexes with chromium(II) ions.

3. The Formation of Organo-Chromium Complexes

Anet and *Leblanc* [11] investigated spectroscopically the reaction of benzyl halides with aqueous chromium(II) perchlorate in perchloric acid, and were thus able to establish the existence of benzylpentaaquochromium(III) perchlorate. On heating in the absence of oxygen, this complex gave bibenzyl through the formation of benzyl radicals. However, in the presence of oxygen the main product was benzaldehyde. Reduction of

[8] *R. Royer*, J. chem. Soc. (London) *1949*, 1663.

[9] *W. Cole* and *P. L. Julian*, J. org. Chemistry *19*, 131 (1954).

[10] *H. Taube* and *H. Myers*, J. Amer. chem. Soc. *76*, 2103 (1954).

[11] *F. A. L. Anet* and *E. Leblanc*, J. Amer. chem. Soc. *79*, 2649 (1957).

[12] *D. H. R. Barton*, *N. K. Basu*, *R. H. Hesse*, *F. S. Morehouse*, and *M. M. Pechet*, J. Amer. chem. Soc. *88*, 3016 (1966).

[13] *C. E. Castro*, J. Amer. chem. Soc. *83*, 1601 (1961).

[14] *J. K. Kochi* and *F. F. Rust*, J. Amer. chem. Soc. *83*, 2017 (1961).

[15] *L. H. Slaugh* and *J. H. Raley*, Tetrahedron *20*, 1005 (1964).

[16] *H. Taube* and *E. L. King*, J. Amer. chem. Soc. *76*, 4053 (1954).

[17] *D. L. Ball* and *E. L. King*, J. Amer. chem. Soc. *80*, 1091 (1958).

[18] *R. M. Milburn* and *H. Taube*, J. physic. Chem. *64*, 1776 (1960).

[19] *D. K. Sebera* and *H. Taube*, J. Amer. chem. Soc. *83*, 1785 (1961).

[20] *R. T. M. Fraser* and *H. Taube*, J. Amer. chem. Soc. *83*, 2239 (1961).

[21] *E. S. Gould* and *H. Taube*, J. Amer. chem. Soc. *86*, 1318 (1964).

[22] *R. C. Linek* and *H. Taube*, J. Amer. chem. Soc. *85*, 2187 (1963).

benzyl chloride with chromium(II) chloride in aqueous hydrochloric acid gave toluene. The complex $[Cr(H_2O)_4ClCH_2C_6H_5]^{2+}$ formed initially contains a chloride ion as well as water molecules in the coordination sphere of the metal ion. In this position the chloride ion favors reduction by bridging with a further chromium(II) ion in the reducing agent. The chromium(II) complex thus formed can dissociate to benzyl anions, which in turn react with the solvent to give toluene. Allyl chloride and phenacyl chloride are likewise reduced by chromium(II) perchlorate.

In a further study, *Anet* [23] investigated the reduction of chloroform by chromium(II) perchlorate in aqueous solution and established the presence of chloropentaaquochromium(III) perchlorate and of $[Cr(H_2O)_5CHCl_2]^{2+}$, whose structure is analogous to

$$CHCl_3 + 2\,Cr^{2+} + 10\,H_2O \rightarrow Cr(H_2O)_5Cl^{2+} + Cr(H_2O)_5CHCl_2^{2+}$$

that of the complex $[Cr(H_2O)_5CH_2C_6H_5]^{2+}$ obtained [11] from benzyl chloride.

The structure of these complexes, like that of other chromium complexes, involves octahedral coordination in which five water molecules and the dichloromethyl anion form the ligands. The stability of these organochromium ions is consistent with the substitution inertness of chromium(III) complexes [24].

Although the benzyl complex decomposes on heating to give bibenzyl, the dichloromethyl complex does not give tetrachloroethane or its reduction product, dichloroethylene; instead, chloride ions are formed. Furthermore, the dichloromethyl complex does not react with oxygen, sulfur dioxide, mercuric chloride, nor is it reduced by hydrogen in the presence of palladium catalyst; it thus behaves differently from its benzyl analog [11].

The reduction of chloroform could involve the following steps. Firstly, a one-electron reduction in which there is a direct transfer of a chlorine atom to chromium.

$$CHCl_3 + Cr^{2+} + 5\,H_2O \rightarrow [Cr(H_2O)_5Cl]^{2+} + {}^{\bullet}CHCl_2$$

Two processes may then occur: the free radicals may either dimerize, or react further with chromium(II) ion present to give organochromium ion:

$${}^{\bullet}CHCl_2 + Cr^{2+} + 5\,H_2O \rightarrow [Cr(H_2O)_5CHCl_2]^{2+}$$

If the latter step is fast, less dimerization will be observed.

Investigations by *Kochi* and *Rust* [14] have shown that the reaction may not be as simple as this. The reaction of *tert*-butylhydroperoxide with a reducing metal in aqueous solution produces methyl radicals

$$(CH_3)_3COOH + M^{n+} \rightarrow (CH_3)_3CO^{\bullet} + M(OH)^{n+}$$
$$(CH_3)_3CO^{\bullet} \rightarrow CH_3COCH_3 + {}^{\bullet}CH_3$$

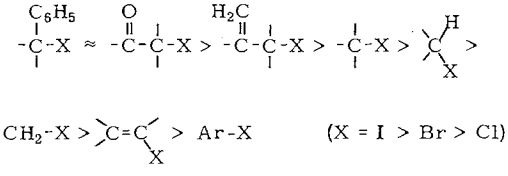
For example, if titanium(III) chloride is the reducing agent [cf. [25]] then the relative yields of ethane and methane depend on the presence of added metal ions. In particular, the ions of the transition metals are effective in promoting dimerization of methyl radicals. Even traces of such ions in the reducing agent may affect the results.

There is a further consequence of the existence of metal ion-free radical complexes. Such complexes may have a longer lifetime than simple alkyl radicals and a lesser tendency to abstract hydrogen from, for example, the solvent.

4. The Reduction of Alkyl Halides

The reduction of alkyl halides by chromium(II) salts represents one of the best known uses of these reagents. Some examples of the systems that have been studied are presented in Table 1.

The reactivity of the various types of halide decreases in the following order [26]:



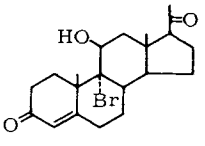
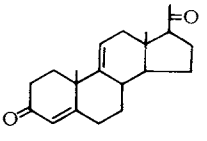
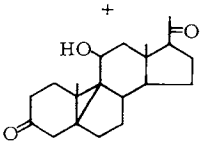
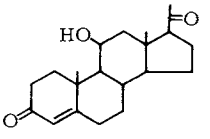
From the results shown in Table 1 it is clear that a number of products are possible. For example monohalides give mainly the products of reduction or dimerization. On the other hand, halides with an adjacent halogen, hydroxyl, or other anionic substituents give rise to olefins. With suitably oriented α,β-unsaturated ketones cyclization can also occur.

The formation of these products can be rationalized in mechanistic terms. In investigations on the reduction of carbonium ion to a free radical by strongly reducing transition metal salts in their low valency states, the influence of added halide ions was particularly noted. It was shown [13] that chromium(II) salts alter the course of reactions of the 1,1-diphenylethyl cation to give dimeric products instead of the radical, provided halide ions are present. The interpretation placed on these results was that an intermediate organic halide was required. It has been subsequently suggested [15] that halide ions are beneficial but not mandatory – in their absence, the reaction merely proceeds more slowly.

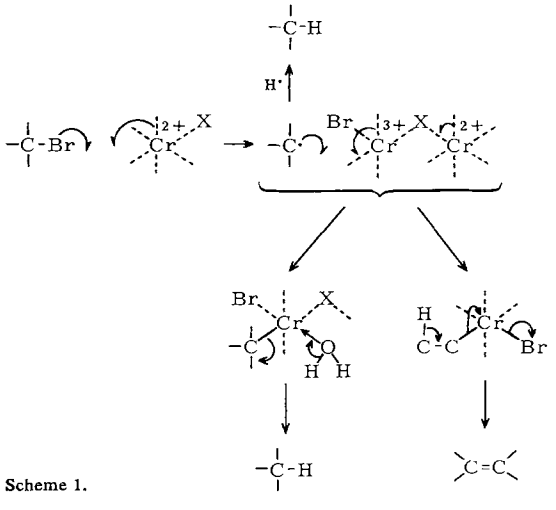
The first step in the reduction of an alkyl halide may be envisaged as the attack of the chromium(II) ion on the halogen atom. The second stage involves a migration of the alkyl residue to form a new carbon-chromium bond. This process is accompanied by a one-electron transfer from a second chromium(II) ion through a bridging anion. The subsequent decomposition of this intermediate by elimination, protonolysis, or attack on unchanged organic halide, can account for the majority of the products.

[23] *F. A. L. Anet*, Canad. J. Chem. *37*, 58 (1959).
[24] *H. Taube*, Chem. Reviews *50*, 69 (1952).
[25] *W. T. Dixon* and *R. O. C. Norman*, J. chem. Soc. (London) *1963*, 3119.
[26] *C. E. Castro* and *W. C. Kray*, J. Amer. chem. Soc. *85*, 2768 (1963); *64*, 4603 (1964).

Table 1. The reactions of organic halogen compounds with chromium(II) salts.

Compound	Reducing agent	Solvent	Product	Yield (%)	Ref.
$CHCl_3$	$Cr(ClO_4)_2/HClO_4$	H_2O	$Cr(H_2O)_5CHCl_2^{2+}$		[23]
$CH_3-CH_2-CH_2Br$	$CrSO_4$	DMF	$CH_3-CH_2-CH_3$		[26]
CH_2Cl-CO_2H	$CrCl_2/HCl$	H_2O	CH_3-CO_2H		[3]
$CH_2=CH-CH_2Cl$	$Cr(ClO_4)_2/HClO_4$	H_2O	$CH_2=CH-CH_3$		[11]
$CH_2=CH-CH_2Cl$	$CrSO_4/H_2O$	THF/H_2O	$CH_2=CH-CH_3$		[13,26]
$CH_2=CH-CH_2Br$	$CrSO_4/H_2O$	THF/H_2O	$CH_2=CH-CH_3$	95	[15]
	$CrCl_2/H_2O$	THF	$(CH_2=CH-CH_2)_2$	83	
cis-$ClHC=CH-CH_2Cl$	$CrSO_4/H_2O$	DMF	$CH_2=CH-CH_3$		[26]
$BrCH_2-CH_2Br$	$CrSO_4/H_2O$	DMF	$CH_2=CH_2$		[26]
$BrCH_2-CH_2OH$	$CrCl_2/HCl/H_2O$	H_2O	$CH_2=CH_2$		[27]
$BrCH_2-CH_2-NH_3Br$	$CrCl_2/HCl/H_2O$	H_2O	$CH_2=CH_2$		[27]
$BrCH_2-CHBr-CH_2Cl$	$CrSO_4$	DMF/H_2O (5 min)	$CH_2=CH-CH_2Cl$		[26]
$CH_2=CBr-CH_2Br$	$CrSO_4$	DMF	$CH_2=CH-CH_3$	74	[26]
			$CH_2=C=CH_2$	26	
$CH_2=C(C_6H_5)_2$	$CrSO_4/HClO_4/HCl$	Dioxane	2,2,3,3-Tetraphenylbutane		[13]
p-$Br-C_6H_4-CO-CH_2Br$	$CrSO_4/H_2O$	DMF	*p*-$C_6H_4-CO-CH_3$		[26]
$C_6H_5-CH=CH-CCl=N-C_6H_5$	$CrCl_2$	Ether	$C_6H_5-CH=CH-CHO$		[6]
2-Bromocholestan-3-one	$CrCl_2$	Acetone	Cholestan-3-one		[28]
	$Cr(CH_3COO)_2$	THF/H_2O			[12,29]
	$Cr(CH_3COO)_2$	$DMSO/H_2O$	+ 		
	$Cr(CH_3COO)_2$ n-C_4H_9SH	DMSO			

The intervention of a free-radical stage prior to the formation of the carbon-chromium bond is supported [12,29] by the action of hydrogen-donor reagents such as *n*-butanethiol, 1,4-cyclohexadiene, 1-benzyl-1,4-dihydronicotinamide, *etc.* In the presence of these reagents, the reduction of 9β-bromo-11β-hydroxy steroids by chromium(II) halides rapidly yields the 11β-hydroxy steroids. These pathways may be summarized according to Scheme 1.

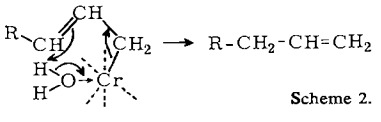


Scheme 1.

There are a number of interesting consequences of this reaction.

For example chromium(II) chloride reduction of 9α-bromo-$\Delta^{1,4}$-3-keto steroids and their 1,2-dihydro analogs, gives rise to 5,9-cyclosteroids – a Grignard type addition of the organochromium derivative occurring to the α,β-unsaturated ketone. The intervention of a bridged complex in the second one-electron transfer step and hence the obvious influence of other groups in the coordination sphere of the chromium ion, suggest a reason for dependence of the reaction on the anion associated with the chromium ion and the influence of the solvent.

The formation of a complex may also account for double-bond isomerizations which have been observed [26] (Scheme 2).



Scheme 2.

The reduction of geminal and vicinal dihalides follows a similar pattern. The dehalogenation of vicinal dihalides by chromium(II) ion proceeds [26] much faster

[27] *F. A. L. Anet* and *E. Isabelle*, Canad. J. Chem. *36*, 589 (1958).

[28] *G. Rosenkranz, J. Pataki, J. Gatica*, and *C. Djerassi*, J. Amer. chem. Soc. *72*, 4081 (1950); *J. J. Beereboom, C. Djerassi, D. Ginsburg*, and *L. F. Fieser, ibid. 75*, 3500 (1953).

[29] *D. H. R. Barton* and *N. K. Basu*, Tetrahedron Letters *1964*, 3151; *C. H. Robinson, O. Gnoj, E. P. Oliveto*, and *D. H. R. Barton*, J. org. Chemistry *31*, 2749 (1966).

than that of the corresponding monohalides and leads to the formation of the corresponding olefins. In the absence of a radical trapping agent this parallels the reduction of α-hydroxy- and α-aminoalkyl halides [27, 30]. There have been a number of preparative uses of this reaction in the introduction and protection of double bonds in the steroid series [31, 32]. (It was not possible to selectively remove the bromine atom from 1,2-bromofluorides.) The possibility of double bond migration is again also present. Indeed the method permits a smooth sequence in the conversion of Δ^5-3-hydroxy steroids to Δ^4-3-ketones by addition of bromine, oxidation to the ketone, and reductive elimination with chromium(II) chloride [33].

The rate of formation of the corresponding olefins follows the sequence [26]

C_6H_5–CHBr–CH_2Br > CH_3–CHBr–CHBr–CH_3 > $BrCH_2$–CH_2Br ≈ CH_2=CBr–CH_2Br > CH_3CHCl–$CHClCH_3$ > $ClCH_2$–CH_2Cl > *o*-dibromobenzene > BrCH=CHBr.

Competitive rate studies support the suggestion of participation by the neighboring halogen in facilitating the reaction. Thus the following relationship was found:

$$\frac{k(\text{1,2-dichloroethyl})\text{benzene}}{k(\text{1-chloroethyl})\text{benzene}} = 20$$

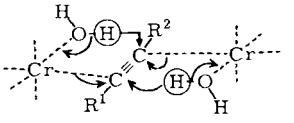
A bromine atom further facilitates reaction, presumably by the easier formation of a bridging system.

$$\frac{k(\text{1-chloro-2-bromoethyl})\text{benzene}}{k(\text{1-chloroethyl})\text{benzene}} = 50$$

However, allylic halides with a second halogen substituent on the vinylic carbon do not show any marked rate enhancement.

5. The Reduction of Unsaturated Systems

There are a number of examples of the reduction of multiple bonds by the low-valency states of transition metal ions. The reduction of alkynes by chromium(II) sulfate in dimethylformamide leads to *trans*-substituted olefins [34]. The ease of reduction depends on the presence of an accessible coordination site in the molecule. The specific reduction of an α-hydroxyallene to an olefin has also been reported in a vitamin A synthesis [35]. A study of the reduction of alkynes suggests that reversible formation of a chromium(II)-alkyne complex is followed, in the rate determining step, by the attack of a second chromium(II) ion on this complex. A transition stage of the type shown in Scheme 3 has been postulated.



Scheme 3.

Appropriately substituted olefins can be reduced to alkanes by chromium(II) sulfate in aqueous dimethylformamide. For reduction to occur in acidic solution the olefin must form part of an enedione or an α,β-unsaturated ketone attached to an aromatic ring. In the majority of cases the yields [36] are high although coupling products have been isolated [2] in certain cases. There are plenty of examples in the alicyclic series in which simple α,β-unsaturated ketones are not attacked by acidic solutions of the reagent. Recently, ammoniacal solutions of chromium(II) ions have been shown to rapidly reduce α,β-unsaturated ketones to the saturated ketones [37]. An extension of this type of reagent uses [38] chromium(II) ion complexed with ethylenediamine. Some examples of the systems that have been studied are given in Table 2.

Table 2. The reduction of unsaturated systems with chromium(II) ions.

Compound	Reducing agent	Solvent	Product	Yield (%)	Ref.
$HOCH_2$–C≡C–CH_2OH	$CrSO_4$	H_2O	*trans*-2-Butene-1,4-diol		[34]
C_6H_5–C≡C–CO_2H	$Cr(OH)_2$	Petroleum ether	C_6H_5–CH_2–CH_2–CH_2H		[1,3]
C_6H_5–CH=CH–CO_2H	$CrCl_2$ or $CrSO_4$	H_2O/DMF	C_6H_5–CH_2–CH_2–CO_2H	89	[1,36]
Maleic acid	$CrSO_4$	H_2O	HO_2C–CH_2–CH_2–CO_2H	86	[1,36]
Fumaric acid	$CrSO_4$	H_2O	HO_2C–CH_2–CH_2–CO_2H	91	[1,36]
C_6H_5–CH=CH–CO–CH_3	$CrCl_2$	C_2H_5OH/H_2O	C_6H_5–CH–CH_2–CO–CH_3 C_6H_5–CH–CH_2–CO–CH_3		[2]
$(CH_3)_2$C=CH–CO–CH_3	$CrCl_2/NH_3$	NH_3/H_2O	$(CH_3)_2$CH–CH_2–CO–CH_3		[37]

The mechanism of the reduction of unsaturated systems probably involves the formation of an olefin-metal complex which is subsequently attacked by a second chromium(II) ion [36]. In the ammoniacal system, species of the following type have been invoked [37].

[30] *F. Fried* and *E. Sabo*, J. Amer. chem. Soc. *79*, 1130 (1957).

[31] *C. H. Robinson, L. Rinckener, E. P. Oliveto*, and *D. Gould*, J. Amer. chem. Soc. *81*, 2191 (1959).

[32] *A. Bowers, L. C. Ibanez, E. Denot*, and *R. Becerra*, J. Amer. chem. Soc. *82*, 4001 (1960).

[33] *P. L. Julian, W. Cole, A. Magnani*, and *E. W. Meyer*, J. Amer. chem. Soc. *67*, 1128 (1945).

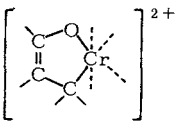
[34] *C. E. Castro* and *R. D. Stephens*, J. Amer. chem. Soc. *86*, 4358 (1964).

[35] *W. Oroshnik, A. D. Mebane*, and *G. Karmas*, J. Amer. chem. Soc. *75*, 1050 (1953).

[36] *C. E. Castro, R. D. Stephens*, and *S. Moje*, J. Amer. chem. Soc. *88*, 4964 (1966).

[37] *K. D. Kopple*, J. Amer. chem. Soc. *84*, 1586 (1962).

[38] *J. K. Kochi* and *P. E. Mocadlo*, J. Amer. chem. Soc. *88*, 4094 (1966).



Related to this is the reduction[39] of oxalate to glycolate by chromium(II) perchlorate.

6. Reduction of Epoxides

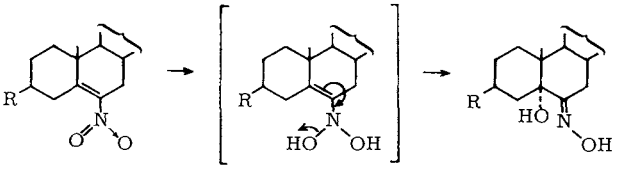
A number of α,β-epoxy ketones have been reduced by acidic solutions of chromium(II) chloride or acetate. Whereas chromium(II) chloride leads to the formation of the α,β-unsaturated ketone, use of chromium(II) acetate under less acidic conditions enables the β-hydroxyketone to be isolated. The main application of this reduction has been in the steroid series. For example reduction of 16α,17α-epoxyprogesterone with chromium(II) chloride gives 16,17-didehydroprogesterone whilst with chromium(II) acetate 16α-hydroxyprogesterone is formed[40]. Chromium(II) chloride has been regularly used[41] in the deoxygenation of the limonoid group of triterpenes in which ring D bears an α,β-epoxy-δ-lactone.

[39] *R. M. Milburn* and *H. Taube*, J. physic. Chem. *64*, 1776 (1960).

[40] *W. Cole* and *P. L. Julian*, J. org. Chemistry *19*, 131 (1954).

7. Reduction of Nitro Compounds

The early observation[1] that chromium(II) chloride does not reduce nitrites and hydroxylamine has not yet been explained. Reduction of a nitroolefin, 6-nitrocholesteryl-acetate *(1)*, and some related 5-chloro-6-nitro steroids with acidic solutions of chromium(II) chloride resulted[42] in the formation of the 5α-hydroxy-6-hydroxyimino steroids.



(1)

The above survey illustrates the wide range of application of the chromium(II) ion, whose reducing properties often complement those of the hydrides or dissolving metals.

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[41] *D. Arigoni, D. H. R. Barton, E. J. Corey*, and *O. Jeger*, Experientia *16*, 41 (1960); *A. Akisanya, C.W.L. Bevan, T.G. Halsall, J.W. Powell*, and *D. A. H. Taylor*, J. chem. Soc. (London) *1961*, 3705; *D. E. U. Ekong* and *O. E. Olagbemi*, *ibid.* (C) *1966*, 944.

[42] *J. R. Hanson* and *E. Premuzic*, Tetrahedron Letters *1966*, 5441; Tetrahedron, in press.

Problems and Possibilities of Modern Trace Analysis[**]

BY H. SPECKER[*]

As a result of the development of measuring techniques, analytical chemists can now determine very small quantities as well as trace concentrations of the order of 10^{-8} % with good accuracy. In exceptional cases it is even possible to detect 10^5 atoms of an element. In this review, definitions of important analytical terms are outlined and a critical appraisal of the principal methods of trace analysis is given.

1. Introduction

During the past two decades, inorganic analytical chemistry has been especially concerned with the problems and methods of trace determination. One reason for this is the importance of trace elements, only recently recognized in biological problems, in the chemistry of very pure substances, in the prevention of pollution of air and water, and in the catalysis of chemical and biological processes.

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[**] Based on plenary lectures to the 2nd International Symposium on Very Pure Substances in Dresden, 1965, and to the Fachgruppentagung Analytische Chemie 1966 in Lindau.

In trace detection and determination, the analyst has at his disposal only very small quantities of the trace elements, which occur in the original substance together with large excesses of other elements, the principal components. The ratio of principal components to trace components is by definition at least 10^3, and in extreme cases 10^{10} or even higher. The analytical problem of trace determination is immediately obvious from this ratio; the methods or the procedures devised must permit the accurate determination of very small quantities of one substance in the presence of large excesses of others. Since classical gravimetric and volumetric methods are clearly unsuitable for determination of such small quantities, only physical methods can be considered. These are:

1. electrochemical methods,
2. photometry and fluorescence analysis,

3. spectrochemical analysis in the broad sense,
4. activation analysis,
5. mass spectroscopy, and
6. catalytic detection reactions.

Electrochemical, photometric, and catalytic methods always require chemical preparation, whereas the other three methods permit examination of the sample as submitted for analysis. Direct analysis offers important advantages; these will be discussed in detail.

2. Definitions

Before discussing the possibilities and limitations of the various methods and analytical principles, we shall first define three terms used in trace determination and present examples to illustrate them:

1. the sensitivity of an analytical method,
2. the detection limit of an analytical procedure, and
3. the limit of guarantee for purity.

The use of the term "sensitivity" has lead to many misunderstandings in analytical chemistry. In modern analysis, *i.e.* in electrochemical methods, photometry, spectrochemistry, and activation analysis the sensitivity of an analytical method is measured by the slope of the calibration line. This definition is particularly clear in photometric analysis where it is well known that the slope of the calibration line is given by:

$$\Delta E/\Delta c = \varepsilon \cdot d$$

(E = extinction, c = concentration, ε = extinctivity, d = thickness of absorption cell).

This is illustrated in Figure 1 for the reactions used in the photometric determination of iron [1]. It can be seen that the method using *o*-phenanthroline (line 2) is about five time as sensitive as that using 2,6-pyridinedicarboxylic acid (line 3). In both cases the thickness of the cell was 1 cm. As can be seen from the equation, the sensitivity of any photometric determination can in principle be increased by increasing the thickness of the absorption cell.

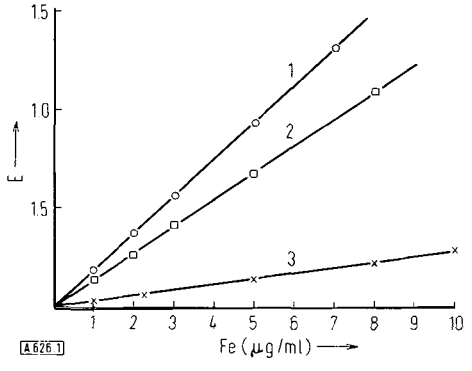

Fig. 1. Calibration lines for the photometric determination of iron (definition of sensitivity). Line 1: with 2-pyridinealdoxime, $\Delta E/\Delta c$ = 0.18; line 2: with *o*-phenanthroline $\Delta E/\Delta c$ = 0.14; line 3: with 2,6-pyridinedicarboxylic acid, $\Delta E/\Delta c$ = 0.028. The thickness of the cell is 1 cm. Ordinate: Extinction. Abscissa: Iron concentration.

[1] *H. Specker*, Z. Erzbergbau Metallhüttenwes. *17*, 132 (1964).

Another example illustrating the sensitivity of a detection reaction is the determination of lead and copper by inverse voltammetry with a hanging drop of mercury (Fig. 2). The slope of the calibration line for copper is much less steep than that for lead. This is because a complexing agent (pyridine) must be added during the determination of copper to separate the redissolution potential of copper from that of mercury. The abscissa in Figure 2 is calibrated in micrograms and not in molarities. Conversion of the results into molarities shows that the inverse voltametric determination of lead is about seven times as sensitive as the determination of copper.

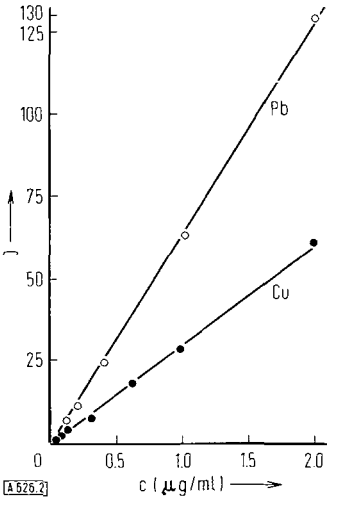

Fig. 2. Calibration lines for the inverse voltammetric determination of lead and copper (definition of sensitivity). Ordinate: I in scale divisions. Abscissa: Concentration (µg/ml). Pb line: dI/dc = 66 (scale divisions/µg); Cu line: dI/dc = 29 (scale divisions / µg).

A careful distinction must be made between the sensitivity of a method and the detection limit of an analytical procedure [*]; the detection limit of an analytical procedure was introduced in its present form by *Kaiser* [2] for spectrochemical analysis, and was later extended to all analytical procedures [3]. The detection limit is a characteristic numerical value (figure of merit) for an analytical procedure; it can be objectively determined, and has a definite significance. In each case it refers to a definite "complete analytical procedure" used for the solution of a given analytical problem in accordance with a precisely established set of instructions. There is no such thing as a general detection limit, *e.g.* for spectrochemistry, photometry, or mass spectroscopy.

The detection limit is derived from the standard deviation of the blank values. Many blank determinations (at least 25) are carried out by the procedure in question; *e.g.* for a photometric detection reaction, all the reagents must be present except the element to be determined, and the standard deviation of the blank values is calculated from the results. The value

[*] For definition of detection power, see Section 4.

[2] *H. Kaiser*, Spectrochim. Acta *3*, 40 (1947/48).

[3] *H. Kaiser* and *H. Specker*, Z. analyt. Chem. *149*, 46 (1956).

of the measured quantity at the detection limit is then given by

$$\underline{x} = 3\,\sigma_{Bl} + \bar{x}_{Bl}$$

(σ_{Bl} = standard deviation of the blank values, $\bar{x}_{Bl}$ = average of the blank values). The factor 3, *i.e.* a probability of error of only 0.14 %, is chosen to ensure that only one value is really necessary in all cases of practical importance, even when the results deviate from the normal distribution. The concentration $\underline{c}$ at the detection limit is found from the analytical function $c = f(x)$ to be

$$\underline{c} = f(\underline{x}).$$

The value of the blank is of no importance; the deciding factor is the scatter of the blank values, from which the standard deviation can be calculated. A constant blank value, whatever its magnitude, can always be eliminated by means of a correction. This is also true of the constant component of fluctuating blank values, which is given by the statistical mean $\bar{x}_{Bl}$ of the values. The significance of the detection limits found in this way is shown by Figure 3 for the photometric determination of iron with *o*-phenanthroline. The value of $\underline{c}$ was found to be 0.04 μg Fe/ml.

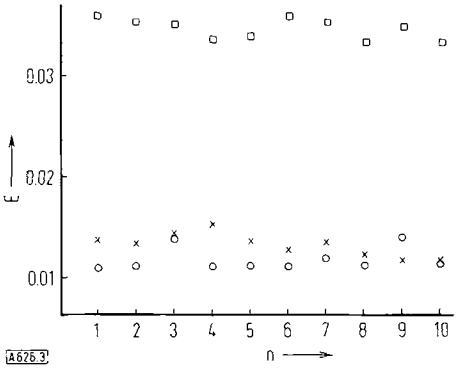

Fig. 3. Detection limit $\underline{c}$ of the photometric determination of iron with *o*-phenanthroline. ○ = blank value, × = 0.02 μg of Fe/ml, □ = 0.1 μg of Fe/ml. $\underline{c}$ = 0.04 μg of Fe/ml. Ordinate: Extinction. Abscissa: Number of measurements (measurements carried out at the Institut für Spektrochemie, Dortmund).

The extent to which the detection limit for an accurately defined procedure can depend on the external conditions may be illustrated by two examples. The indicated value of 0.04 μg of Fe/ml for the detection limit of iron was determined by more than 100 blank measurements in unpurified laboratory air. When the experiments were repeated in a dust-free room, the detection limit with the same reagents was 0.013 μg of Fe/ml. The poor detection limit in the first case was due to the unavoidable presence of dust particles (which contained iron) from the air around the industrial area of Dortmund. These stray dust particles increased the standard deviation of the blank values, and so gave a poor detection limit.

The detection limit is improved only slightly, if at all, by an increase in the thickness of the cell; this can be seen from Figure 4, which shows the blank values for the photometric determination of nitrate in water at cell thicknesses of 1 cm (left) and 5 cm (right). The detection limit at 1 cm is 0.3 mg/l, while that at 5 cm

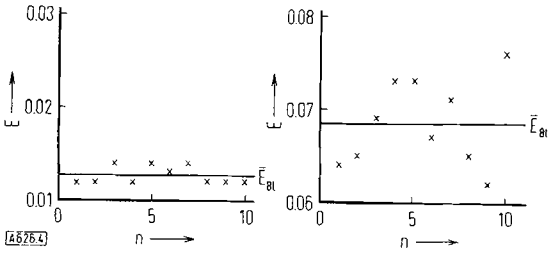

Fig. 4. Blank values for the photometric determination of nitrate with α-naphthylamine and sulfanilic acid. Left: thickness of the cell d = 1.002 cm, detection limit $\underline{c}$ = 0.3 mg of NO_3^-/l; right: d = 5 cm, $\underline{c}$ = 0.27 mg of NO_3^-/l. $\bar{E}_{Bl}$ are the average blank values.
Ordinate: Extinction. Abscissa: Number of measurements.

is 0.27 mg/l. The sensitivity, on the other hand, increases in proportion to the cell thickness, as was mentioned earlier. In the examples given, and in general in processes involving chemical pretreatment, the variations in the blank values are due, not to the measuring apparatus, but to the reagents and to stray components introduced from the atmosphere. The only variations caused by a photometer are about two orders of magnitude smaller, and are not significant in such determinations [4]. For this reason, lower (*i.e.* better) detection limits are achieved in processes that can be carried out without chemical preparation. In these cases, the scatter of the results, and hence the standard deviation of the blank values, is due only to the measuring apparatus. All experimental work in modern trace analysis is aimed at the improvement of the detection limits, *i.e.* at the reduction of the scatter of the blank values and in general of the "noise level" of a procedure.

The "limit of guarantee for purity" is a relatively new concept in trace analysis. It is required when an analysis leads to a negative result, *i.e.* when the experimental result x is smaller than the value $\underline{x}$ at the known detection limit. In such cases, the analyst is asked what purity he can guarantee for the sample. The obvious answer is to say that the concentration in the sample is definitely below the concentration $\underline{c}$ at the detection limit. However, this is wrong, since it is quite possible for a concentration slightly above $\underline{c}$ to give an experimental result smaller than $\underline{x}$ owing to a strong chance fluctuation, so that this experimental value cannot be accepted as correct. The reason for this state of affairs is known in mathematical statistics as an "error of the second type".

The significance and statistical derivation of the "limit of guarantee for purity" was first formulated by *Nalimov et al.* [5,6], and later by *Roos* [7]. This concept was subsequently discussed in detail mainly at the instigation of *Ehrlich* [8], and has been described in a clear and understandable manner by *Kaiser* [8]. According

[4] *H. Specker, E. Jackwerth,* and *H. Hartkamp,* Z. analyt. Chem. *139,* 163 (1958).

[5] *V. V. Nalimov*: The Application of Mathematical Statistics to Chemical Analysis. Pergamon Press, Oxford 1963.

[6] *V. V. Nalimov, V. V. Nedler,* and *N. P. Mensova,* Zav. Labor. *27,* 861 (1961).

[7] *J. B. Roos,* Analyst *87,* 832 (1962).

[8] *H. Kaiser,* Z. analyt. Chem. *209,* 1 (1965).

to this author the limit of guarantee for purity is given by

$$c_G = \bar{x}_{Bl} + 6\,\sigma_{Bl}$$

where $\bar{x}_{Bl}$ is again the mean of the blank values and σ_{Bl} is the standard deviation of the blank values. The analyst can guarantee with "certainty" that the concentration of a given element in the sample is not higher than c_G when the analysis gives a negative result.

We shall again compare the "detection limit" of an analytical procedure ($\underline{c}$) and the "limit of guarantee for purity" of a sample (c_G)

1. What is the lowest content in a sample that can be "reliably" detected by the analyst? Answer: $\underline{c} = f(\bar{x}_{Bl} + 3\,\sigma_{Bl})$.

2. What purity can be guaranteed with "certainty" if a substance that might be present cannot be detected (experimental value smaller than the value at the detection limit)? Answer: $c_G = f(\bar{x}_{Bl} + 6\,\sigma_{Bl})$.

3. Enrichment Processes

Chemical and physical enrichment processes have proved very useful for the improvement of detection limits. If the introduction of impurities can be avoided in chemical enrichment processes, the detection limits, as with physical enrichment, can generally be improved by one to two powers of ten. Interference is decreased by the removal of the principal components, and the absolute quantity of the trace components subjected to analysis is also increased.

The following is a simple example from spectrochemical analysis. In a directly excited sample of aluminum, approximately 10 mg are analyzed. If this sample contains *e.g.* 10^{-4} % of copper, the analytical signal is based on 10^{-6} g of copper. If, on the other hand, we begin with 1 g of sample, remove the aluminum, and quantitatively excite the trace element, then 10^{-4} g of copper are available for the analytical signal. In *Pohl*'s procedure[9], the trace elements are separated from the principal component by precipitation and solvent extraction, and are then determined spectrochemically.

Another interesting example of chemical concentration of trace components by extraction of the trace elements was described by *Wunderlich*[10]. Very pure germanium chloride (50 to 100 g) is extracted directly with 6 N hydrochloric acid; the two phases are immiscible. Several cations, including arsenic, can then be determined down to 0.01 ppm. The danger of accidental contamination in this case is extremely low, since the 6 N hydrochloric acid can be prepared in a very pure state.

Physical enrichment processes generally do not involve dissolution of the sample, and so are not subject to chemical sources of interference. Such methods are particularly suitable for combination with spectrochemical analysis and X-ray fluorescence analysis.

With the aid of zone melting, *Abakumov* and *Konovalov*[11] obtained detection limits of 10^{-6} to 10^{-7} % for Ag, Cu, and Tl in very pure bismuth. The vaporization method presents two possibilities: (i) vaporization of the principal component and (ii) vaporization of the trace components, which are then collected. In case (i), the matrix is often removed by chlorination or fluorination; thus by vaporization of V, B, and Si in the form of the chlorides 5×10^{-5} % of W, 10^{-6} % of Ta, and 2×10^{-8} % of Mn can be detected spectrochemically in samples of a few grams of these substances.

In a method described by *Geilmann*[12] and *Neeb*[13], the sample is heated in a furnace, and the volatile components are carried by a current of gas through a nozzle onto a cold collecting surface; this collector is then excited directly. The *Geilmann* process has proved very useful for the determination of Tl, Zn, As, Bi, and Cd. Simultaneous concentration of several trace elements in tungsten oxides was achieved by *Lounamaa*[14]. In this process, the tungsten is first converted into the extremely nonvolatile tungsten carbide at low temperatures. It was possible by this procedure to improve the detection limits of 15 elements by two powers of ten.

4. Possibilities and Limitations of the Various Methods

We shall now consider the limits of the various methods in the light of the present position of trace analysis. The question of the absolute limit of a method or of an analytical principle is not very meaningful, since there are processes used in nuclear physics by which it is possible to detect individual atoms or elementary particles. However, one would hardly call these analytical procedures. Consequently, one can only consider an idealized analytical procedure isolated from the apparatus available at any given time, and ask oneself if it approaches the limit imposed by the quantized nature of energy.

Considerations of this type are already important in connection with the detection power[*] of X-ray fluorescence and spectrochemical analysis. Only a small number of investigations that can be accurately evaluated have been carried out on the detection power of modern electrochemical processes[15]. In inverse voltammetry on the hanging mercury drop and on the graphite electrode, we found that the detection power for lead, cadmium, and silver was 0.2 ng/ml, *i.e.* approximately 10^{-9} M solutions. Modern polarographs are also capable of detection in the nanogram range. According to the latest publications and the manufacturers' data, some cations and anions

[9] *F. A. Pohl*, Z. analyt. Chem. *142*, 19 (1954).

[10] *E. Wunderlich* and *E. Göhring*, Z. Erzbergbau Metallhüttenwes. *18*, 121 (1965).

[11] *G. Abakumov* and *E. E. Konovalov*, Zav. Labor. *29*, 1506 (1963).

[12] *W. Geilmann* and *A. de Alvato Esterbaranz*, Z. analyt. Chem. *194*, 60 (1962).

[13] *K. H. Neeb*, Z. analyt. Chem. *194*, 255 (1963).

[14] *N. Lounamaa*, Suomalaisen Tiedeakatemian Toimituksia (Ann. Acad. Sci. fenn.) Ser. A II *63*, 1 (1955).

[*] In accordance with a suggestion by *Kaiser*, the term "detection sensitivity" or "sensitivity" that was frequently used in the past is replaced by "detection power". This means that the term "sensitivity" is now reserved exclusively for the measured value/scale division, *i.e.* in analysis, for the slope of the calibration line.

[15] *R. Neeb*, Article in Reinststoffanalytik, 2. Internationales Symposium „Reinststoffe in Wissenschaft und Technik". Vol. 2, Akademie-Verlag, Berlin 1966, p. 573.

can be determined in solutions as dilute as 10^{-9} to 10^{-10} M.

To emphasize clearly the distinction between the terms used, we again stress that the detection power referred to here is not to be confused with the statistically defined detection limit of a complete analytical process. The detection power applies to an analytical principle embodied in an "idealized" procedure that is not subject to interference by external influences. It is usually one to two powers of ten lower than the detection limit.

4.1. Photometry

Owing to the chemical pretreatment of the sample and the reagents required, the detection limit in photometry, as was mentioned earlier, depends on the reagents and on the scatter of the blank values due to the outside atmosphere. We have been able to achieve detection limits of 0.008 to 0.02 μg of metal/ml by the use of specially purified reagents in a dust-free room. In the present state of photometric measuring techniques, this is the order of magnitude of the detection power of this analytical principle, which is determined by the extinctivity [16]. With few exceptions [17] ε_{max} is given by

$$\varepsilon_{max} = 9 \cdot 10^{19} \cdot P \cdot a \leqq 10^5$$

if the entire system contains only one chromophore. In this equation, P is the probability of transition, and a is the square dimension of the chromophore. The extinctivities in the photometric procedures used for the determination of trace elements are between 10000 and 30000, and between 50000 and 80000 for dithizonates. If one assumes that an extinction of 0.01 can still be reproducibly measured, it can be deduced from the well known equation

$$E = \varepsilon \cdot c \cdot d$$

that by making use of all possibilities, it is just possible to carry out an accurate measurement on a 10^{-7} M solution. Thus trace contents of less than 10^{-5} % cannot be determined photometrically without previous enrichment. This limit was determined for absorption photometry; it is not valid for fluorescence analysis, in which visual and photometric measurement is still possible in some cases for 10^{-10} to 10^{-12} M solutions. However, routine fluorescence analysis is not particularly popular in inorganic chemistry, owing to its susceptibility to interference.

4.2. Spectrochemical Analysis

The most important method of inorganic trace analysis at present is emission and absorption atomic spectroscopy. This method has the following advantages over other methods [18].

The samples can be analyzed directly, *i.e.* without chemical preparation. The spectrochemical methods are specific, and the identification of the element is conclusive. For these reasons, many elements in the same sample can be determined qualitatively and quantitatively at the same time. Low detection limits can be achieved, and the accuracy (standard deviation) is satisfactory over wide concentration ranges; moreover, only small quantities of material are required (sometimes as little as 1 μg is sufficient). Once a procedure has been established, the time taken for preparation of the sample and analysis is short. Combination of spectrochemical analysis with enrichment processes, though not so universally applicable, leads to very low detection limits and relatively high accuracies [18].

The problem of the detection limit and its improvement has received more attention in recent years in spectrochemistry than in any other analytical method [18]. The detection power of this analytical principle has been discussed by *Mandel'stam* and *Nedler* [19]. Because of the simplifications and assumptions made, the authors regard their treatment as qualitative rather than as quantitative. They calculate the spectrochemical detection power for individual elements in absolute quantities, and conclude that 10^{-12} g can be detected in an arc and 10^{-13} g in a hollow cathode. The corresponding concentrations are 10^{-9} and 10^{-10} % respectively. This means that 10^9 atoms can be detected in a sample with the aid of the hollow cathode, and 10^{10} atoms with the aid of an arc.

That these limits have occasionally almost been reached in practice is illustrated in Table 1, where column a) refers to analysis of pure solutions and column b) to the analysis of U_3O_8 with a carrier. The Table clearly shows the difference between the detec-

Table 1. Spectrochemically detectable quantities (after *Korovin* [19a], abridged) (a) in pure solutions, (b) in technical U_3O_8 (enrichment of the sample by fractional distillation with a carrier).

Element	a) (ng)	b) (ng)
Al	10	500
Ag	0.03	5
B	1	1
Be	0.03	10
Cd	30	7
Co	0.3	100
Cr	1	300
Cu	0.03	30
Fe	10	100
Ga	0.03	–
K	10	200
Li	0.1	10
Mg	0.03	50
Mn	0.03	100
Na	0.03	50
Ni	1	200
P	30	5000
Pb	10	100
Sb	100	1000
Si	1	300
Sn	10	100
Zn	3	2000

[16] *H. A. Staab*: Einführung in die theoretische organische Chemie. Verlag Chemie, Weinheim 1951, p. 298.

[17] *D. Thierig* and *F. Umland*, Z. analyt. Chem. *211*, 161 (1965).

[18] *K. Laqua*, Z. analyt. Chem. *221*, 44 (1966), and further literature cited there.

[19] *S. L. Mandel'stam* and *V. V. Nedler*, Optics and Spectroscopy (USSR) (Engl. Translation) *10*, 196 (1961).

[19a] *Yu. I. Korovin*, Ž. analit. Chim. *16*, 494 (1961).

tion limits in pure solutions and those in an industrial analytical sample.

Of the many spectrochemical investigations that have been carried out, we shall consider only one interesting piece of work on the analysis of very pure substances. *Haftka*[20] studied the purification of high-purity aluminum by zone melting, with particular reference to the elements magnesium and silicon. The detection limits in this case are about 10^{-6} %. Some trace elements that could not be detected spectrochemically in the initial bar were very obvious after zone melting. *Haftka* followed the purification of zone-refined bismuth spectrochemically and by conductance measurements. Whereas the conductance along the bar changed only by a factor of 2, concentration changes of several powers of ten were found spectrochemically. Thus spectrochemical analysis is much more suitable for purity control in this case.

An even more recent spectrochemical method of trace analysis is atomic absorption spectroscopy[21]. This method developed surprisingly rapidly after the first investigations by *Walsh*[22]. The analytical principle is simple, and the apparatus inexpensive. A hollow cathode made from the element that is to be determined is caused to emit radiation (a continuum may also be used), which is then passed through the vaporized sample. The atoms of the element to be determined absorb in particular at the wavelengths of their resonance lines, and this absorption is measured. Since the number of atoms absorbing the light determines the detection limit, the latter may be decreased by increasing the optical path or the residence time of the atoms present in the gaseous phase. This second alternative was realized by *L'vov*[23] by means of the graphite cell. When the sample or the solution is introduced directly into a graphite tube about 10 cm long and heated to a high temperature it evaporates, and the atoms remain for a long time in the gas space. The versatility and handling of the absorption cell was recently considerably improved by *Massmann*[24]. By this technique, it was possible to obtain detection limits of 10^{-11} g of aluminum and 10^{-12} g of zinc in atomic absorption spectroscopy. The detection power as defined in Section 4 is about 10^{-14} g for favorable elements. Though atomic absorption spectroscopy cannot achieve the importance of emission spectral analysis, it has gained a firm place in optical spectral analysis because of its very low detection limits and the relatively inexpensive apparatus required. However, a number of technical difficulties still remain to be overcome before it can be used for routine analysis on a large scale.

4.3. Activation Analysis

The trace analysis method having the best detection power is activation analysis. The reasons for this are the high specificity (due to specific half-lives and specific radiation energies), the possibility of the simultaneous determination of several elements, the ease of separation by carriers, and the absence of blank values, since the sample is irradiated without preliminary treatment and any surface impurities can be removed by etching after activation.

Thermal neutrons are the particles most frequently used in activation analysis. When a sample is irradiated with neutrons or other particles, the number of atoms A activated is

$$A = Nf\sigma\,(1-e^{-\lambda t})$$

N is the number of atoms present, f is the neutron flux, σ is the effective cross section (which is a measure of the probability of capture of the particles by the element in question), λ is the half-life, and t is the irradiation time. The effective cross section differs from one element to another by several powers of ten. This difference and the difference in the half-lives give rise to the different detection limits for the various elements under otherwise identical conditions. Some idea of the detection limits found is given in Table 2. By increasing the neutron flux by one to two powers of ten, which is now possible, the detection limits given here can be further improved, and short-lived activated emitters can be determined more readily. Thus *Neeb et al.*[27] were recently able to determine 10^{-10} % of gold in high-purity aluminum at a neutron flux of 8×10^{13} n cm^{-2} sec^{-1}.

Table 2. Detection limits for activation analysis by neutron radiation in a flux of 10^{13} n cm^{-2} sec^{-1}.

10^{-11} g	10^{-12} g	10^{-13} g	10^{-14} g
Sb	As	Lu	Eu
Ar	In	Dy	—
Cs	Ir	Au	—
Er	Kr	Ho	—
Gd	Mn	—	—
Ga	Re	—	—
Hf	Sm	—	—
Co	Sc	—	—
Cu	Tb	—	—
La	Tm	—	—
Li	W	—	—
Na	Yb	—	—

The activation analysis of high-purity substances has recently been reviewed by *Alimarin et al.*[28] (see Table 3). The detection limits for most impurities, irrespective of the matrix, are between 10^{-6} and 10^{-8} %. (For further reviews on detection limits for 70 elements by this analytical principle, see the articles by *Lukens*[25] and *Jule*[26].)

Activation analysis is not confined to the use of slow neutrons. Fast neutrons, protons, deuterons, α-particles, ^{3}He, and γ-radiation can also be used for activation. "Inverse" activation is also possible. Owing to its high neutron capture cross section, boron (0.1 to 0.008 %) can be determined indirectly in steel from the reduced ^{59}Fe activity.

[20] *F. J. Haftka*, Mikrochim. ichnoanalyt. Acta (Wien) *1965*, 331.

[21] *H. Massmann*, Chimia *21*, 217 (1967), and further literature cited there.

[22] *A. Walsh*, Austral. Pat. 163586 (23041/53) (Nov. 17, 1953).

[23] *B. V. L'vov*, Inž.-fiz. Ž. *2*, 44 (1959).

[24] *H. Massmann* in [15], p. 297.

[25] *H. R. Lukens*, Analytica chim. Acta *34*, 9 (1966).

[26] *H. P. Jule*, Analytic. Chem. *38*, 818 (1966).

[27] *K. H. Neeb*, *H. Stöckert*, and *W. Gebauhr*, Z. analyt. Chem. *219*, 69 (1966).

[28] *J. P. Alimarin*, *Ju. V. Jakovlev*, and *N. N. Dogadkin* in [15], p. 437.

Table 3. Detection limits in the activation analysis of impurities in high-purity substances after radiochemical separation (after *Alimarin* [28]).

High-purity substance	Detection limits of the impurities (%)															
	Cu	Zn	Mn	Ga	As	Sb	P	Au	Rare earths (above Eu)	Ni	Co	S	Se	Te	Mo	Cr
Si	1×10^{-8}	1×10^{-7}	5×10^{-9}	5×10^{-8}	5×10^{-7}	1×10^{-8}	–	1×10^{-8}	1×10^{-7}	1×10^{-6}	–	–	–	–	–	–
Ge	1×10^{-8}	5×10^{-5}	–	–	–	1×10^{-7}	–	–	1×10^{-7}	–	–	–	–	–	1×10^{-6}	–
Ga	1×10^{-7}	–	–	–	3×10^{-7}	–	2×10^{-4}	1×10^{-7}	–	–	–	–	–	–	–	–
In	3×10^{-7}	5×10^{-5}	–	–	1×10^{-6}	6×10^{-6}	–	1×10^{-7}	–	–	–	–	–	–	–	–
P	5×10^{-8}	5×10^{-6}	–	–	1×10^{-7}	5×10^{-7}	–	1×10^{-8}	–	–	–	2×10^{-4}	4×10^{-5}	3×10^{-6}	–	–
As	3×10^{-7}	3×10^{-6}	–	5×10^{-6}	–	3×10^{-6}	1×10^{-5}	5×10^{-8}	–	5×10^{-5}	5×10^{-5}	–	5×10^{-4}	2×10^{-6}	–	–
Sb	1×10^{-7}	8×10^{-7}	5×10^{-8}	5×10^{-7}	5×10^{-7}	–	8×10^{-6}	–	–	–	–	–	–	–	–	5×10^{-4}
GaAs	3×10^{-7}	–	–	–	–	4×10^{-6}	–	1×10^{-7}	–	–	–	–	1×10^{-3}	3×10^{-6}	–	–
Pb	5×10^{-8}	5×10^{-7}	–	–	5×10^{-8}	5×10^{-7}	–	2×10^{-8}	–	1×10^{-6}	–	–	2×10^{-5}	2×10^{-6}	–	–
Bi	2×10^{-7}	1×10^{-7}	1×10^{-8}	–	1×10^{-7}	4×10^{-7}	–	–	5×10^{-7}	–	–	–	–	–	1×10^{-6}	–
Zn	–	–	–	–	5×10^{-7}	3×10^{-7}	–	–	–	–	–	–	–	1×10^{-6}	–	–

In addition to the advantages mentioned, activation analysis also has certain disadvantages. It cannot be used to obtain a general picture of the composition of a sample, as can spectrochemical analysis or mass spectroscopy, since the elements to be determined must be known in advance. Another disadvantage is the high cost of production and manipulation of radioactive elements. Nevertheless, activation analysis must be used whenever the most rigorous demands of the chemistry of pure substances have to be met. It is in fact indispensable in certain special cases.

4.4. Mass Spectroscopy

One of the great advantages of spectrochemical analysis is that it can be used for very fast, rough analysis to gain a general picture of the composition of a sample. The same possibility is offered by mass spectroscopy. This method again requires no chemical preparation of the sample. Consequently, contamination by the outside air and by reagents is reduced, and the detection power is accordingly greatly improved. The ion source used almost exclusively in inorganic mass-spectroscopic analysis is the high-frequency high-vacuum spark type, in which the composition of the ion beam corresponds closely to the composition of the sample. On the basis of this assumption, it is possible to determine all components directly to within an uncertainty factor of 3, and without special calibration. The ions of the elements present are generally recorded on a photographic plate. Mass spectroscopy is finding increasing use, particularly in the analysis of very pure substances. Table 4 lists the detection power for the impurities in very pure silicon as determined by such a method.

Table 4. Detection limits $\underline{c}$ for mass spectrographic trace determinations in high-purity silicon [28a].

Element	$\underline{c}$ (Atom-ppb)	Element	$\underline{c}$ (Atom-ppb)
Bismuth	1	Arsenic	3
Lead	2	Gallium	6
Gold	10	Zinc	5
Tungsten	3	Copper	5
Tantalum	30	Nickel	50
Europium	2	Iron	30
Cerium	100	Manganese	1000
Antimony	2	Chromium	10
Tin	3	Calcium	10
Indium	30	Chlorine	10
Silver	6	Phosphorus	10
Molybdenum	10	Magnesium	10
Niobium	3	Boron	3

[28a] The data are taken from AEI Technical Information Sheet A 16.

In a fundamental study, *Ehrlich* and *Mai* [29] have accurately determined detection limits in the analysis of very pure substances on a statistical basis. In semiconductor silicon, the detection limits for about 50–60 elements are less than or about 10 atom-ppb (billion $\equiv 10^9$), and for a further 10 elements between 10 and 100 ppb; only three elements have detection limits between 100 and 200 ppb in the mass-spectroscopic analysis of high-purity silicon. By very careful elimination of the strong background blackening in the neighborhood of the principal lines of the matrix (cut-outs are made in the photographic plates and the interfering ions of the principal components pass through), *Mai* [30] achieved detection limits of 0.3 ppb for favorable elements in high-purity aluminum. Conversion of the values given here into absolute quantities, *i.e.* the quantities that fall on the photographic plate and give rise to the analytical signal, shows that as little as 10^{-12} to 10^{-16} g can be recorded mass-spectroscopically; thus 10^5 atoms can be detected. This brings us into a range that is also reached in special cases by activation analysis.

However, it should be mentioned that the results of mass spectroscopic analysis can be falsified by external influences. Sources of error include contaminants from the outside air, contacts made during transport, materials entrained through the ion source, and particularly the "memory effect" (errors due to remaining traces of the previous analytical sample). Moreover, the performance of accurate inorganic analysis of solids is still very difficult, and requires extensive cooperation between chemists and physicists. A great deal of fundamental research and improvement of the equipment will be required before routine inorganic mass-spectroscopic analysis in the ppb range will become practicable.

[29] *G. Ehrlich* and *H. Mai*, Z. analyt. Chem. *218*, 1 (1966).
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4.5. Catalytic Detection Reactions

Catalytic or kinetic analytical methods make use of the dependence of catalytic reactions on the concentration of the catalyzing element. These reactions can be divided into three groups [31, 32, 32a]

1. activation of the reactant by coordination,
2. formation of a charge transfer complex between the catalyst and the reactant, and
3. activation of the reactant by conversion into the free radical form.

The first group consists mainly of reactions of elements that occur in only one oxidation state. The increase in the reaction rate is generally slight and the detection power is of the order of 10^{-4} to 10^{-7} g/ml. A well known example is the catalytic determination of iodide ions with hydrogen peroxide in the presence of molybdenum, zirconium, hafnium, niobium, and tantalum, all of which form complexes with hydrogen peroxide.

The formation of a charge transfer complex requires overlapping between the free orbitals of the reactant and the occupied orbitals of the catalyst or *vice versa*. For this reason, the favored elements are those with partly occupied d shells, *i.e.* those which form characteristic complexes of this type with aromatic anions and phenols. It is possible in such reactions to attain a detection power of 10^{-9} to 10^{-12} g/ml.

If a catalyst is to form free radicals, it must be readily oxidizable or reducible, with loss of or acceptance of an electron. The radicals formed are extremely reactive, a fact which leads to a very marked increase in the reaction rate and consequently to an extremely good detection power (in the picogram range). Some examples are the catalytic detection reactions with hydrogen peroxide in alkaline media, the oxidation of thiosulfate to tetrathionate, and the reduction of peroxodisulfate to sulfate.

Catalytic detection reactions are known at present for 35 elements. The only elements for which specific reactions exist are copper [33] and cobalt. Copper(II) salts react specifically with *p*-dimethylamino-α-benzoylaminocinnamic acid, a compound which exhibits green fluorescence in the presence of copper. By means of such a process it is possible to determine 0.001 μg of Cu/ml and it is used at present for the determination of very low copper contents in high-purity hydrochloric acid and chlorosilanes.

The number of selective catalytic detection reactions is greatly increased if selectivity is related to the same reaction for three to five other elements. Reactions of this type exist for chromium, molybdenum, tungsten, uranium, manganese, rhenium, iron, nickel, ruthenium, palladium, vanadium, platinum, gold, mercury, fluorine, bromine, iodine, sulfur, selenium, and tellurium. Less selective reactions are known for titanium, zirconium, hafnium, thorium, niobium, tantalum, zinc, cadmium, germanium, silicon, and phosphorus. Selectivity for some of the elements in the last group can be greatly increased by preliminary complexing of one of the accompanying elements.

This and other recent results show considerable promise for the future of trace determination by catalytic detection reactions, particularly in trace analysis of high-purity substances.

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[33] *E. A. Bozevol'nov, S. U. Krejngol'd, R. P. Lastovskij,* and *V. V. Sidorenko,* Doklady Akad. Nauk SSSR *153*, 97 (1963).

Conductance of Electrolyte Solutions

BY J. BARTHEL [*]

The present article deals with methods and results of conductance studies with special reference to nonaqueous solvents, e.g. ethanol, dioxane, dimethylformamide, acetonitrile, nitromethane, and acetone, in some cases mixed with water, as well as NH_3, SO_2, I_2, etc. On the basis of a model in which the ions are represented as charged spheres and the solvent as a homogeneous isotropic medium, the conductance theory can (at least for low electrolyte concentrations) give a more or less complete representation of the problem. A new statistical treatment of the transport problem confirms important results of this representation. The present state of the investigation is finally outlined in a review of recent publications.

1. Introduction

Conductance measurements are among the most accurate of all electrochemical measurements. The investigation of conductance as a function of concentration gives the conductivity at infinite dilution, the ion mobilities, the dissociation constants of ionogens, the association constants of ionophores, ionic radii, and in many cases information about the structure of the electrolyte solutions in the vicinity of the ions. Parameters available in studies of this nature include the temperature, the pressure, and the strength and frequency of the external electric field, as well as the properties of the ions and of the solvent. In the theoretical treatment, there is no fundamental difference between water and nonaqueous solvents.

Ionophores [2] (true electrolytes [1]) are substances which in the pure state already exist as ionic crystals, *e.g.* the alkali metal halides. Ionogens [2] (potential electrolytes [1]), such as acetic acid, form ions only by chemical reaction with solvent molecules.

Ionophores are completely dissociated in solution; however, in solvents with sufficiently low dielectric constants, Coulomb forces between oppositely charged ions lead to the formation of associates, which, in symmetrical electrolytes (charges on cation and on anion equal in magnitude), cannot transport current, *e.g.*

$$Na^+ + Cl^- \underset{CH_3COCH_3}{\rightleftharpoons} [Na^+Cl^-]^0$$

The reaction of ionogens with the solvent to form ions does not proceed to completion

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

Both processes are described by the thermodynamic equilibrium constants K_A (association constant) or K_D (dissociation constant) [**].

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[1] *G. Kortüm*: Lehrbuch der Elektrochemie. 4th Edit., Verlag Chemie, Weinheim 1966.

[2] *R. M. Fuoss* and *F. Accascina*: Electrolytic Conductance. Interscience, New York 1959.

[**] The symbols used are given in the following list in the approximate order in which they occur.

K_A	= association constant [l/mole]
K_D	= dissociation constant [mole/l]
Λ	= molar conductance [ohm^{-1} cm^2 mole^{-1}]
Λ_c	= equivalent conductance [ohm^{-1} cm^2 equiv^{-1}]
Λ_0	= limiting conductance for $c \to 0$
σ, σ_c	= specific conductance [ohm^{-1} cm^{-1}]
σ_L	= specific conductance of the solvent
n_e	= electrochemical valence of electrolyte $[K^{z+}_{\nu+}A^{z-}_{\nu-}]$ $n_e = \nu_+ z_+ = \nu_- z_-$
R, R_L	= resistance [ohm] also hydrodynamic ionic radius R, R_∞, R^+, R^- [cm]
A	= cell constant [cm^{-1}] also coefficient of the Fuoss-Onsager theory
$\vec{P}(\vec{r})$	= establishment of a point by the vector $\vec{r}$
n_i, n_ν, n_+, *etc.*	= analytical concentration [ions/ml] of i ions ν ions, cations, *etc.*
$n_{ij}(\vec{r_1}, \vec{r_{21}})$	= density of j ions at a distance $\vec{r_{21}}$ from an i ion at $\vec{P}(\vec{r_1})$
D	= relative dielectric constant
η	= viscosity [poise]
$n^0_{ij}(r)$	= density of j ions at a distance r from an i ion in spherically symmetrical non-disturbed equilibrium distribution
z_i, z_ν, z_+, *etc.*	= valence of an i ion, an ν ion, a cation, *etc.*
$f_{ij}(\vec{r_1}, \vec{r_{21}}), f^0_{ij}(r)$	= distribution functions; for definition, see eq. (2) and eq. (3).
$\psi_i(\vec{r_1}, \vec{r_{21}}), \psi'_i(\vec{r_1}, \vec{r_{21}}), \psi^0_i(r)$	= electrostatic potentials
ρ, ρ_i	= charge density
e_0	= electronic charge = 4.80223×10^{-10} e.s.u.
k	= Boltzmann constant = 1.38026×10^{-16} erg deg^{-1} molecule^{-1}
N_ν	= occupancy in the Wicke-Eigen and Falkenhagen-Kelbg theories
μ, μ_i, μ_0	= chemical potential
f_i, γ_i, y_i	= activity coefficients
$f_\pm$, $\gamma_\pm$, $y_\pm$	= mean activity coefficients of electrolytes
x	= mole fraction
m	= molality [mole/1000 g of solvent]
c	= molarity [mole/l]
τ	= for definition cf. eq. (10)
$\varkappa$	= parameter in the Debye-Hückel theory, for definition see eq. (11)
b	= parameter of the Bjerrum theory, for definition see eq. (10)
a, a_i, a_J, a_K, *etc.*	= ionic radii (distance parameters)
Λ_I	= relaxation term
Λ_{II}	= electrophoretic term

(This footnote is continued on opposite page)

The theory of electrolytes is primarily concerned with completely dissociated electrolytes. The results of this treatment are then extended to account for the behavior of the free ions of associating ionophores or ionogens.

2. Measurement of the Concentration-Dependence of the Conductance of Electrolytes

The determination of the properties of electrolytes from the dependence of their electric conductance on concentration demands very accurate experimental data. To obtain an accuracy of 0.01 % in the determination of the limiting conductance Λ_0 by extrapolation, the measurement of the individual Λ values and of the corresponding concentrations in dilute solutions (10^{-4} to 10^{-2} mole/l) must be equally accurate. Association constants $K_A \geqslant 10$ can be determined with this accuracy; values found for association constants much lower than this are not meaningful, owing to the limits of accuracy of K_A.

An accuracy of 0.01 % for the individual values can be achieved even in nonaqueous solvents. The prime requirement in this case is that the solvents used should be so pure that no correction of the electrolytic conductance is necessary. This is often possible only if all preparations (chemical purification, distillation) of the solvent and of the electrolyte, as well as the measurements themselves, are carried out under a carefully purified protective gas.

The concentration-dependence of the electrolytic conductance can be determined by three methods:

1. independent preparation of each sample and subsequent introduction into the measuring apparatus,

2. stepwise dilution of a concentrated electrolyte solution in the apparatus shown in Fig. 1,

3. stepwise concentration, starting with the pure solvent, by addition of the pure electrolyte or of a concentrated stock solution in the apparatus shown in Fig. 2.

In our experience, the stepwise concentration method (Fig. 2) has certain advantages over the dilution method. The sample used in the measurement of the conductance of the solvent is that used for the preparation of all the solutions. The quantity of solvent is small, however large the number of concentration steps, and the accuracy of measurement, which is to be identified with the accuracy with which the concentration of the most dilute solution is known, is higher than in a dilution method, in which the error increases from the most concentrated to the most dilute solution. (For other measuring arrangements of this type see [5,6].)

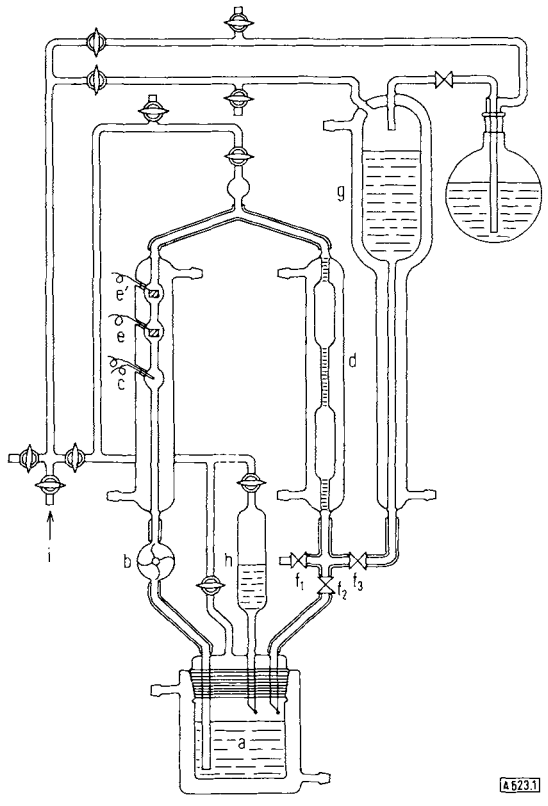

Fig. 1. Recirculation apparatus for the determination of the concentration dependence of electrolytic conductance under a protective gas by the stepwise dilution method [7]:

a electrolyte container; b recirculating pump; c thermistor; e,e' large-surface cylindrical electrodes in the measuring segment; d burette (a known quantity of electrolyte solution is run out through the valve f_1 with f_2 closed, and is replaced by pure solvent from the solvent reservoir g through the valve f_3); h concentrated stock solution; i protective gas inlet. All tubes are thermostatted or insulated.

To achieve an accuracy of 0.01 %, the temperature in the measuring cell must be kept constant to within about 0.001 °C. The resistance is measured by a bridge arrangement (for a discussion of the effects of the measuring cell, the measuring bridge, and the recorded reading in precision measurements cf. [3,7,8]; for the phase jump method cf. [6,9]). The electrolytic conductor obeys Ohm's law.

The cell constant ($A[\mathrm{cm}^{-1}] = l/q$) of the measuring cell is the ratio of the length (l) of the electrolytic conductor to its cross section (q). It is generally found with the aid of the equation $A = R \cdot \sigma_c$ by measurement of the resistance (R) of an electrolyte whose specific conductance $\sigma_c = \Lambda_i \cdot c \cdot n_e 10^{-3}$ is known, and can then be used to determine the specific

S, E', J_1, J_2, L, A, F = coefficients of the Fuoss-Onsager theory
$\mathfrak{F}$ = Faraday constant = 96493 abs. Coul/equiv.
C = velocity of light = 2.997902×10^{10} cm sec^{-1}
$v_{ij}(\vec{r}_1, \vec{r}_{21})$ = velocity of the j ions at a distance $\vec{r}_{21}$ from an i ion at $P(\vec{r}_1)$
α = degree of dissociation
$(1-\alpha)$ = degree of association
w_{ij} = number of j ions at a distance between r and $r + \Delta r$ from an i ion
l_0, l_{0j}, l_{0+} = ion mobilities [ohm^{-1} cm^2 equiv^{-1}]
$\mathfrak{A}$ = matrix of the A_{ik}, cf. Fig. 7
$\vec{X}$ = vector (X_1, X_2, X_3), cf. Fig. 7
$\vec{B}$ = vector (B_1, B_2, B_3), cf. Fig. 7
N = in Fig. 7, number of pairs of values (c_i, Λ_i), otherwise Avogadro's number = 6.0238×10^{23} molecules mole^{-1}

[3] Cf., *e.g.*, *R. A. Robinson* and *R. H. Stokes*: Electrolyte Solutions. 2nd Edit., Butterworths, London 1959.

[4] *J. Barthel, M. Knerr, G. Schwitzgebel,* and *R. Wachter*, unpublished.

[5] *J. L. Hawes* and *R. L. Kay*, J. physic. Chem. *69*, 2420 (1965).

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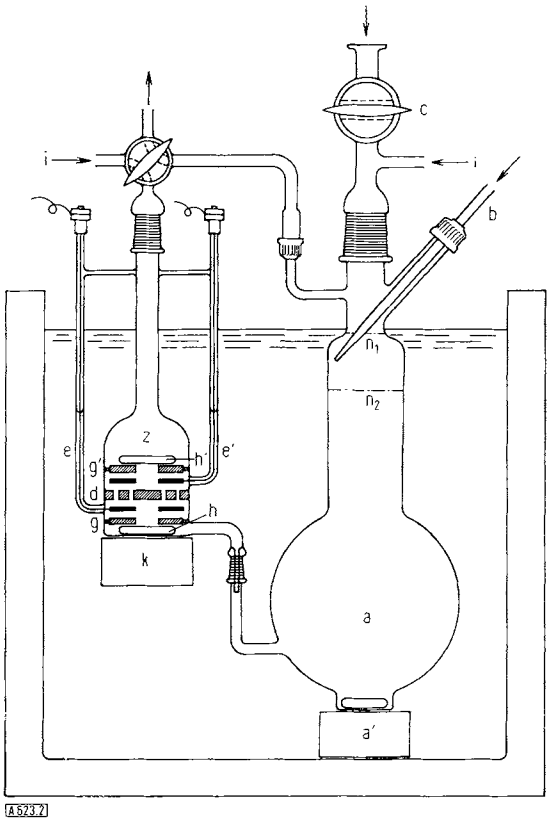

A 623.2

Fig. 2. Apparatus for the determination of the concentration dependence of electrolytic conductance under a protective gas by the method of stepwise increase of concentration [4]:

a electrolyte container and mixing vessel with stirrer; a' stirrer motor; z measuring cell with large-surface annular electrodes e,e' facing narrow conduction paths (capillary ring d); g,g' glass rings to protect the electrodes; h,h' stirrers; k stirrer motor. The mixing vessel contains the solution up to the level n_1, and the measuring cell is filled (new level n_2 in a) and emptied by inert gas pressure. A stock solution may be introduced into b from a weighing burette (tip of the burette shown), or the electrolyte may be introduced through the cap c; i protective gas inlet.

conductance σ_c or the equivalent conductance Λ_c of any electrolyte solution from resistance measurements. When the solvent used is not completely pure, the resistance value R_{exp} found for the solution must be corrected by means of the formula $1/R = 1/R_{exp} - 1/R_L$, where R_L is the resistance found for the solvent used. This correction allows only for additivity of the conductance values, and its validity is therefore often doubtful (cf. Section 7.4).

Since conductance measurements on electrolyte solutions are generally referred to standard KCl solutions, it is necessary to ensure that the accuracy of these with respect to the cell constant is compatible with the desired accuracy in Λ_c. If the usual standard solutions[18] (1 N, 0.1 N, 0.01 N KCl) cannot be used because their electrolyte concentration is too high, it is advantageous to use aqueous KCl solutions having $c < 0.01$ mole/l, which satisfy the equation

$$\Lambda_c = 149.93 - 94.65c^{1/2} + 58.74c \log c + 198.46c \qquad (1)$$

with an accuracy of 0.01 %[10]. The cell constant should be independent of concentration in the range in which measurements are carried out.

[10] *J. E. Lind, J. J. Zwolenik*, and *R. M. Fuoss*, J. Amer. Chem. Soc. *81*, 1557 (1959).

3. Distribution Functions

The theory of electrolytes is built up around the distribution functions of the ions. Electrolytes in solution give ions of the types 1,2,....*i*,*j*,...*m* in the concentrations $n_1, n_2, \ldots n_i, n_j, \ldots n_m$ ions/ml. The distribution of the ions in the solution depends on the forces acting between all the particles, ions and solvent molecules. External forces are also involved in the description of transport properties. The distribution of ions is described by distribution functions[11] (cf. also [2, 17, 18]).

$$f_{ij}(\vec{r}_1, \vec{r}_{21}) = n_i(\vec{r}_1) n_{ij}(\vec{r}_1, \vec{r}_{21}) = n_j(\vec{r}_2) n_{ji}(\vec{r}_2, \vec{r}_{12}) = f_{ji}(\vec{r}_2, \vec{r}_{12}) \qquad (2)$$

In this equation, $n_{ij}(\vec{r}_1, \vec{r}_{21})$ represents the density of *j* ions [ions/ml] at a distance $\vec{r}_{21}$ from an *i* ion at $P_1(\vec{r}_1)$ (cf. caption to Fig. 3).

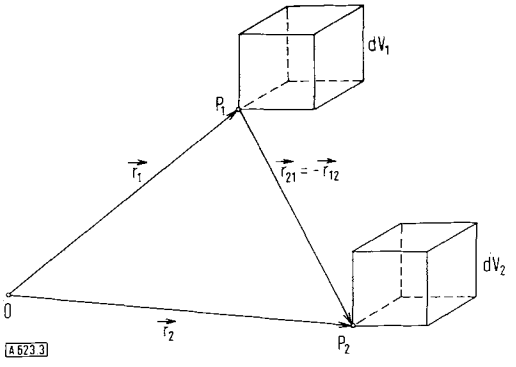

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Fig. 3. Derivation of the distribution function eq. (2).
To find the ion distribution, let an observer at a point 0 record the population of *i* ions in a volume element dV_1 and the population of *j* ions in a volume element dV_2 over a period Δt. The two volume elements with their solvent-permeable and ion-permeable walls are immovably fixed in relation to the observer at the positions $P_1(\vec{r}_1)$ and $P_2(\vec{r}_2)$ in the solution. The observer notes a time Δt_i for the residence of an *i* ion in dV_1. This is proportional to the particle density n_i, the size of the volume element dV_1, and the observation period Δt, *i.e.* $\Delta t_i = \alpha n_i\, dV_1\, \Delta t$ (where α is the proportionality factor). Similarly, he records a time $\Delta t_j = \alpha n_j\, dV_2\, \Delta t$ for the residence of a *j* ion in dV_2. He also determines a time $\Delta t_{ij} = \alpha n_{ij}\, dV_2\, \Delta t_i$ for the presence of a *j* ion in dV_2 with the condition that there is also an *i* ion in dV_1, and finally a time $\Delta t_{ji} = \alpha n_{ji}\, dV_1\, \Delta t_j$. Since $\Delta t_{ij} = \Delta t_{ji}$, we obtain eq. (2) (cf. also [2]).

As is confirmed *e.g.* by the behavior of KCl in aqueous solution at low concentrations, a small group of ionophores exists in solution almost entirely as free cations and anions, and can therefore be used for the direct experimental investigation of the properties of an electrolyte that is theoretically completely dissociated.

In the absence of external forces, the ions assume a spherically symmetrical equilibrium distribution, in which n_i is independent of position P_1 and $\vec{r}_{12} = r$, and which is described by the function

$$f_{ij}^0(r) = n_i\, n_{ij}^0(r) = n_j\, n_{ji}^0(r) = f_{ji}^0(r) \qquad (3)$$

The ions exert long-range Coulomb forces on one another, which are stronger than the induction and

[11] *L. Onsager*, Physik. Z. *28*, 277 (1927).

dispersion forces acting between all the particles in the solution. There is as yet no theory that takes into account all intermolecular forces.

In the classical model of an electrolyte solution, the ions (valences $z_1 \ldots . z_m$) are represented as charges in a homogeneous and isotropic solvent (dielectric constant D, viscosity η). If $\psi_i^0(r)$ is the electric potential at a distance r from an ion i in the absence of external forces, and if it is assumed that only Coulomb forces act between the ions, the position-dependent concentration of j ions in the vicinity of the i ions is obtained as a result of a Boltzmann distribution in the form of eq. (4).

$$f_{ij}^0 = n_i n_j \exp\left[\frac{e_0 z_j \psi_i^0(r)}{kT}\right] = n_i n_j \sum_{\nu=0}^{\infty} \frac{1}{\nu!}\left[\frac{e_0 z_j \psi_i^0(r)}{kT}\right]^\nu \quad (4)$$

In the Debye-Hückel theory[12], the expansion of the series is stopped after the linear term

$$f_{ij}^0 = n_i n_j \left[1 - \frac{e_0 z_j \psi_i^0(r)}{kT}\right] \quad (5)$$

For symmetrical electrolytes, the further expanded distribution function (6) leads to the same Poisson

$$f_{ij}^0 = n_i n_j \left[1 - \frac{e_0 z_j \psi_i^0(r)}{kT} + \frac{1}{2}\left(\frac{e_0 z_j \psi_i^0(r)}{kT}\right)^2\right] \quad (6)$$

equation (8) as equation (5), since the charge density

$$\rho_i = \frac{1}{n_i} \sum_{j=1}^{m} f_{ij}^0 e_0 z_j$$

for electrolytes of this type contains no powers with even exponents.

Higher powers in the expansion (4) were taken into account, though only for a binary electrolyte in solution, in the work of *Gronwall, Sandved*, and *La Mer*[13] for symmetrical electrolytes up to $\nu = 5$ and of *La Mer, Gronwall*, and *Greiff*[14] for unsymmetrical electrolytes up to $\nu = 3$.

According to *Wicke* and *Eigen*[15], contrary to the Boltzmann distribution, the volume occupied by the ions should restrict the sites available for the ν ions in a unit volume to a number N_ν. For this case, *Falkenhagen* and *Kelbg*[16] give a distribution function

$$f_{ij}^0 = n_i n_j \frac{\exp\left[\frac{e_0 z_j \psi_i^0(r)}{kT}\right]}{1 + \sum_{\nu=1}^{m} \frac{n_\nu}{N_\nu}\left[\exp\left(\frac{e_0 z_\nu \psi_i^0(r)}{kT}\right) - 1\right]} \quad (7)$$

which changes into the form previously given by *Eigen* and *Wicke* for $m = 2$ and equal occupancies for the cation and the anion, and into equation (4) for infinitely large occupancies.

Each of the electrostatic potentials $\psi_i^0(r)$ of equations (4) to (7) satisfies a Poisson equation

$$\Delta\psi_i^0(r) = -\frac{4\pi}{D}\cdot\rho_i = -\frac{4\pi}{Dn_i} \sum_{j=1}^{m} f_{ij}^0 e_0 z_j \quad (8)$$

and can be determined from this and the boundary conditions of the problem.

If the charge on the ions in solution is assumed to be built up from zero to its full value, $\psi_i^0(r)$ can be used to find the activity coefficients f_i, γ_i, or y_i of the species i (solvent index $i = 0$), which explain the thermodynamic properties of the electrolyte solution in the range of validity of the distribution function in question (cf. *e.g.*[1,17,18]) according to

$$\mu_i = \mu_i^{0(x)} + RT \ln x_i f_i = \mu_i^{0(m)} + RT \ln m_i \gamma_i = \mu_i^{0(c)} + RT \ln y_i c_i$$
$$\mu_i^{0(x)} = \lim_{x_0 \to 1} [\mu_i - RT \ln x_i]\,; \quad \lim_{x_0 \to 1} f_i = 1 \quad (9)$$

The mean activity coefficient $y_\pm$ that occurs in the conductance equation of associating ionophores and ionogens is discussed in connection with this equation. For point ions (ions with zero radius), the activity coefficient of a binary electrolyte in dilute solution, which is the one encountered most frequently, is found from the distribution (5) to be

$$-\ln y_\pm = \tau = \frac{1}{2} ba\varkappa\,, \quad b = \frac{|z_+ z_-| e_0^2}{aD\,kT} \quad (10)$$

$$\varkappa^2 = \frac{4\pi e_0^2 Nc}{1000\,D\,kT}(\nu_+ z_+^2 + \nu_- z_-^2) \quad (11)$$

In this article we give only the basic principles that lead to conductance equations in the classical theory of electrolytes. For the calculation of the thermodynamic properties of electrolyte solutions by statistical-mechanical methods, the reader is referred to recent summaries[20,21].

4. The Conductance of Completely Dissociated Electrolytes

With the exception of a limiting law, conductance equations have been derived only for solutions containing a single binary electrolyte. In these equations the specific conductance σ [ohm^{-1} cm^{-1}], or more frequently the molar conductance $\Lambda = 1000\ \sigma/c$ [ohm^{-1}cm^2 mole^{-1}] or the equivalent conductivity

[12] *P. Debye* and *E. Hückel*, Physik. Z. *24*, 185 (1923).

[13] *T. H. Gronwall, V. K. La Mer*, and *K. Sandved*, Physik. Z. *29*, 358 (1928).

[14] *V. K. La Mer, T. H. Gronwall*, and *L. J. Greiff*, J. physic. Chem. *35*, 2245 (1931).

[15] *E. Wicke* and *M. Eigen*, Z. Elektrochem., Ber. Bunsenges. physik. Chem. *56*, 551 (1952); *57*, 319 (1953); Z. Naturforsch. *8a*, 161 (1953); *M. Eigen* and *E. Wicke*, J. physic. Chem. *58*, 702 (1954).

[16] *H. Falkenhagen* and *G. Kelbg*, Ann. Physik (6) *11*, 60 (1952); *14*, 393 (1954).

[17] *H. Falkenhagen*: Elektrolyte. 2nd Edit., S. Hirzel Verlag, Leipzig 1953.

[18] *H. S. Harned* and *B. B. Owen*: The Physical Chemistry of Electrolytic Solutions. 3rd Edit. Reinhold Publ. Corp., New York 1958.

[19] *B. E. Conway* and *R. G. Barradas*: Chemical Physics of Ionic Solutions. Wiley, New York 1966.

[20] *J. C. Poirier* in [19], p. 9.

[21] *G. Kelbg* in [19], p. 29.

$\Lambda_c = \Lambda/n_e$ [ohm^{-1} cm^2 equiv^{-1}] is expressed as a function of the electrolyte concentration c.

$$\Lambda_c = f\,[c;\,\Lambda_0,a,D,\eta,T]$$

In addition to c, this function contains the limiting values ($c \rightarrow 0$) of the equivalent conductance Λ_0, a parameter a that is generally taken to represent the ionic radius, and the viscosity η, dielectric constant D, and temperature T of the solution. The influence of the frequency and strength of the applied field are not shown in this equation. The dependence on c is frequently written as a dependence on the parameter $\varkappa$ (cf. eq. (11)) of the Debye-Hückel theory.

No experimental confirmation can be found for an equation $\Lambda = \Lambda_0$, such as that on which Ostwald's Law for ionogens is based. The main inhibiting effects are defined by a relaxation term Λ_I, resulting from the unsymmetrical charge distribution about a migrating ion due to the external field, and an electrophoretic term Λ_{II}, due to the migration of this ion in relation to the solvent, which is displaced in countercurrent by the ion cloud.

$$\Lambda_c = \Lambda_0 - \Lambda_I\,(c;\,\Lambda_0,a,D,T) - \Lambda_{II}\,(c;\,a,D,\eta,T) \tag{12}$$

In the form

$$\Lambda_c = \Lambda_0 - Sc^{1/2} + E'c\ln c + J_1c - J_2c^{3/2} \tag{13}$$

which was first established in the Fuoss-Onsager theory [23,24], all the coefficients S, E', J_1, and J_2 contain components due to both effects.

The disturbed ion distribution due to the external field is described by the unsymmetrical function

$$f_{ij}(\vec{r}_1,\vec{r}_{21}) = f_{ij}^0(r) + f'_{ij}(\vec{r}_1,\vec{r}_{21}) \tag{14}$$

to which is assigned, for pure Coulomb interaction between the ions, a potential

$$\psi_i = \psi_i^0(r) + \psi'_i(\vec{r}_1,\vec{r}_{21}) \tag{15}$$

in accordance with eq. (8) and

$$\Delta\psi'_i = -\frac{4\pi}{Dn_i}\sum_{j=1}^{m} f'_{ij}e_0z_j \tag{16}$$

The continuity equation for the stationary case

$$\mathrm{div}_2(f_{ij}\vec{v}_{ij}) + \mathrm{div}_1(f_{ji}\vec{v}_{ji}) = 0 \tag{17}$$

where the velocities $\vec{v}_{ij}(\vec{r}_1,\vec{r}_{21})$ and $\vec{v}_{ji}(\vec{r}_2,\vec{r}_{12})$ ($\vec{v}_{ij}$ = velocity of a j ion out of the vicinity of the i ion) are related to the forces responsible for the unsymmetrical distribution (cf. [18]), and *via* these to the potential $\psi'_i(\vec{r}_1,\vec{r}_{21})$, can be used together with the Navier-Stokes equation for the movement of spherical ions to calculate the components [25,27] Λ_I and Λ_{II} or the coefficients [2,23,33] S, E', J_1, and J_2.

The information that can be provided by a conductance equation therefore depends

1. on the form of the ion distribution f_{ij}^0 on which it is based,

2. on the form of the boundary conditions of the problem,

3. on the approximations used in the calculation of ψ'_i, and

4. on the nature of the factors affecting ion mobility that are also taken into account.

The limiting equation (*Onsager* [11,22], *Debye* and *Falkenhagen* [26]) with

$$\Lambda_I = \frac{|z_+z_-|e_0^2}{3\,D\,kT}\,\frac{q}{1+\sqrt{q}}\,\Lambda_0\,\varkappa \tag{18}$$

$$\Lambda_{II} = (|z_+| + |z_-|)\,\frac{\mathfrak{F}\,e_0\,10^8}{6\pi\eta C}\,\varkappa \tag{19}$$

$$q = \frac{|z_+z_-|}{|z_+| + |z_-|}\,\frac{l_{0+} + l_{0-}}{|z_+|l_{0-} + |z_-|l_{0+}} \tag{20}$$

is the simplest solution of the conductance problem for point ions (ionic radius $a = 0$) obtained with the distribution (5).

Consideration of (11) leads directly to a form

$$\Lambda = \Lambda_0 - S_{(\Lambda)}\,c^{1/2} \tag{21}$$

whose coefficient $S_{(\Lambda)}$ has the value S given in Table 1, for 1,1 electrolytes since $q = {}^1/_2$.

With $a \neq 0$, *Onsager* and *Fuoss* [29] obtained an electrophoretic term Λ_{II} which, for symmetrical electrolytes, contains the factor $(1 + \varkappa a)^{-1}$ that is not present in eq. (19). Also for $a \neq 0$, *Kaneko* [30] gives a relaxation term Λ_I that also contains the factor $(1+\varkappa a)^{-1}$ not present in (18) on linear approximation of the exponential function $\exp[(1-\sqrt{q})\varkappa a]$ occurring in the Kaneko expression. This result explains an equation proposed by *Robinson* and *Stokes* [3,31]

$$\Lambda = \Lambda_0 - S_{(\Lambda)}\,(1 + \varkappa a)^{-1}\,c^{1/2} \tag{22}$$

The validity of the limiting law is often confined to such low ion concentrations in nonaqueous solutions that it is outside the range of accurate measurement. The experimental data can be reproduced over a wider range with the aid of eq. (22).

Conductance equations in the complete form (13) or equations of similar and corresponding content in the form (12) have been obtained on revision of the

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[23] *R. M. Fuoss* and *L. Onsager*, J. physic. Chem. *61*, 668 (1957).

[24] *R. M. Fuoss* and *L. Onsager*, Proc. nat. Acad. Sci. U.S.A. *41*, 274, 1010 (1955).

[25] *H. Falkenhagen* and *G. Kelbg* in *J. O'M. Bockris*: Modern Aspect of Electrochemistry. No. 2, Butterworths, London 1959, p. 1.

[26] *P. Debye* and *H. Falkenhagen*, Physik. Z. *29*, 401 (1928).

[27] *H. Falkenhagen* and *G. Kelbg* in [28], p. 109.

[28] *B. Pesce*: Electrolytes. Pergamon Press, Oxford 1962.

[29] *L. Onsager* and *R. M. Fuoss*, J. physic. Chem. *36*, 2689 (1932).

[30] *S. Kaneko*, J. chem. Soc. Japan *56*, 793, 1320 (1935).

[31] *R. A. Robinson* and *R. H. Stokes*, J. Amer. chem. Soc. *76*, 1991 (1954).

Table 1. Coefficients [*] of the conductance equation

$\Lambda = \Lambda_0 - Sc^{1/2} + E'c \ln c + J_1 c - J_2 c^{3/2}$

for 1,1 electrolytes (eq. (13)). For the meanings of b and $\varkappa$, see equations (10) and (11).

Fuoss-Onsager equation: coefficients S_1, S_2, E', J_1 according to [2]; J_2 according to [33].

Pitts equation: coefficients according to [38].

	Onsager	*Fuoss-Onsager*	*Pitts*	*Falkenhagen-Kremp*
S	$S = S_1\Lambda_0 + S_2$; $S_1 = \frac{e_0^2\varkappa}{3DkT(2+\sqrt{2})c^{1/2}}$; $S_2 = \frac{\mathfrak{F}e_0\varkappa\cdot 10^8}{3\pi\eta Cc^{1/2}} \approx \frac{e_0^2 N\varkappa\, 10^{-11}}{27\pi\eta_i c^{1/2}}$			
E'	0	$E' = E_1'\Lambda_0 - E_2'$; $E_1' = \frac{(\varkappa ab)^2}{24c}$; $E_2' = S_2\cdot\frac{\varkappa ab}{16c^{1/2}}$		$E' = E_1'\Lambda_0$
J_1	0	$J_1 = \sigma_1\Lambda_0 + \sigma_2$		
		$\sigma_1 = \frac{(\varkappa ab)^2}{12c}\left[-\frac{1}{b^3}+\frac{2}{b^2}+\frac{2}{b}+0.9074+\ln\frac{\varkappa a}{c^{1/2}}\right]$	$\sigma_1 = \frac{(\varkappa ab)^2}{12c}\left[\frac{2}{b}+1.7718+\ln\frac{\varkappa a}{c^{1/2}}\right]$	$\sigma_1 = \frac{(\varkappa ab)^2}{12c}\left[-\frac{1}{b^3}+\frac{1}{b^2}+\frac{9}{4b}+0.96+\ln\frac{\varkappa a}{c^{1/2}}\right]$
		$\sigma_2 = S_2\left[S_1+\frac{11\varkappa a}{12c^{1/2}}-\frac{\varkappa ab}{8c^{1/2}}(1.0170+\ln\frac{\varkappa a}{c^{1/2}})\right]$	$\sigma_2 = S_2\cdot\frac{\varkappa a}{c^{1/2}}\left[1+\frac{b}{8}(0.01387-\ln\frac{\varkappa a}{c^{1/2}})\right]$	$\sigma_2 = S_2\cdot\frac{\varkappa a}{c^{1/2}}$
J_2	0	$J_2 = \sigma_3\Lambda_0 + \sigma_4$		0
		$\sigma_3 = \frac{\sqrt{2}}{24}\frac{(\varkappa ab)^3}{c^{3/2}}\left[\frac{1}{b^3}+\frac{2}{b^2}-\frac{1.0776}{b}\right]$	$\sigma_3 = \frac{(\varkappa ab)^3}{6c^{3/2}}\left[\frac{1.2929}{b^2}+\frac{1.5732}{b}\right]$	
		$\sigma_4 = S_2\frac{(\varkappa a)^2}{c}$	$\sigma_4 = S_2\frac{(\varkappa a)^2}{c}(1+0.07828\cdot b)$	

[*] The value of the Faraday constant $\mathfrak{F}$ in absolute coulomb/equivalent and that of the electronic change in esu must be used in the equations of the coefficients in this Table, in agreement with the work of *Fuoss* and *Onsager*. The equations can also be applied to symmetrical electrolytes having ions of higher valences by taking the magnitude of the charge into account in the coefficients.

approximations for the relaxation term and the electrophoretic term, taking into account extended distribution functions and the formulation of appropriate boundary conditions [*].

The first equation (13), which was proposed by *Fuoss* and *Onsager* [23], is based on the distribution (6); the boundary conditions are taken as

$$\left(\frac{\delta\psi_i'}{\delta r}\right)_\infty = 0\ ;\ \psi_i'(a-0) = \psi_i'(a+0)\ ;\ \left(\frac{\delta\psi_i'}{\delta r}\right)_{a-0} = \left(\frac{\delta\psi_i'}{\delta r}\right)_{a+0}; \tag{23a}$$

$$([f_{ij}\vec{v}_{ij} - f_{ji}\vec{v}_{ji}]\vec{r})_{r=a} = 0 \tag{23b}$$

The conditions (23a) describe the behavior of the disturbing potential at the field boundaries, while (23b) states that the ions, as rigid spheres, move with only a tangential velocity component on meeting. The terms S, E', J_1, and J_2 contain two components: both the contributions of the electrophoretic effect and the evaluation of the relaxation term by an approximation that takes the velocity field completely into account (in the limiting law, only the component in the field direction is considered). Though it does not include all the terms that are linear in the concentration dependence [23,25], this equation [2] takes into account a conductance-increasing kinetic effect that results in the accumulation of ions behind the migrating ion. A viscosity component to allow for the change in the viscosity of the solution on introduction of the electrolyte can be taken into account by means of the Einstein relation [32]. Λ in eq. (13) is then replaced by the quantity $\Lambda_\eta = \Lambda(1 + Fc)$, where $F = 6.308\times 10^{21} R^3$ (R = hydrodynamic radius of the ion), or else eq. (13) takes the form [48]:

$$\Lambda = \Lambda_0 - Sc^{1/2} + E'c \ln c + J_1 c - Fc\Lambda_0 + O(c^{3/2}) \tag{24}$$

A term J_2 for the Fuoss-Onsager theory is given by *Fuoss* and *Berns* [33] and in a revised form by *Justice* [33a]. However, this term is used by *Fuoss et al.* only in rare cases in the evaluation of experimental data, and in the conductance theory it is discussed only in the residual term $O(c^{3/2})$ of (13) or (24) in view of the incompleteness of J_1 [34]. *Fuoss, Onsager,* and *Skinner* [35] have reported a new equation resulting from further revision [36] of the fundamental principles; this equation will be discussed in Section 5.

The extended distribution function (4) for symmetrical electrolytes [13] forms the basis of the conductance equation proposed by *Pitts* [37]. Here the boundary conditions are postulated in a different manner and additional effects are not taken into account. The equation, which has a claimed validity range of up to 0.1 N for 1,1 electrolytes in aqueous solution, was deduced as a complex expression with the aid of tabulated functions, but was modified to the form (13) by *Fernández-Prini* and *Prue* [38].

[*] Equations in this section of the present article are formulated so as to be valid for 1,1 electrolytes.

[32] *A. Einstein*, Ann. Physik *19*, 289 (1906); *34*, 591 (1911).

[33] *D. S. Berns* and *R. M. Fuoss*, J. Amer. chem. Soc. *82*, 5585 (1960).

[33a] *J. C. Justice*, Thèse *1967*, N° d'enregistrement au C.N.R.S. A.O. 1558.

[34] *R. M. Fuoss* in [19], p. 463.

[35] *R. M. Fuoss, L. Onsager,* and *J. F. Skinner*, J. physic. Chem. *69*, 2581 (1965).

[36] *R. M. Fuoss* and *L. Onsager*, J. physic. Chem. *66*, 1722 (1962); *67*, 621, 628 (1963); *68*, 1 (1964).

[37] *E. Pitts*, Proc. Roy. Soc. (London) *217A*, 43 (1953).

[38] *R. Fernández-Prini* and *J. E. Prue*, Z. physik. Chem. *228*, 373 (1965).

Falkenhagen, Leist, and *Kelbg*[39] give a conductance equation based on the Eigen-Wicke distribution function[15], in which an a parameter is also taken into account in the boundary conditions. *Leist*[40] attacked the problem again, using the generalized distribution (7) given by *Falkenhagen* and *Kelbg*, and with a viscosity correction for 1,1 electrolytes.

Kelbg[41] introduced the boundary condition (23) in the derivation of another conductance equation (see also[25,27]). The equations are obtained in the form (12). The Kelbg equation for symmetrical electrolytes[25] then contains

$$\Lambda_I = \frac{e_0^2}{6\,D\,kT} \cdot \frac{(2-\sqrt{2})\,\Lambda_0\,\varkappa}{(1+\varkappa a)\,(1+\frac{1}{2}\sqrt{2}\,\varkappa a+\frac{1}{6}\,\varkappa^2 a^2)} \qquad (25)$$

$$\Lambda_{II} = \frac{e_0^2\,N\cdot 10^{-11}}{27\,\pi\eta} \cdot \frac{\varkappa}{1+\varkappa a}$$

(Compare with the equation given by *Fuoss* and *Onsager*, see[25]).

In all extensions of the Onsager limiting law, the short-range forces in the neighborhood of an ion are taken into account by the a parameter. The stipulation of a rigid sphere by means of the boundary conditions corresponds to the simplest form of a repulsion potential[34]. The importance of the distribution function f_{ij}^0 becomes clear in the new conductance equation given by *Fuoss, Onsager,* and *Skinner* (cf. Section 5).

Only a few experimental data have been evaluated by several equations. In these cases, the experimental values for aqueous solutions with $c < 0.02$ mole/l can be reproduced equally well by the Fuoss-Onsager, Pitts, Leist, and Kelbg equations, though with different a values[25,42]. The viscosity correction of the Leist equation permits the description of the experimental data up to the saturation range of 1,1 electrolytes[40]. By far the majority of the experimental results were evaluated with the Fuoss-Onsager equation. This equation has also been repeatedly confirmed by experimental results in nonaqueous solutions.

Important results of the classical theory of electrolytes are confirmed by a new treatment of the conductance problem, which is based on the statistical-mechanical theory of irreversible processes, and is independent of the basic principles of the foregoing description. The limiting law is confirmed by the theories of *Friedmann*[43], *Falkenhagen* and *Ebeling*[44], and *Résibois et al.*[45]. *Falkenhagen* and *Kremp*[46] give a new conductance equation of the form (13). The coefficients of this equation are shown in Table 1; the electrophoretic term S_2 is written in a form of the classical limiting law that differs from the form given in the original article.

The conductance equations cannot be easily applied to solutions containing more than two ionic species[17,29,47]. Though the electrophoretic term Λ_{II} for each individual ion in the limiting law for electrolyte mixtures is independent of the nature of the other ions, the relaxation term Λ_I depends in a complex manner on the nature and concentration of all the ions in the solution.

5. Conductance of Ionogens and Associating Electrolytes

In charge transport, ion pairs formed by symmetrical electrolytes

$$K^+ + A^- \rightleftharpoons [K^+\,A^-]^0 \qquad K_A = \frac{[K^+\,A^-]^0}{[K^+]\,[A^-]} \qquad (26)$$

behave in the same way as the undissociated molecules of ionogens.

$$KA \rightleftharpoons K^+ + A^- \qquad K_D = \frac{[K^+]\,[A^-]}{[KA]} \qquad (27)$$

The association constant K_A of ionophores and the dissociation constant K_D of ionogens are related to the degree of dissociation α [$(1-\alpha)$ is thus the degree of association] by

$$K_A = K_D^{-1} = \frac{(1-\alpha)y_0}{\alpha^2 c y_\pm^2} \qquad (28)$$

where $y_\pm$ is the mean activity coefficient of the dissociated electrolyte; the activity coefficient y_0 of the associate or of the undissociated molecule can generally be taken as equal to unity ($y_0 = 1$).

Only the free ions of ionogens and of associated ionophores contribute to their conductance. Since the concentration of these ions in the solution is $c' = \alpha c$, the conductance equation for electrolytes of this type is

$$\Lambda = \alpha\,[\Lambda_0 - \Lambda_I(c') - \Lambda_{II}(c')] \qquad (29)$$

or

$$\Lambda = \alpha\,[\Lambda_0 - Sc'^{1/2} + E'c'\ln c' + J_1 c' - J_2 c'^{3/2}] \qquad (30)$$

based on eqs. (12) and (13) of Section 4. Eq. (30) can be related to the law of mass action (28), and it then gives the conductance equation reported by *Fuoss*[2,48–50] for associating electrolytes ($J_1 = J$, and J_2 is disregarded).

$$\Lambda = \Lambda_0 - S(\alpha c)^{1/2} + E'\alpha c \ln(\alpha c) + J\alpha c - K_A y_\pm^2\,\Lambda\alpha c + O(c'^{3/2}) \qquad (31)$$

Table 2. Dependence of the association constants on the activity coefficients used [51]. Alkali metal ethoxides in ethanol (25 °C), $10^{-4} < c < 10^{-3}$ mole/l, water content of the ethanol about 0.001 %.

	Λ_0	$J^{(1)}$	$K_A^{(1)}$	$K_A^{(2)}$	$K_A^{(3)}$
$LiOC_2H_5$	39.99	1853	176	181	197
$NaOC_2H_5$	43.35	1397	49	52	58
KOC_2H_5	46.62	1359	36	38	42
$RbOC_2H_5$	47.73	1315	39	43	46
$CsOC_2H_5$	49.47	1241	65	68	74

[39] *H. Falkenhagen, M. Leist,* and *G. Kelbg,* Ann. Physik (6) *11,* 51 (1952).

[40] *M. Leist,* Z. physik. Chem. *205,* 16 (1955).

[41] *G. Kelbg,* Dissertation, Universität Rostock 1954, [25].

[42] *J. E. Prue*: Ionic Equilibria. Pergamon Press, Oxford 1966.

[43] *H. L. Friedmann,* Physica *30,* 509, 537 (1964); J. chem. Physics *42,* 450, 462 (1965); in [22], p. 487.

[44] *H. Falkenhagen* and *W. Ebeling,* Mber. dtsch. Akad. Wiss. Berlin *5,* 615 (1963).

[45] *P. Résibois* and *N. Hasselle-Schuermanns,* J. chem. Physics *43,* 1016 (1965); *H.T. Davies* and *P. Résibois, ibid. 40,* 3276 (1964).

[46] *H. Falkenhagen* and *D. Kremp,* Z. physik. Chem. *230,* 85 (1965); Ann. Physik (7) *14,* 322 (1964).

[47] *H. L. Friedmann,* J. chem. Physics *42,* 462 (1965).

[48] *R. M. Fuoss,* J. Amer. chem. Soc. *81,* 2659 (1959).

[49] *R. M. Fuoss,* J. Amer. chem. Soc. *79,* 3301 (1957).

[50] *R. M. Fuoss,* J. Amer. chem. Soc. *80,* 3163 (1958).

[51] *J. Barthel, G. Schwitzgebel,* and *R. Wachter,* Z. physik. Chem. N. F. *55,* 33 (1967).

The equation for the activity coefficient $y_{\pm}$ depends on the concentration range. It must be remembered in this connection that the association constant depends to a certain extent on the activity coefficient used (Table 2). The constants $K_A^{(1)}$, $K_A^{(2)}$, and $K_A^{(3)}$ are based on

$$-\ln y_{\pm}^{(1)} = \tau = 4.202 \times 10^6 \cdot (DT)^{-3/2} (\alpha c)^{1/2} \quad \text{(cf. (10))} \tag{32}$$

$$-\ln y_{\pm}^{(2)} = \tau(1 + \varkappa a)^{-1} \tag{33}$$

$$-\ln y_{\pm}^{(3)} = \tau(1 + \tau)^{-1} \tag{34) [52, 53]}$$

Eqs. (30) and (31) can be deduced from any conductance equation of the form (13). They were derived and discussed by *Fernández-Prini* and *Prue*[54] for the Pitts equation. An equation of the form (29) was derived by *M. Leist* [40] from her equation for completely dissociated electrolytes and related to the law of mass action using an activity coefficient that takes into account the volume occupied by the ions.

The work involved in the use of the complete equation (31) can be avoided for strongly associated electrolytes and nearly always for ionogens since the concentration of free ions in the solution in these cases is so small that it falls within the range of application of the Onsager limiting law. For incompletely dissociated electrolytes this law is written in the form

$$\Lambda = \alpha\,[\Lambda_0 - S(\alpha c)^{1/2}] \tag{35}$$

or

$$\Lambda = \Lambda_0 - S(\alpha c)^{1/2} - K_A y_{\pm}^2\,\Lambda\alpha c\,; \quad -\ln y_{\pm} = \tau \tag{36}$$

An acceptable guiding figure for the use of these equations is an association constant $K_A = 10^4$ ($K_D = 10^{-4}$) in aqueous solution.

Among the extensions of the Onsager limiting law, the equation given by *Marshall* and *Grunwald*[55] could also be mentioned.

$$\Lambda = \Lambda_0 - \frac{S(\alpha c)^{1/2}}{1 + \tau} - K_A y_{\pm}^2 \Lambda\alpha c\,; \quad -\ln y_{\pm} = \frac{\tau}{(1 + \tau)^{3/2}} \tag{37}$$

Table 3. Comparison of conductance data from various conductance equations (experimental data from [51] and [4]).

	Equation	$CsOC_2H_5/C_2H_5OH$		$LiOC_3H_7/C_3H_7OH$	
		Λ_0	K_A	Λ_0	K_A
Limiting law	(36)	49.47	100	20.54	1238
Marshall and *Grunwald*	(37)	49.51	130	20.53	1275
Fuoss and *Onsager*	(31)	49.47	65	20.39	1090

The Ostwald dilution law $\Lambda = \Lambda_0 - K_A\Lambda\alpha c$ with $\alpha = \Lambda/\Lambda_0$ is nearly always an inadequate approximation [55a].

Under conditions that do not permit the use of the limiting law, most experiments are evaluated with the aid of the Fuoss equation.

The Leist equation, *e.g.* with $a = 1.8$ Å, gave $K_A = 220$ and $\Lambda_0 = 44.8$ for $AgNO_3$ in ethanol in the concentration range $c < 0.6$ mole/l [40]. According to *Parfitt* and *Smith*[56], the values obtained with the aid of the Fuoss-Onsager method ($c < 0.02$ mole/l) are $K_A = 210$, $\Lambda_0 = 44.88$ and, $a_J = 3.85$ Å.

If the dissociation constant K_D of the ionogen and the association constant K_A of the ionophore are introduced into the conductance equations in the same way, *via* the postulated law of mass action, no allowance is made for the essential difference between these two quantities. The dissociation of ionogens results from the breaking of a nonpolar bond, whereas the association of ionophores (and sometimes also ionogens) is a consequence of the distribution of the ions in a given solvent. The ions retain their identity in the associate. The association constant can be calculated from the forces that determine the distribution of the ions.

For oppositely charged ions, the number w_{ij} of j ions at a distance between r and $r + \Delta r$ from an i ion

$$w_{ij} = 4\pi r^2\,\Delta r\,nj \exp\left(-\frac{z_i z_j e_0^2}{DkTr}\right) \tag{38}$$

has a minimum at

$$r = q = -\frac{z_i z_j e_0^2}{2\,D\,kT} \tag{39}$$

This minimum moves toward greater distances r as the dielectric constant of the solvent decreases (Fig. 4). According to *Bjerrum*[57], ions at a distance $r < q$ apart are to be regarded as associated, so that the

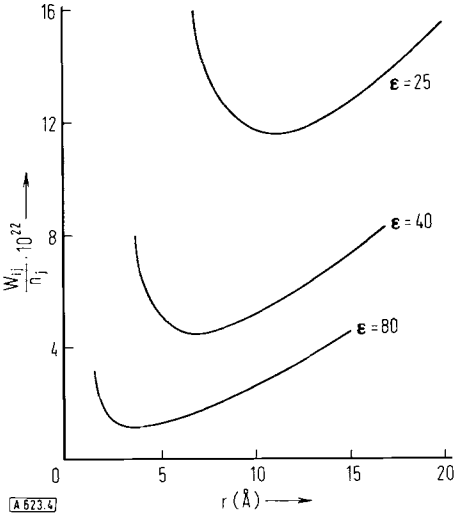

Fig. 4. Number of negative ions in a spherical shell ($\Delta r = 0.1$ Å) at a distance r from a positive central ion in solvents of different dielectric constants ($\varepsilon = D$).

[52] *R. M. Fuoss* and *L. Onsager*, Proc. nat. Acad. Sci. U.S.A. *47*, 818 (1961).

[53] *J. F. Skinner* and *R. M. Fuoss*, J. Amer. chem. Soc. *86*, 3423 (1964).

[54] *R. Fernández-Prini* and *J. E. Prue*, Trans. Faraday Soc. *62*, 1257 (1966).

[55] *H. P. Marshall* and *E. Grunwald*, J. chem. Physics *21*, 2143 (1953).

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[56] *G. D. Parfitt* and *A. L. Smith*, Trans. Faraday Soc. *59*, 257 (1963).

[57] *N. J. Bjerrum*, Kgl. danske Vidensk. Selsk., mat.-fysiske Medd. *7*, No. 9 (1926).

degree of association (1 - α) of a binary electrolyte (for definition of b see equation 10) is

$$(1-\alpha)=\frac{4\pi Nc}{1000}\int_{a}^{q} r^2 \exp(ba/r)\,dr=\frac{4\pi Nca^3b^3}{1000}Q(b) \qquad (40)$$

$$Q(b)=\int_{2}^{b} x^{-4}e^{x}dx$$

The function $Q(b)$ has been tabulated [1,18]. In dilute solutions ($\alpha^2 \approx 1$, $y_{\pm} \approx 1$), it is found that

$$K_A=\frac{1-\alpha}{c}=\frac{4\pi Na^3b^3}{1000}Q(b) \qquad (41)$$

The Bjerrum association theory, in principle, correctly reproduces the change in K_A with the dielectric constant and temperature of the solvent [1,18,58,59] when there are no specific interactions between ions and solvent molecules, but sometimes leads to anomalies with respect to the a parameter. In eq. (40), *Fernández-Prini* and *Prue* [54] take the dielectric saturation in the field of the ions into account by inclusion of a position-dependent dielectric constant in the Boltzmann factor. This leads to much better agreement of the a parameter with the crystallographic radii of the ions in the cases studied by the authors. *Prue* [60] also raises the question of whether the Bjerrum distance q for which the potential energy of the ion pair becomes $2kT$, really takes into account the ions that cannot contribute to the charge transport; as a result of the consideration of this question, he replaces the upper integration limit in eq. (40) by an arbitrary distance d, which is discussed as a further parameter on the basis of the experimental data.

Fuoss [61] interprets the association constant by counting the contact pairs (according to *Prue* [60], $d = 4a/3$):

$$K_A=\frac{4\pi Na^3}{3000}e^{b} \qquad (42)$$

From thermodynamic considerations, *Denison* and *Ramsay* [62] had found $K_A = e^b$, and *Gilkerson* [63] extended this relationship by inclusion of the entropy component from the partition functions of the free and associated ions. A specific solvation in the association process is taken into account in this equation.

With E_s as the molar free energy of solvation (free ions → ion pair), it is found [61,63,64] that

$$K_A = K_0\, e^{b}\, e^{E_s/RT}, \text{ and according to } Fuoss\ K_0=\frac{4\pi Na^3}{3000} \qquad (43)$$

The mass-action constant of the ion-pair formation required in the *ad-hoc* hypothesis is no longer necessary in a new conductance equation given by *Fuoss*, *Onsager*, and *Skinner* [35] for symmetrical ionophores. The retention of the complete Boltzmann factor in the distribution function (4) gives an expression $A(a)$ for the decrease in conductance due to ion contact pairs, which asymptotically approaches the value of K_A given by eq. (42) with decreasing dielectric constant of the solvent.

$$\Lambda=\Lambda_0-Sc^{1/2}+E'c\ln\tau^2+L(a)c-A(a)\Lambda_0 c\,e^{-2\tau} \qquad (44)$$

τ is as defined in eq. (10). Eq. (44) covers the equation (31) given by *Fuoss* [48] in 1959 as a limiting form. For low concentrations, and since $\tau^2 = 6E'_1c$, equation (44) can be converted into eq. (31) with $L+E'\ln 6E'_1 = J$ in the low dielectric constant range. In dilute solutions with higher dielectric constants, on the other hand, $e^{-2\tau} \approx 1$, and collection of the linear terms as $J = L(a)-\Lambda_0A(a)+E'\ln 6E'_1$ leads to the 1957 Fuoss-Onsager equation [23] (13) for unassociated electrolytes [34]. Since it is the only conductance equation for ionophores, eq. (44) is the solution of an old theoretical problem.

In the new statistical treatment of the problem, again without postulation of the law of mass action, *Ebeling*, *Kraeft*, and *Kremp* [65] derived a form

$$K_A=\frac{4\pi Na^3}{1000}\,\frac{e^{b}}{b} \qquad (45)$$

which is obtained by asymptotic expansion of the function $Q(b)$ in eq. (41).

The distance parameter a can be determined in three ways from the conductance data for associating electrolytes: First from the J or L term in accordance with Table 1 as $a_J(a_L)$; secondly from K_A as a_K; and finally, in conjunction with Stokes law, as a_Λ from Λ_0. However, the relationship $a_K = a_J = a_\Lambda$ is generally not satisfied. The observed deviations form the starting point for the discussion of the structure in the immediate neighborhood of the ions.

In solvents having low dielectric constants ($D < 12$), another ion can arrange itself in the field of the ion pair dipole of 1,1 electrolytes to form an ion triplet [66] (cf. also [1,18,67]).

$$[K^+A^-]^0 + K^+ \rightleftharpoons[K'_3] [K^+A^-K^+]^+$$

$$A^- + [K^+A^-]^0 \rightleftharpoons[K''_3] [A^-K^+A^-]^-$$

On the assumption of spherical ions with spherically symmetrical charge distributions, $K'_3 = K''_3 = K_3$. The ion triplets contribute to the charge transport and have a limiting conductance $\Lambda_0^{(3)}$; however, this conductance cannot be directly determined by experiment. No complete theoretical treatment of the conductance problem including ion triplets or even higher associates has yet been carried out. The equation

$$\Lambda=\Lambda_0 K_A^{-1/2}c^{-1/2}+\Lambda_0^{(3)}K_3K_A^{-1/2}c^{1/2} \text{ (see ref. [66])}$$

[58] *R. M. Fuoss*, Chem. Rev. *17*, 27 (1935).

[59] *R. M. Fuoss* and *C. A. Kraus*, J. Amer. chem. Soc. *55*, 1019 (1933).

[60] *J. E. Prue* in [19], p. 163.

[61] *R. M. Fuoss*, J. Amer. chem. Soc. *80*, 5059 (1958).

[62] *J.T. Denison* and *J. B. Ramsay*, J. Amer. chem. Soc. *77*, 2615 (1955).

[63] *W. R. Gilkerson*, J. chem. Physics *25*, 1199 (1956).

[64] *H. R. Sadek* and *R. M. Fuoss*, J. Amer. chem. Soc. *81*, 4507 (1959).

[65] *W. Ebeling*, *W. D. Kraeft*, and *D. Kremp*, J. physik. Chem. *70*, 3338 (1966).

[66] *R. M. Fuoss* and *C. A. Kraus*, J. Amer. chem. Soc. *55*, 2387 (1933).

[67] *A. Gemant*: Ions in Hydrocarbons. Interscience, New York 1962.

as a functional type correctly reproduces the observed concentration dependence. It gives the observed minimum of Λ and its displacement with the dielectric constant of the solvent. K_A and K_3 can be determined from the position of the minimum and an assumption [18] regarding $\Lambda_0^{(3)}$, *e.g.* $\Lambda_0:\Lambda_0^{(3)} = 1:3$.

6. Evaluation of the Experimental Data

6.1. Graphic Methods

For completely dissociated electrolytes, the values of Λ_0 and J_1 are obtained from a plot of

$$\Lambda = \Lambda_0 - Sc^{1/2} + Ec \log c + J_1 c\,; \quad E = 0.4343\,E' \tag{46}$$

An approximate value ${}_0\Lambda_0$ is found by extrapolation in the Λ-$c^{1/2}$ diagram or with the aid of equation (51), and S and E' from Table 1 are used to calculate a function

$$\Lambda_1 = \Lambda + Sc^{1/2} - Ec \log c \tag{47}$$

$$S = 0.8204\times10^6\,\Lambda_0/(DT)^{3/2} + 82.501/\eta(DT)^{1/2} \tag{48}$$

$$E = 6.7747\times10^{12}\,\Lambda_0/(DT)^3 - 0.9977\times10^8/\eta(DT)^2 \tag{49}$$

A plot of $\Lambda_1 = \Lambda_0 + J_1 c$ gives an improved extrapolated value ${}_1\Lambda_0$, with which the rapidly converging process is repeated [2]. J_1 is found from the slope of the linear function (Fig. 5). A nest method may be used to find a_J from $J_1^{(exp)}$.

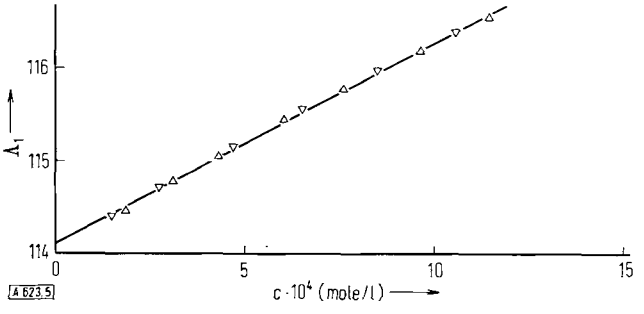

Fig. 5. Determination of Λ_0 and J in accordance with eq. (46). $CsOCH_3$ in CH_3OH (25 °C) [69]; Δ and ∇ are points obtained for different sets of experiments; $\Lambda_0 = 114.11$, $J = 2120$.

Two values a' and a'' are chosen such that $J_1(a') < J_1^{(exp)} < J_1(a'')$. The difference between a' and a'' is narrowed in the subsequent steps. The complete equation (13) with J_2 is best evaluated numerically.

Evaluation with the aid of the limiting law would give Λ_0. *Shedlovsky* [68] has shown that the function

$$\Lambda_0^c = \frac{\Lambda + S_2 c^{1/2}}{1 - S_1 c^{1/2}} \tag{50}$$

calculated from (21) does not give constant Λ_0 values even in very dilute solutions, and that this approximation is reached only by linear extrapolation of the Λ_0 value after plotting the experimental Λ_0^c values as

$$\Lambda_0^c = \Lambda_0 + Bc \tag{51}$$

The equation (22) given by *Robinson* and *Stokes* can also be used for extrapolation from higher concentration ranges [31].

The conductance equation for incompletely dissociated electrolytes

$$\Lambda = \Lambda_0 - S(\alpha c)^{1/2} + E\alpha c \cdot \log(\alpha c) + J_1 \alpha c - K_A y_\pm^2 \Lambda \alpha c \tag{52}$$

can be evaluated graphically [2,49,70]; an estimated or extrapolated ${}_0\Lambda_0$ value is taken, and the quantity

$$\Lambda' = \Lambda + S(\alpha c)^{1/2} - E\alpha c \log(\alpha c) \tag{53}$$

is used to construct a function $y = (\Lambda' - \Lambda_0)(\alpha c)^{-1}$. When plotted against $x = y_\pm^2 \Lambda$ by a graphic nest method to find Λ_0, this function gives an equation

$$y = J_1 - K_A x \tag{54}$$

that is suitable for iteration (Fig. 6).

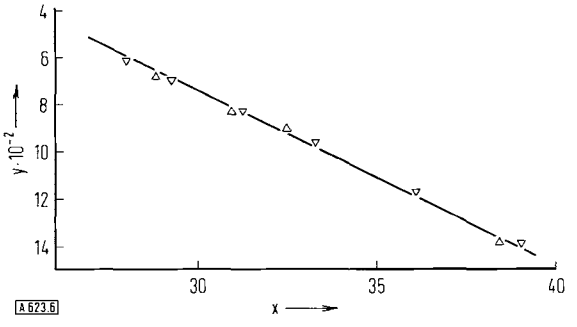

Fig. 6. Determination of conductance data by the x–y method. $CsOC_2H_5$ in C_2H_5OH (25 °C) [71]; Δ and ∇ are points for different sets of experiments; $\Lambda_0 = 49.49$, $J = 1460$, $K_A = 73$.

Apart from the first iteration step, in which one takes $\alpha = \Lambda/{}_0\Lambda_0$, it is necessary to determine α iteratively from equation (30) (with $J_2 = 0$) for each subsequent step in the determination of Λ_0, J_1, and K_A for each experimental value, so that the process is very time-consuming.

A procedure described by *Fuoss* and *Kraus* [72] can be used for evaluations in accordance with the limiting law

$$\Lambda = \alpha[\Lambda_0 - S(\alpha c)^{1/2}] \tag{55}$$

With an auxiliary variable $z = {}_0\Lambda_0^{-3/2}(\Lambda c)^{1/2}S$ and a corresponding tabulated function [73] $F(z) = 1\text{-}z[1\text{-}z[1\text{-}...]^{-1/2}]^{1/2}$ equation (55) can be written in conjunction with the law of mass action as

$$\frac{F(z)}{\Lambda} = \frac{1}{\Lambda_0} + \frac{K_A}{\Lambda_0^2}\,\frac{c\,\Lambda y_\pm^2}{F(z)} \tag{56}$$

Λ_0 and K_A are obtained in a rapidly converging iteration process on plotting of $F(z)\Lambda^{-1} = f(c\Lambda y^{2+}\,[F(z)]^{-1})$. A process described by *Shedlovsky* [74] using an auxiliary function that has also been tabulated [75] is based on an empirical extension of the limiting law. A comparison of the two procedures is described by *Fuoss* and *Shedlovsky* [76]. The sensitivity of this

[68] *Th. Shedlovsky*, J. Amer. chem. Soc. *54*, 1405 (1932).

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[74] *Th. Shedlovsky*, J. Franklin Inst. *225*, 739 (1938).

[75] *H. M. Dagett*, J. Amer. chem. Soc. *73*, 4977 (1951).

[76] *R. M. Fuoss* and *Th. Shedlovsky*, J. Amer. chem. Soc. *71*, 1496 (1949).

process to fluctuations of the experimental values and solvent corrections was described by *Kortüm et al.* [77, 230].

The extrapolation to Λ_0 is sometimes inaccurate for weakly dissociated electrolytes; in cases of this type, it is advantageous to obtain Λ_0 from the additivity of the ion mobilities [78, 79].

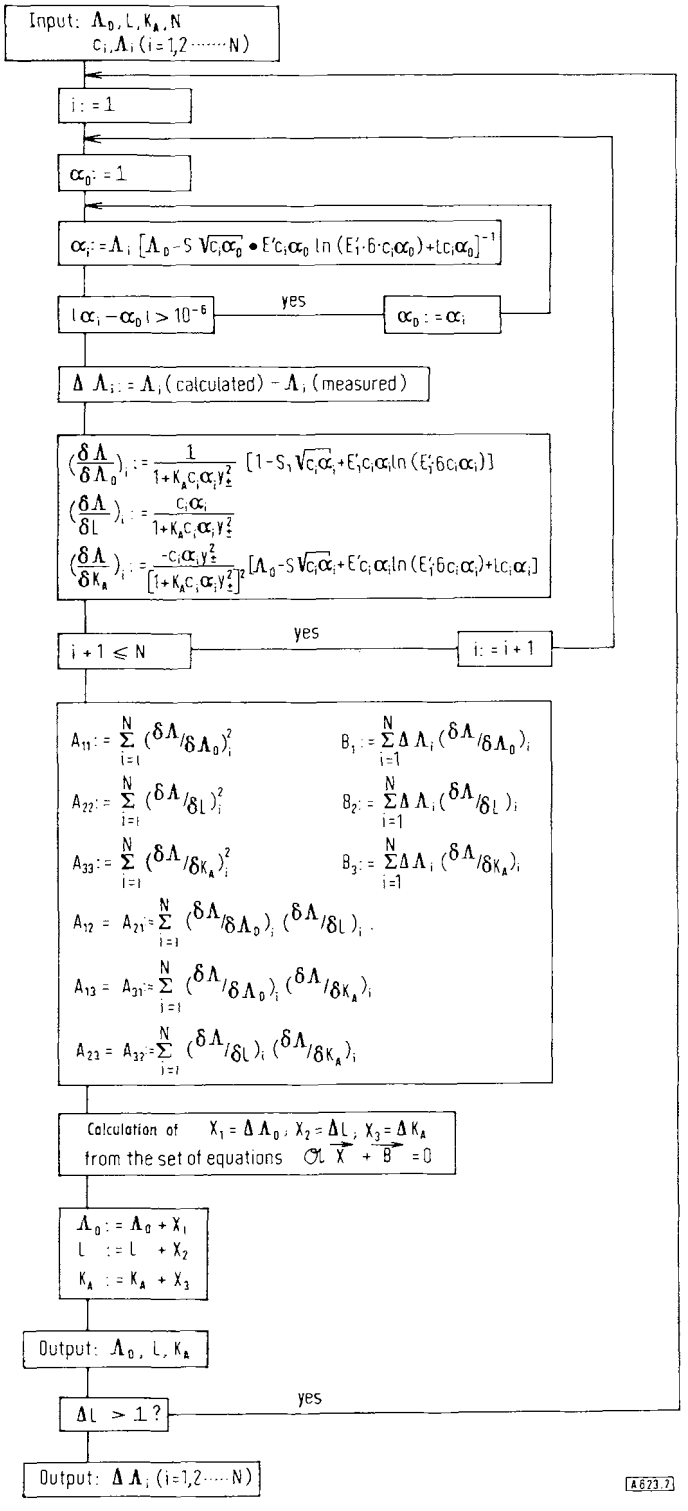

Fig. 7. Flow diagram for the evaluation of experimental data in accordance with eq. (44) in the form

$$\Lambda = \Lambda_0 - S(\alpha c)^{1/2} + E'\alpha c \ln(6E'_1\alpha c) + Lc - K_A\Lambda\alpha c y_\pm^2$$

for associated electrolytes. N = number of pairs of values c_i, Λ_i. For higher association constants ($K_A > 500$), it is preferable to start with α_0: = Λ_i/Λ_0. The equation

$$\mathfrak{A}\vec{X} + \vec{B} = 0$$

is solved by the Gauss-Banachiewicz method [*].

6.2. Numerical Methods

The basic principles for the establishment of a numerical compensation ("adjustment of observations") process were deduced by *Kay* [80, 81]. The conductance equation in the form (13) or in a similar form is expanded in accordance with

$$\Lambda({}_0\Lambda_0 + \Delta\Lambda, {}_0J_1 + \Delta J_1 \ldots) = \Lambda({}_0\Lambda_0, {}_0J_1 \ldots) + \frac{\delta\Lambda}{\delta\Lambda_0}\Delta\Lambda_0 + \frac{\delta\Lambda}{\delta J_1}\Delta J_1 + \ldots \quad (57)$$

using preselected approximate values ${}_0\Lambda_0$, ${}_0J_1$, *etc.* Iterative improvements $\Delta\Lambda_0$, $\Delta J_1 \ldots$ are calculated with the aid of a compensation program until the improvements fall below a predetermined limit. Figure 7 shows the flow diagram of a general process of this type used by us for the evaluation of experimental data and as an example of the use of equation (44). The predetermined limit in this case is $\Delta L < 1$. Differing from *Kay* we prefer to calculate the coefficients J_1, J_2, *etc.* from the conductance data of a direct calculation of a, since these coefficients are the same for all equations (cf. Table 1). The a parameters are determined from these quantities with the aid of special programs. Computer programs for the treatment of conductance equations are also given by *de Maine* and *Seawright* [82].

7. Results of Recent Conductance Investigations

The foregoing sections described the conductance theory and the hydrodynamic and electrostatic continuum model on which it is based. This model and the conductance equations derived from it, with a few exceptions that can be seen from the text, form the basis of the following investigations. As with any model, there exists the difficulty of assigning the parameters of the equations to the molecular dimensions of the solvent-electrolyte system; however, it is possible by a systematic series of experiments to demonstrate functional relationships which, sometimes in conjunction with results obtained by other methods, enable one to draw correct conclusions concerning the true molecular data, the structure of the electrolyte solutions, and reactions in solutions.

In the discussion of the results, no special role has been assigned to water as a solvent, and concentrated aqueous solutions have been completely disregarded (cf. [89]).

Contributions to this problem have also been made in Russian publications, but we have not been able to make systematic use of these.

Work on electrolytic conductance up to 1964 was reviewed in reports by *Fischer, Winkler,* and *Jander* (1958) [83], *Prue*

[77] *G. Kortüm* and *H. Wenck*, Ber. Bunsenges. physik. Chem. *70*, 435 (1966).

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[79] *Th. Shedlovsky* in *W. J. Hamer*: The Structure of Electrolytic Solutions. Wiley, New York 1959, p. 268.

[*] For a computer program, see *D. Müller*, Programmierung elektronischer Rechenanlagen. Bibliographisches Institut, Mannheim 1964, p. 175.

[80] *R. L. Kay*, J. Amer. chem. Soc. *82*, 2099 (1960).

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[83] *L. Fischer, G. Winkler,* and *G. Jander*, Z. Elektrochem., Ber. Bunsenges. physik. Chem. *62*, 1 (1958).

(1960)[84], *Evers* and *Kay* (1960)[85], *Covington* and *Prue* (1963)[86], *Scatchard* (1963)[87], and *Agar* (1964)[88]. Only the more recent literature will therefore be considered in the following discussions.

7.1. Conductance and Association of 1,1 Electrolytes

In agreement with the Bjerrum association theory, 1,1 ionophores generally exist exclusively as free ions in aqueous solutions at low concentrations; association is generally observed in solvents having a dielectric constant of about 50.

Hawes and *Kay*[5] carried out very accurate measurements in ethanol-water mixtures, and found $K_A = 3 \pm 0.4$ for CsCl at $D = 54.9$ and for KCl at $D = 43.3$. The corresponding values in pure ethanol ($D = 24.3$, $\sigma_L \approx 10^{-8}$) are $K_A(CsCl) = 158.1 \pm 0.6$ and $K_A(KCl) = 95 \pm 3$. In an extensive study of alkali metal halides in dioxane-water mixtures, *Fuoss et al.*[90] found no measurable association above $D = 50$. LiCl and $AgNO_3$ are associated in dimethylformamide ($D = 36.7$), whereas KI and perchlorates are not[91]. *Bury* and *Justice*[92] do not give association constants for $KClO_4$ in dioxane-water mixtures above $D = 25.3$; at $D = 25.3$, K_A has a value of 15.3. In the same solvent mixture, *Accascina* and *D'Aprano*[93] observed a similar behavior for $KClO_3$ ($K_A = 18$ at $D = 28.5$). 1,1 Electrolytes are not associated in formamide ($D = 109.5$)[94]. *Hoover*[95] found abnormally low a values for KCl in *N*-methylpropionamide ($D = 176$), and regarded this specific solvent effect as evidence of slight association.

Accascina et al. found an anomaly at low dielectric constants: $LiClO_4$ exhibits no association in dioxane-water mixtures[96] down to a dielectric constant of 10, in which *e.g.* LiCl[90] and $LiClO_3$[97] are strongly associated ($K_A \approx 1000$), or in methanol-butanol mixtures[98] down to a dielectric constant of 18, though it is associated in acetone ($K_A \approx 5000$)[99]. In solvents of low dielectric constant, in agreement with theory, this nonassociating electrolyte showed the second intersection ($c_1 = 0$, $c_2 = 10^{-J/E}$) of the limiting line $\Lambda = \Lambda_0 - Sc^{1/2}$ with the complete function $\Lambda = \Lambda_0 - Sc^{1/2} + Ec \log c + Jc$, which is situated too close to c_1 in solutions having higher dielectric constants[100]. For comparison, $K_A = 268$ at $D = 15.7$ for $KClO_4$ in dioxane-water[92]; $KClO_4$ and $NaClO_4$ are completely dissociated in methanol[101], in dimethylformamide[91], and in dimethylacetamide[102].

The validity of rules concerning the relationship between the properties of the electrolyte and the solvent and the magnitude of the association constant is only limited. *Fuoss et al.*[90] found in their studies on the conductance of alkali metal halides in dioxane-water mixtures that, for a given anion, the association constant increases with the atomic weight of the cation (as a result of decreasing solvation), while for a given cation, the association constant decreases with increasing atomic weight, *i. e.* with increasing volume, of the anion. On re-evaluation of earlier data for alkali metal salts in other solvents with the aid of the conductance equations (13) and (31), *Kay*[80] found partial agreement with the above rule. In methanol ($D = 32.6$), only CsCl ($K_A = 15$; subsequent redetermination[103] gave $K_A = 8.9$) is weakly associated, whereas all the nitrates studied are associated ($10 < K_A < 40$). The alkali metal picrates[104] also deviate from the Fuoss rule. *Evans*, *Zawoyski*, and *Kay*[105] report that the association constant for ion pair formation in the approximately isodielectric solvents ($D = 36$) acetonitrile, nitromethane, and nitrobenzene and in acetone ($D = 20.5$) increases with decreasing crystallographic radius of the ions. LiCl and LiBr are strongly associated in sulfolane[54] ($D = 43.3$ at 30 °C) the values of K_A being 1.4×10^4 and 278 respectively, whereas alkali metal iodides and other alkali metal salts exhibit only slight association. LiCl[106] and NaCl[107] are not associated in water-glycerol mixtures. NaCl is also unassociated in water-ethylene glycol mixtures[108].

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[91] *J. E. Prue* and *P. J. Sherrington*, Trans. Faraday Soc. *57*, 1795 (1961).

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[94] *P. H. Tewari* and *G. P. Johari*, J. physic. Chem. *67*, 512 (1963).

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For further data on alkali metal and silver halides, nitrates, chlorates, and picrates in several solvents and solvent mixtures, see [56, 109–120].

Janz, Marcinkowsky, and *Ahmad* [121] studied the electric conductance and viscosity of $AgNO_3$ in acetonitrile and benzonitrile up to a concentration of 6 moles/l; these authors observed ion pair formation, and at higher salt concentrations ion triplet formation. The results were evaluated with the aid of the semi-empirical conductance equation given by *Wishaw* and *Stokes* [122], which is applicable at high salt concentration when a viscosity correction [25] is applied.

Large ions having a central charge, such as tetraalkylammonium and tetraphenylborate ions, are characterized in many series investigations by constancy of the a parameter.

Among the tetraalkylammonium halides R_4NX (R = CH_3, C_2H_5, C_3H_7, C_4H_9, X = Cl, Br, I), tetrabutylammonium iodide is associated in water ($K_A \approx 3$). This behavior is due to the structure of the environment of the large hydrophobic ions rather than to direct electrostatic interaction of the charge carriers [123]. Low association constants have also been found for tetraalkylammonium salts by *Quintin, Justice*, and *Justice* [124]. *Davies* and *Taylor* [125] found that R_4NX, $R_3(n\text{-}C_{18}H_{37})NX$, $R_2(n\text{-}C_{12}H_{25})_2NX$, and $R_2(n\text{-}C_{12}H_{25})(n\text{-}C_{18}H_{37})NX$ (R = CH_3, C_2H_5, C_3H_7, C_4H_9, X = Cl, I, NO_3, Pi (picrate)) behaved normally in hydrocyanic acid (18 and 25 °C), *i.e.* the experimental values agreed with the eq. (13) for unassociated electrolytes.

Information about the limiting range for association (methanol at 25 and 10 °C) is given in a comprehensive report by *Kay, Zawoyski*, and *Evans* [126], which contains results of measurements on 23 tetraalkylammonium salts of type R_4NX and $(iso\text{-}C_5H_{11})_3RNX$ (R = CH_3, C_2H_5, C_3H_7, C_4H_9, $n\text{-}C_5H_{11}$, $iso\text{-}C_5H_{11}$; X = Cl, Br, I, Pi, $B(C_6H_5)_4$). $(C_4H_9)_4NB(C_6H_5)_4$ is the most strongly associated salt ($K_A = 37$); the association is uncertain for some of the salts in this series. A similar situation is found in acetonitrile [105, 127], and in nitrobenzene the occurrence of association cannot be definitely established in many cases. Association is pronounced, however, in acetone ($(CH_3)_4NF$ with $K_A = 1140$). (For further data on tetraalkylammonium salts and borates, alkylsulfonates, phosphonium salts, and other salts, see [120, 128–148, 191–193].)

Since the sizes of the cation and the anion are approximately equal, $(C_4H_9)_4NB(C_6H_5)_4$ can be used as the reference electrolyte for the determination of ion mobilities in accordance with

$$l_{0+} = l_{0-} = 1/2\,\Lambda_0 \qquad (58)$$

with an accuracy of about 1 % [128]. $(iso\text{-}C_5H_{11})_3(C_4H_9)NB(C_6H_5)_4$ is equally suitable [130] and $(iso\text{-}C_5H_{11})_4NB(iso\text{-}C_5H_{11})_4$ even gives an accuracy of

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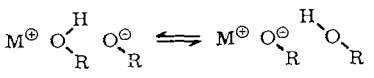
0.1 %[129]. (For other ion mobility measurements, also by other methods, see[120,125,149–159].)

Investigations with D_2O as the solvent have been carried out by *Kay* and *Evans*[160] on tetraalkylammonium halides, by *Horne* and *Johnson*[161] on KCl between −2 and +12 °C, and by *Swain* and *Evans*[162] on other salts.

Barthel et al.[4,51,69] were able to evaluate accurate measurements on alcoholic solutions containing bases (MOR) in low concentrations by means of the new conductance equations (13), (31), and (44). The variation of the association constant, which had not previously been observed in salts (decreasing from LiOR to KOR and increasing again from KOR to CsOR (R = C_2H_5, C_3H_7) cf. Table 2) is explained by ion pair formation according to two possible mechanisms:

1. the partial or complete penetration of the solvent sheaths by ions, generally accepted for salts, or
2. as a consequence of protolysis of a solvate molecule.



The second effect is more significant with small cations. The alkali metal methoxides are not associated in methanol[69].

7.2. Conductance and Association of Polyvalent Electrolytes

The normal limiting region of association for symmetrical electrolytes generally occurs at higher dielectric constants for electrolytes containing ions of higher valence. Mg, Ni, and $Cu(en)_2$ sulfates exhibit no association in formamide (D = 110)[163]. $MgSO_4$, MgC_2O_4, $CaCrO_4$[164], and many other 2,2 electrolytes are associated in water, and $MgSO_4$ is associated even in formamide-dioxane mixtures having a dielectric constant (D = 81, K_A = 88) higher than that of water[165]. However, the Ca salts of disulfonic acids do not form associates in water[166]. *Staples* and *Atkinson*[167] used benzenesulfonates (BS^-), *p*-benzenedisulfonates (BDS^{2-}), 4,4′-biphenyldisulfonates ($BPDS^{2-}$), and 4,4′′-terphenyldisulfonates ($TPDS^{2-}$) to study the association of polyvalent electrolytes having widely separated charge centers (bolaform electrolytes) in dioxane-water mixtures. The 1,1-electrolyte KBS and the 1,2 electrolytes K_2BDS and K_2BPDS are associated only in mixtures containing 50 % of dioxane, whereas K_2TPDS is weakly associated even in water.

In the treatment of unsymmetrical electrolytes, it is necessary to take into account conducting ion pairs of the type $[K^+A^{2-}]^-$ as well as $[K^+A^{2-}K^+]^0$. A conductance equation for bolaform electrolytes is given by *Fuoss* and *Edelson*[182].

Dawson, *Vaughn*, *Lester*, *Pruitt*, and *Sears*[183] found that polyvalent electrolytes and complex salts of the transition elements are completely dissociated in *N*-methylacetamide.

The association limit is further displaced for 3,3 electrolytes, such as $La[Co(CN)_6]$. $La[Co(CN)_6]$ is associated (K_A = 243) in formamide, whereas the conductance data of unsymmetrical electrolytes such as $[Co(NH_3)_6]Cl_3$ can be represented by eq. (13)[184]. For other studies on polyvalent electrolytes, see[168–181].

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7.3. Higher Associates

On the basis of nonlinearity of the Shedlovsky plot, *Little* and *Singleterry* [185] concluded that higher associates are formed by cesium dinonylnaphthalenesulfonate (CsDNNS) in nitromethane, nitropropane, ethanol, *n*-butanol, and methyl isobutyl ketone and by LiDNNS in nitroethane, nitropropane, acetone, and methyl isobutyl ketone. LiDNNS forms only ion pairs in methanol, ethanol, and butanol, as does CsDNNS in acetone.

Beard and *Plesch* [186] observed minima in the concentration dependence of the conductance of $(CH_3)(C_2H_5)_3NI$ in CH_2Cl_2 down to low temperatures (−55 °C), and deduced ion triplet formation constants based on the assumption that $\Lambda_0^{(3)} = \Lambda_0/3$. *Strohmeyer*, *Seifert*, and *Landsfeld* [187] studied the effect of the ligands R on the electrolytic conductance of organometallic compounds of the type MR_2. Compounds MgR_2 form ion triplets in diethyl ether and tetrahydrofuran, whereas dialkylzincs do not; the cyclopentadiene derivatives of zinc behave similarly to the dialkylmagnesiums. Sodium tetracarbonylcobaltate associates in tetrahydrofuran to form ion pairs and higher associates [188]. *Vreugdenhil* and *Blomberg* [189] studied the conductance of Grignard compounds in diethyl ether.

According to *Bearcroft* and *Nachtrieb* [190], several associates are involved in charge transport in the system I_2 (liq.)/KI, as follows:

$$nI_2 \rightleftharpoons I^+ + I_{2n-1}^-, \quad K^+I^- \rightleftharpoons K^+ + I^-, \text{ and } K^+I^- + K^+ \rightleftharpoons K_2I^+$$

7.4. Interaction of the Electrolyte and the Solvent

This group of problems was first studied by *Walden*, who expressed his findings in the rule

$$\Lambda_0 \eta = \text{const.} = \frac{e_0^2 N \times 10^{-11}}{54\pi}\left(\frac{1}{R^+} + \frac{1}{R^-}\right) \tag{59}$$

Equation (59) is the form for 1,1 electrolytes (R^+, R^- = hydrodynamic radii of the ions). It can be deduced from Stokes' law and the definition of ion mobility. The accuracy with which it is satisfied generally increases with increasing size of the ions and with decreasing tendency of the solvent toward association. In addition to eq. (59), the relationship

$$l_{0j}\eta = \text{const.} = \frac{|z_j| e_0^2 N \times 10^{-11}}{54\pi} \cdot \frac{1}{R_j} \tag{60}$$

is also valid under the same conditions.

The Walden rule can be used for the estimation of a first Λ_0 value, such as is required *e.g.* in the iteration process. It provides information about the movement of spherical ions in a hydrodynamic continuum, and has been used in many of the investigations mentioned above for the estimation of the interaction of the ion with its surroundings. Examples are to be found in the work of *Fuoss* [90, 208, 209, 211, 212] and of *Kay et al.* [160, 191–193].

The approximation of the Walden rule is improved if the ionic radius R is expressed as depending on the dielectric constant of the solvent [194] (s = empirical constant)

$$R = R_\infty \left(1 + \frac{s}{D}\right) \tag{61}$$

This takes into account the orientation of the solvent dipoles by the migrating ion. *Boyd* [195] and *Zwanzig* [196] have provided a theoretical basis for the semiempirical equation (61). For a discussion of the limiting conductance on the basis of a kinetic theory see Section 7.6.

A second group of investigations was concerned with the discussion of the association constants as $\ln K_A = f(1/D)$ in accordance with $K_A = K_0 e^b$ (cf. eq. (43)). The results obtained in series of solvents were often satisfactorily reproduced by this relationship. Deviations from linearity in the $\ln K_A - 1/D$ diagram can be explained by $E_s \neq 0$ (cf. eq. (43)), and have even been quantitatively explained in a few cases (cf. *e.g.* [63]). For a complete understanding it is necessary to introduce a variable dielectric constant for the continuum surrounding the ion [54, 197] or to take into account the molecular structure of the solvent [60].

In another group of investigations, a further polar component is added to the solvent-electrolyte system, this component interacting with one of the ions to form an ion-dipole associate whose formation constant competes with K_A. The association of tetrabutylammonium picrate in dioxane/*p*-nitroaniline mixtures differs considerably from that in isodielectric mixtures (D = 13.2) of dioxane with water, methanol, and acetonitrile [198]. The picrate anion forms an associate with *p*-nitroaniline [199]. *Treiner*, *Quintin*, and *Fuoss* [200] concluded from conductance measurements that the phenol component of binary mixtures of acetonitrile with picric acid, *p*-, *m*-, and *o*-nitrophenol, and *p*-methoxyphenol adds on to quaternary ammonium ions as the phenoxide, with liberation of a proton, and that small ions such as Br^- in the mixtures are preferentially solvated by phenols.

The investigations mentioned above are concerned with complex formation between the anion of the electrolyte and an electrophile. Interactions of the

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cation with nucleophiles have been described in a series of articles by *Gilkerson et al.* [201–203]. The cation of tertiary ammonium salts, in this case $(C_4H_9)_3HNPi$, forms 1:1 complexes with added amines in chlorobenzene and *o*-dichlorobenzene, the stability of these complexes increasing in the order 4-cyanopyridine < acetonitrile < tri-*n*-butylamine < pyridine < 4-methylpyridine. The methyltri-*n*-butylammonium cation (introduced as the perchlorate or iodide) associates with triphenylphosphine oxide in *o*-dichlorobenzene and ethylene dichloride. The addition of picric acid to tri-*N*-*n*-butylhydroxylammonium picrate in *o*-dichlorobenzene leads to a considerable decrease in conductance, while the addition of pyridine leads to an increase in conductance.

Specific ion-solvent interactions have also been found by *Day*, *Barnes*, and *Cox* [204] in conductance measurements on $Na[Al(C_2H_5)_4]$ and $Na[Al(iso\text{-}C_4H_9)_4]$ in diethyl ether and toluene. The conductance of $AlCl_3$ in acetonitrile (L) is due to the ions $[AlCl_2L_4]^+$ and $[AlCl_4]^-$, which are formed by complex disproportionation [205] in accordance with

$$2\ AlCl_3(s) + 4\ L \rightarrow [AlCl_2L_4]^+ + [AlCl_4]^-$$

In the same solvent, $CoCl_2$ forms the ions $[CoL_6]^{2+}$ and $[CoCl_3L]^-$ [206], and according to other investigations $[CoCl_4]^{2-}$ [207]. (For investigations that include other types, see [208–212].)

Ebeling, *Falkenhagen*, and *Kraeft* [213] interpret the decrease in conductance with increasing concentration of a neutral component (such as sugar, glycerol, mannitol) with the aid of a molecular theory in which the decrease in conductance is mainly due to the volume occupied by the ions and by the neutral molecules.

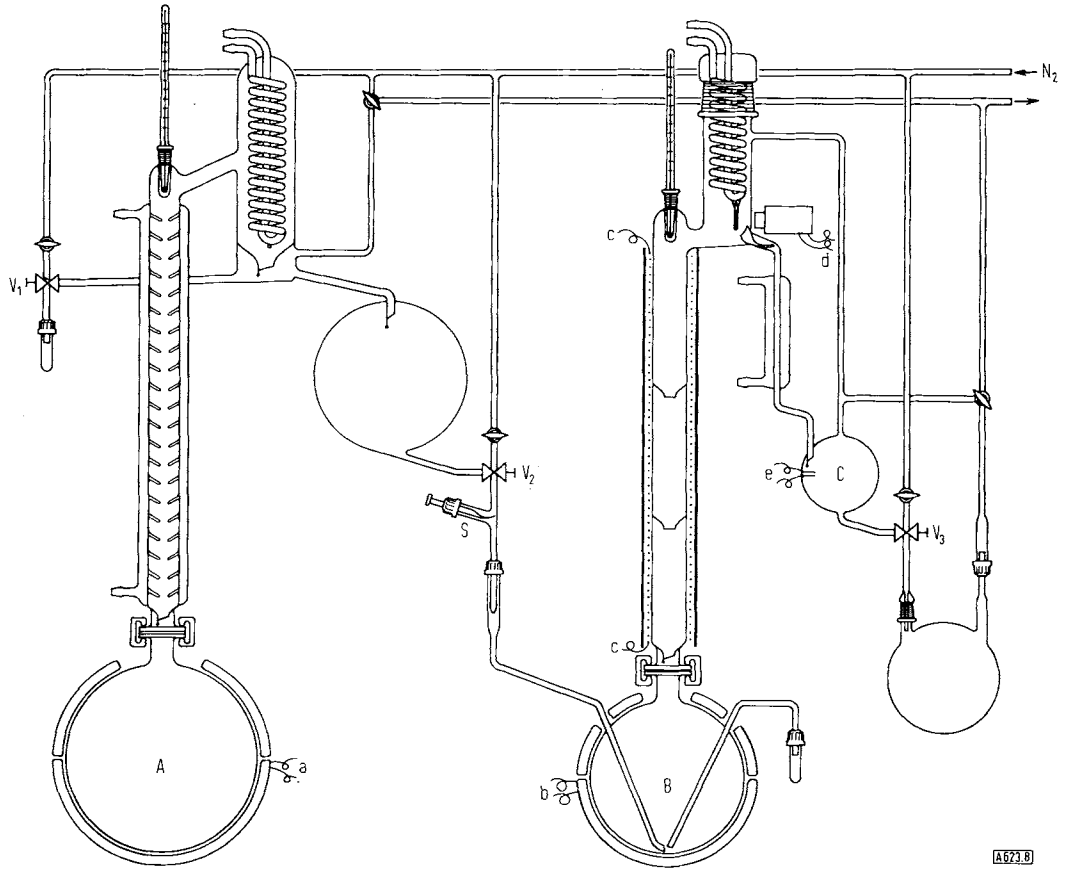

Fig. 8. Apparatus for the purification of solvents [216]. Dehydration of the solvent (isopropanol in this case) in A (approx. 5 l), distillation into B, addition of other reagents (in this case sulfanilic acid) for purification (in this case elimination of basic components) through S, final distillation from B (packed column, about 20 theoretical plates), C fraction collector, a,b,c, controlled heaters, d electromagnetically controlled take-off (adjustable reflux ratio [217]), e conductance measuring cell (A = 0.02 cm^{-1}) for examination of the distillate. V_1, V_2, V_3 nitrogen-purged, grease-free through-flow valves in the distillate line (description [218]). The entire apparatus operates under carefully purified protective gas.

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Mention should also be made in this section of an interaction that is generally disregarded, and which is due to insufficient purification of the solvent. It can be seen from the results discussed above that effects due to impurities frequently cannot be eliminated by correction of the conductance values. Figure 8 shows a purification arrangement used by us. From chemical purification, *via* distillation, until its introduction into the measuring cell, the solvent remains under a protective gas. For example, iso-C_3H_7OH is purified in A over Al powder as described by *Walden, Ulich* and *Laun*[214]. After distillation into B, sulfanilic acid is added through S. The distillation product contains 5 ppm of H_2O, CO_2 is undetectable, and $\sigma_L = 10^{-9}$ ohm^{-1} cm^{-1}.

Figure 9 shows Λ-$\sqrt{c}$ curves for $KOCH_3$ in methanol, highly purified methanol being used in one case (A) and methanol distilled in air in the other (B). The interfering impurity is CO_2, which reacts with the electrolyte to form

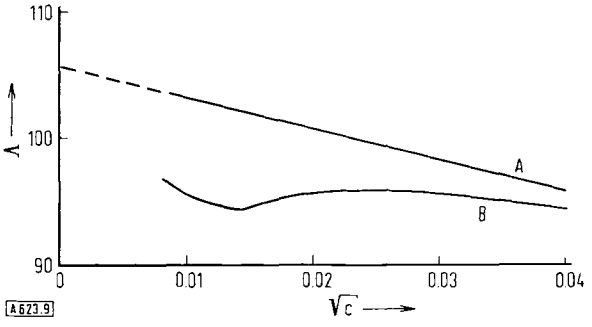

Fig. 9. Influence of the CO_2 content of methanol on the conductance of $KOCH_3$ in this solvent (25 °C) [71]. A: highly purified methanol; B: methanol distilled in air.

potassium methyl carbonate. Special investigations on the purity of the solvent are necessary in many cases (cf. *e.g.* [120, 215]).

The effect of the water content on the conductance is shown in Figure 10. The diagram shows a plot of $\vartheta = \Delta\Lambda$/wt-% of H_2O against the root of the electrolyte concentration for NaCl[215] (line) and for $NaOCH_3$ (circles) in methanol (25 °C).

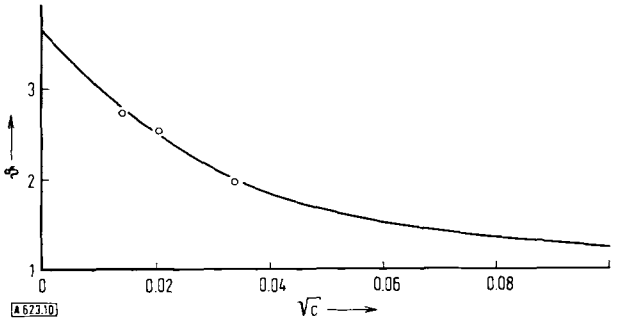

Fig. 10. Effect of the water content of methanol on electrolytic conductance [69]. —: NaCl in methanol, o: $NaOCH_3$ in methanol, (25 °C). $\vartheta = \Delta\Lambda$/wt-% of H_2O.

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Since these electrolytes form their ions by chemical reaction with the solvent, solutions of such electrolytes, by definition, exhibit a specific solvent-electrolyte interaction. No clear-cut distinction from the electrolyte properties discussed in the last section is possible, as is shown by the case of $AlCl_3$/acetonitrile.

For HCl in water/ethanol mixtures (0–100 %)[219] and in water/*n*-propanol mixtures (0–100 %)[220], the conductance data over the entire mixing range can be described by eq. (44); HCl is almost completely dissociated in solutions containing large quantities of water (up to 80 % of ethanol and up to 60 % of propanol, $K_A < 10$). The values of K_A in pure ethanol ($D = 24.3$) and in pure propanol ($D = 20.40$) are 48 and 171 respectively. This is not in conflict with earlier results of very accurate measurements on HCl in water by *Stokes*[221], since *Stokes*' work covered a wider concentration range.

Janz et al.[222–224] studied hydrogen halides HX mainly in acetonitrile and benzonitrile, and explained the conductance data and their time dependence on the basis of multi-step reactions leading to the overall reaction

$$HX + L \rightleftharpoons LH^+ + X_{solv.}$$

and which may be followed by triplet formation

$$HX + X_{solv.} \rightleftharpoons HX_{2,\,solv.}$$

(L = solvent).

The conductance of acetic acid in methanol-water[79] and ethanol-water mixtures[225] has been discussed on the basis of two cations H_3O^+ and ROH_2^+. $(CH_3)_2S$ and $(CH_3)_3N$ give ion triplets in liquid hydrogen halides[226]. (For other investigations in this medium and in ClF_3 and BrF_3, see[226–228] and[229].)

As was shown by *Kortüm* and *Koch*[230], the dissociation constants found from the conductance data for 2,6-dinitrophenol in water-methanol mixtures do not agree, at high methanol contents, with the constants found from optical measurements. Ions that cannot

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contribute to charge transport in the associate, but still retain their identity as ions, give the same spectrum as free ions.

7.6. Dependence of Conductance on Pressure, Temperature, and Frequency

The dependence of the limiting conductance of tetraalkylammonium salts, potassium salts, and picric acid in dimethylformamide on temperature and pressure (25 to 65 °C, 1 to 1900 atm) was discussed by *Brummer* [231] on the basis of a kinetic model [232]. This discussion led to ΔH and ΔV values for the transport mechanism. The theoretical principles of a kinetic study are presented by *Hills* [233].

Horne, *Myers*, and *Frysinger* [234] compared the pressure dependence of the conductance of aqueous solutions (5 to 45 °C, 1 to 7000 atm). While the activation energy of the conductance of a KCl solution shows a variation parallel to that of the viscosity with rising pressure, the behavior of HCl is quite different. As *Horne* also suggested in a different context [235], the protonic conductance in aqueous solution contains components due to a Grotthus mechanism. At pressures below 1380 bar, the rotation of the water molecule is reported to be rate determining, at pressures above this value, the proton jump becomes rate determining. (For such pressure studies on solutions of several electrolytes, cf. [236].)

The conductance of tetraisopentylammonium picrate in diethyl ether and benzene decreases with increasing pressure (up to 5000 atm), owing to an increase in the viscosity of the solvent and a displacement of the ion pair and triplet formation equilibria as a result of an increase in the dielectric constant [237].

The temperature dependence of conductance in nonaqueous solvents is illustrated by the work of *Carvajal*, *Tölle*, *Smid*, and *Szwarc* [238] on various tetraphenylborates in dimethoxyethane (DME) and tetrahydrofuran (THF) (−70 to +25 °C). In both solvents, $(C_4H_9)(C_5H_{11})_3N^+$ forms contact pairs with $(C_6H_5)_4B^-$, and these contact pairs dissociate into unsolvated ions ($\Delta H_{diss.}$ = −1.3 kcal/mole in THF and −2.3 kcal/mole in DME). On the other hand, Na^+ and $(C_6H_5)_4B^-$, form ion pairs with inclusion of solvent molecules; the ion pairs dissociate into a solvated Na^+ and an unsolvated $(C_6H_5)_4B^-$ ($\Delta H_{diss.}$ = −1.3 kcal/mole in THF and −1.8 kcal/mole in DME).

The temperature coefficient of the conductance of copper perchlorate dihydrate as a function of concentration is negative in several solvents [239].

The pressure and temperature dependences of the conductance, as well as of the dissociation constant of ionogens and the association constant of ionophores, are the objects of further studies [157, 186, 240–245].

The decrease in conductance with increasing pressure is explained in the theoretical study by *Ebeling*, *Falkenhagen*, and *Kraeft* [213] as being due to the increase in the number of solvent molecules (which can be treated as neutral components) per unit volume as a result of the increase in pressure. The results of investigations by *Hensel* and *Franck* [246] on the pressure dependence of aqueous salt solutions are satisfactorily described in this way.

The frequency dependence of the conductance (1–100 kHz) of tetrabutylammonium picrate in dichlorobenzene-benzene mixtures was studied by *Nanney* and *Gilkerson* [247]. The results obtained at low salt concentrations are explained by the Debye-Falkenhagen theory, while the relaxation of the ion pair equilibrium is used to explain the variation of the conductance at higher salt concentrations.

The Wien effect was studied by *Spinnler* and *Patterson* [248] for aqueous solutions of uranyl salts (5 to 65 °C).

The numerical calculations for this work were carried out by kind permission of Professor J. Dörr, Computer Center of the Universität des Saarlandes, to whom I am very grateful. I thank Dr. G. Schwitzgebel for carrying out the calculations and for constructing the required programs. Thanks are also due to Fräulein K. Lenz and to Dipl.-Chem. G. Schmeer for their assistance with the preparation of the manuscript and of the drawings.

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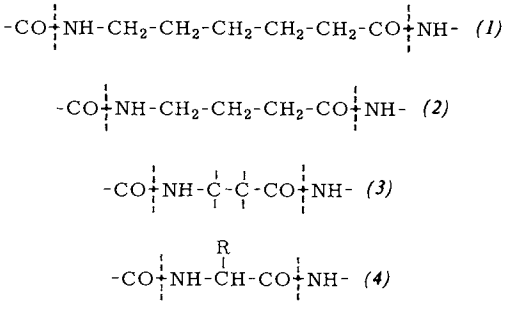
Poly-β-amides [**]

BY H. BESTIAN [*]

High molecular weight poly-β-amides with fiber-forming properties (repeating unit $-NH-CR_2-CR_2-CO-$) differ from the polyamides of the nylon series in that the amide groups are much more closely spaced. These polymers are thus the nearest of the synthetic polyamides to natural silk. The production of poly-β-amides was made possible by a recent synthesis of β-lactams from olefins and chlorosulfonyl isocyanate. The anionic polymerization of the β-lactams gives poly-β-amides containing up to 10000 monomer units in the chain. The molecular weight can be controlled as desired by means of initiators and chain terminators, and the properties can be varied within wide limits by the choice of the β-lactam or by copolymerization of several β-lactams. Remarkable differences are observed between polymers containing structural units in the threo form and those containing erythro structural units. The poly-β-amides can be spun into fibers having valuable textile properties.

1. Introduction

High molecular weight poly-β-amides with fiber-forming properties were still largely unknown a few years ago. These polyamides, in which the repeating unit is a β-amino acid skeleton, differ from polyamides of the nylon series in that the amide linkages are much more closely spaced, so that the polymers are therefore similar to the polypeptides, and to silk fibroin in particular. We have not adopted the term poly-β-peptides, which is also found in the literature, since the name polypeptides should be used only for polymeric α-amino acids. Some polyamides are shown in Scheme 1.



Scheme 1. Repeating units of some polyamides. *(1)* polycaprolactam (nylon 6), *(2)* polypyrrolidone (nylon 4), *(3)* poly-β-amides, *(4)* polypeptides such as fibroin.

While the polyamides containing six or more carbon atoms in the monomer unit became available from ω-amino acids or their lactams soon after their discovery by *W. H. Carothers*, considerable difficulties were encountered in the synthesis of high molecular weight polyamides with short structural units, since the close spacing of the amide linkages leads to lower solubility and raises the melting point into the decomposition range. These polyamides are also less stable to heat, so that the simple but rather vigorous melt condensation cannot be used.

During the past 10 to 15 years, special methods have been developed for each group of polyamides. These methods all involve the use of alkaline catalysts, low polymerization temperatures, and suitable solvents or diluents. Thus the high molecular weight peptides could be obtained from α-amino acids *via* the Leuchs anhydride, and pyrrolidone could be polymerized into a polyamide (nylon 4) having a sufficiently high molecular weight for fiber production.

2. Existing Methods

At roughly the same time as efforts were being made to find a route to synthetic polypeptides, attempts were also being made to prepare poly-β-amides (Table 1).

The polycondensation of β-alanine and its derivatives always led to low molecular weight poly-β-amides [1–4]. *Birkhofer* and *Modic* [5] succeeded in preparing the *N*-carboxy-β-amino acid anhydrides corresponding to the Leuchs compound (*e.g.* *N*-carboxy-β-alanine anhydride) and in synthesizing poly-β-amides containing up to 100 amino acid units. The α,α-disubstituted β-amino acids occupy a special place, since β-elimination, which can lead to loss of ammonia or to cleavage of the polymer chain, is suppressed in these cases. Thus,

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[5] *L.Birkhofer* and *R.Modic*, Liebigs Ann.Chem.*628*,162 (1959).

Table 1. Preparation of poly-β-amides.

Starting material	Reaction conditions	Molecular weight	Ref.
$H_2N-CH_2-CH_2-COOH$	Condensation at 200 °C		[1]
$H_2N-CH_2-CH_2-COOC_2H_5$	Self condensation at 20 °C		[2]
$H_2N-CH_2-CH_2-COCl$	Thermal condensation under vacuum	< 5000	[3]
$HN-CH_2-CH_2-COOH$ $CO-SC_6H_5$	In dioxane at 60–80 °C catalyst: pyridine		[4]
N-Carboxy-β-alanine anhydride	Thermal decomposition at 150 °C	≈ 7000	[5]
$H_2N-CH_2-C(CH_3)_2-COOH$	In cresol at 190 °C	≈ 10000	[6]
$CH_2=CH-CO-NH_2$	In pyridine at 100 °C, alkaline catalyst	76000	[7]

Linkoln[6] was able to convert aminopivalic acid (in cresol at 190 °C) into polyamides whose viscosities correspond to molecular weights of 5000 to 10000.

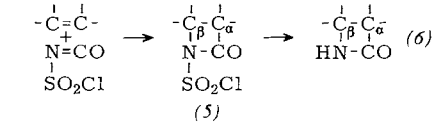
An unconventional method was successfully used by *Breslow*, *Hulse*, and *Matlack*[7] for the synthesis of poly-β-amides. These authors converted acrylamide into poly-β-alanine by alkali-catalyzed polyaddition, and isolated a small yield of a high molecular weight substance from the nonuniform crude product; the molecular weight of this substance as calculated from light-scattering measurements was 76000. The relatively low specific viscosity of 0.639 (measured in formic acid) indicates that the molecular weight of this poly-β-alanine is too low for the production of fibers.

3. β-Lactams as Starting Materials

Graf observed in 1952 that sulfur trioxide and cyanogen chloride combine to form a new isocyanate, *i.e.* *N*-carbonylsulfamoyl chloride[8].

$$SO_3 + ClCN \rightarrow ClO_2S-N=CO$$

This readily available compound is a stable liquid boiling at 108 °C. The reactivity of its isocyanate group is very greatly increased by the sulfonyl chloride group attached to the nitrogen. While investigating the reaction of this isocyanate with olefins, *Graf* discovered a new synthesis of β-lactams[9].



(5) *(6)*

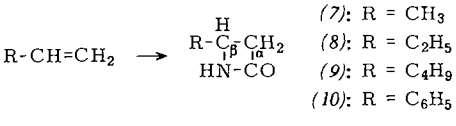
The isocyanate adds on to the olefinic double bond to give *N*-chlorosulfonyl-β-lactams *(5)*, from which free lactams *(6)* can be obtained by removal of the sulfonyl chloride group.

The addition proceeds under mild conditions, and no catalyst is required. Complete conversion of the isocyanate is obtained with even a small excess of olefin. Polar solvents increase the reaction rate and make the reaction easier to control.

The hydrolytic removal of the sulfonyl chloride group without opening the lactam ring initially presented difficulties. The attraction of electrons by the SO_2Cl group weakens the NC bonds. In the alkaline pH range, the ring is opened between N and CO, while in the strongly acidic range it is opened between N and C_β. Moreover, it was also necessary to consider the stability of the β-lactams formed on hydrolysis. *Graf* was able to remove the sulfonyl chloride group with high selectivity by pH-controlled hydrolysis in the weakly acidic range[9].

Many new β-lactams of simple structure have become readily obtainable, even on the industrial scale, by procedures developed on the above basis. The following discussions will be restricted to β-lactams that have been prepared from industrially available olefins and that can be used as starting materials for the preparation of poly-β-amides.

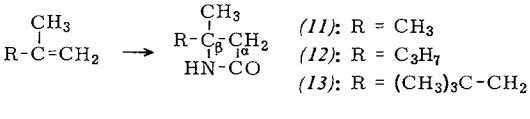
The α-olefins propylene, 1-butene, 1-hexene, and styrene give the β-lactams 4-methyl- *(7)*, 4-ethyl- *(8)*, 4-butyl- *(9)*, and 4-phenyl-2-azetidinone *(10)*.



(7): R = CH_3
(8): R = C_2H_5
(9): R = C_4H_9
(10): R = C_6H_5

As in conventional electrophilic additions, the carbonyl group of the isocyanate becomes attached to the doubly-bonded carbon atom having the higher electron density. Thus the synthesis yields the lactams of the unbranched β-amino acids. β-Butyrolactam *(7)*, which has recently become available from propylene, has particularly attracted our attention for the synthesis of poly-β-amides.

Olefins of the vinylidene type, *e.g.* isobutylene, 2-methyl-1-pentene, and diisobutylene (2,4,4-trimethyl-1-pentene), are much more reactive. The addition of the isocyanate to isobutylene proceeds rapidly even below 0 °C. The direction of addition is the same as that observed with the α-olefins. The vinylidene olefins give lactams of β-methyl-β-amino acids. [*(11)*, *(12)*, and *(13)*]. These lactams are very stable to oxygen, and this property is retained on conversion into poly-β-amides.



(11): R = CH_3
(12): R = C_3H_7
(13): R = $(CH_3)_3C-CH_2$

β-Lactams can also be obtained from olefins containing a double bond in the chain or in a ring[10]. The addition of the isocyanate to 2-butene proceeds as a *cis*

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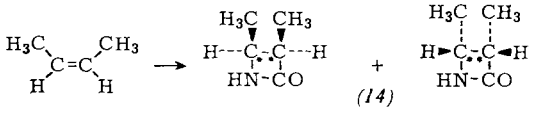
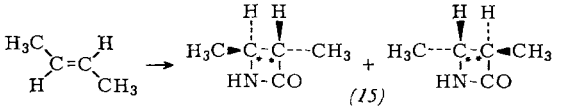
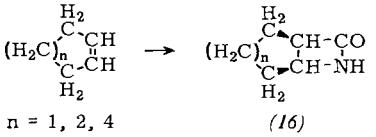
addition with high stereoselectivity. *cis*-2-Butene gives 98–99 % pure *cis*-α-methyl-β-butyrolactam *(14)*. The *trans*-lactam *(15)* having a similar degree of purity can be obtained from trans-2-butene. The α and β carbon atoms in these lactams are centers of unlike asymmetry. Consequently both lactams are formed as racemates. It should be possible to synthesize isotactic poly-β-amides having two centers of chirality in the structural unit from the antipodes (see Section 5).



(14)



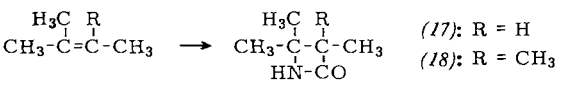
(15)



n = 1, 2, 4 *(16)*

When cyclic olefins of medium ring size are used in this synthesis, bicyclic β-lactams *(16)* with *cis* ring fusion are obtained. These compounds are interesting models for the synthesis of poly-β-amides, in which the mobility of the chain unit is restricted by bridging at the α and β carbon atoms.

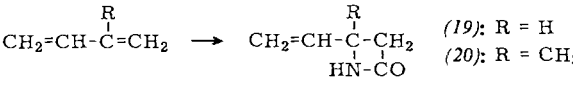
β-Lactams with three and four methyl groups [*(17)*, *(18)*] can be obtained readily and in excellent yields by the Graf method from 2-methyl- and 2,3-dimethyl-2-butene.



(17): R = H
(18): R = CH_3

In the methyl-substituted butenes, the π electrons are more readily available for nucleophilic attack on the isocyanate than in butene. In spite of the steric hindrance due to the methyl groups, the addition of the isocyanate proceeds rapidly and in high yield at room temperature.

The last β-lactams examined for the synthesis of poly-β-amides are the vinyl-β-lactams *(19)* and *(20)*.



(19): R = H
(20): R = CH_3

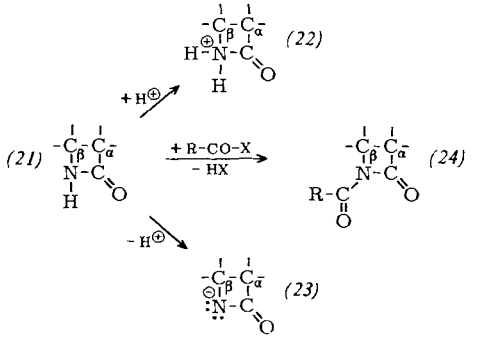
All the β-lactams mentioned here are quite stable, in spite of the strained ring. They can be purified by distillation or crystallization to the degree required for the synthesis of high molecular weight compounds. The IR spectrum shows a strong carbonyl band at 5.7 μm. γ- and δ-Lactams absorb at 5.9 μm.

The new β-lactams mentioned do not include the unsubstituted ring, β-propiolactam. This compound has not so far been obtained by the Graf method owing to the low reactivity of ethylene. β-Propiolactam, which was first obtained by *Holley*[11] from esters of β-alanine in a yield of 0.7 %, was prepared by a new method in sufficient quantities for the study of poly-β-alanine synthesized by the lactam route. The new synthesis begins with the ester of *N*-benzyl-β-alanine, which is readily obtainable from acrylic esters and benzylamine. Cyclization of this ester with ethylmagnesium bromide gives *N*-benzyl-β-propiolactam, which is converted into the unsubstituted β-propiolactam by reductive removal of the benzyl residue with sodium in liquid ammonia. The overall yield is 50 %.

4. Polymerization of the β-Lactams

With the synthesis of β-lactams having no substituents on the nitrogen, it became possible to prepare high molecular weight poly-β-amides[12]. The ring strain in the β-lactams facilitated the opening of the ring at the amide linkage. The head-to-tail linkage of these four-membered structural units leads exclusively to open-chain products and not to cyclic oligomers, which would hinder the formation of the high molecular weight compounds. It follows as a necessary consequence of the high ring strain in the β-lactams that the monomer ⇌ polymer equilibrium for β-lactams can be disregarded, in contrast to the corresponding equilibrium for the homologous lactams having five-, six-, and seven-membered rings. No reformation of the β-lactam ring by depolymerization of the poly-β-amides has been observed.

Since the ring opening has a decisive effect on the course of the polymerization, the β-lactam ring structures involved in the polymerization will now be discussed (Scheme 2).



Scheme 2. β-Lactam ring structures involved in the polymerization.

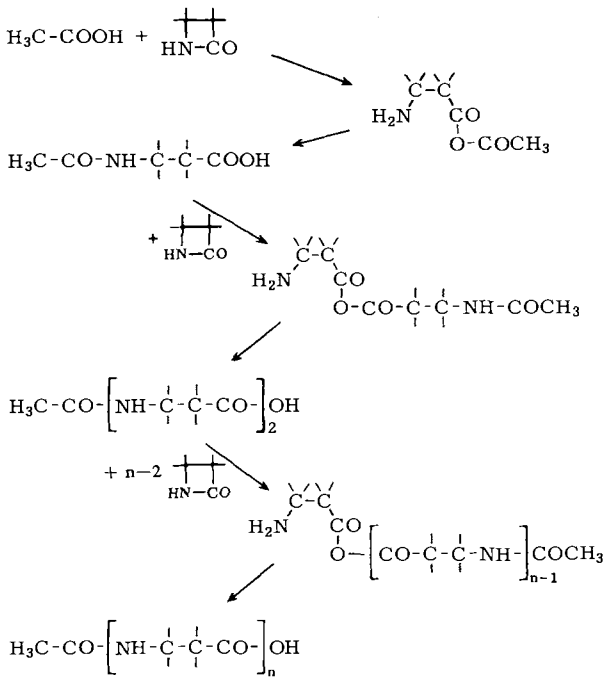
The ring opening in acid polymerization can be best interpreted by protonation on the nitrogen. Cleavage then takes place in the onium form *(22)* of the amide linkage. To initiate the alkaline polymerization, the lactamate anion *(23)* must be formed. The β-lactam ring in the lactamate structure, in contrast to that in the onium structure, is stable. The lactams *(21)*, and especially *(24)*, are opened on nucleophilic attack of the lactamate anion *(23)* at the amide bond (see Section 4.1.).

The acid induced polymerization proceeds as a stepwise polyaddition, as can be shown for the case of

[11] *R. W. Holley* and *A. D. Holley*, J. Amer. chem. Soc. *71*, 2129 (1949).

[12] *R. Graf*, *G. Lohaus*, *K. Börner*, *E. Schmidt*, and *H. Bestian*, Angew. Chem. *74*, 523 (1962); Angew. Chem. internat. Edit. *1*, 481 (1962).

acetic acid (Scheme 3). When stoichiometric quantities of acid and lactam are used, the resulting mixture contains the acetylamino acid together with large quantities of the oligomeric compounds containing two, three, and four monomer units.



Scheme 3. Polyaddition of β-lactams to acetic acid.

To explain the course of the reaction, it may be assumed that the addition of acetic acid leads to the formation of the mixed amino acid anhydride, which immediately changes into the acetylamino acid. Further reaction with unreacted lactam leads, again *via* the anhydride, to the stepwise formation of the oligomeric β-amino acids. The mixture of the oligomeric β-amides can be separated by esterification followed by vacuum distillation. This provides a convenient method for the preparation of the dimeric and trimeric compounds in reasonable quantities, and can be used with a wide variety of starting materials.

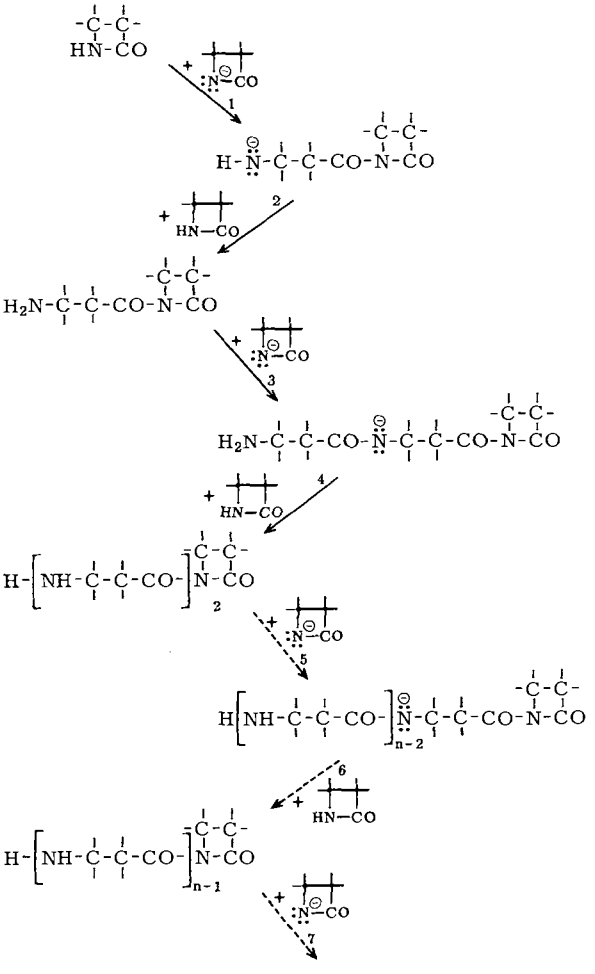
It was to be expected that when the β-lactams were allowed to react at 100 to 150 °C with less than the stoichiometric quantity of carboxylic acid, poly-β-amides having high degrees of polymerization would be formed in accordance with the polyaddition scheme presented for the stoichiometric reaction. This is also true of the formation of poly-β-amides having medium degrees of polymerization (up to about 50). The polyaddition of β-lactams to carboxylic acids is the best method known in this range. The average molecular weight is controlled by the quantity of carboxylic acid used.

High molecular weight poly-β-amides could not be obtained by this method. The stepwise growth of the polymer molecule by addition of lactam to the carboxyl group is a slow reaction, and at very low carboxyl group concentrations, it is necessary to raise the reaction temperature. This leads to side reactions (presumably ring opening between N and C_β) which stop the growth of the polymer chain.

4.1. Anionic Polymerization

The formation of poly-β-amides with high degrees of polymerization is much more strongly favored by the use of alkaline catalysts that also accelerate the polymerization of the lactams having larger rings. Thorough investigations have shown that β-lactams are the ideal structural units for the synthesis of the desired high molecular weight poly-β-amides. The polymer molecules are formed rapidly even at room temperature, with complete consumption of the lactam present. To facilitate the dissipation of the heat of reaction, the polymerization may be carried out in solvents or diluents.

To establish the optimal polymerization procedure, systematic studies were carried out on all parameters that influence the polymerization. Kinetic measurements and planned experiments were made possible by the favorable reaction conditions and by the use of selected model compounds[12]. On the basis of these investigations, it is possible to deduce a detailed picture of the course of the polymerization (Scheme 4).



Scheme 4. Anionic polyaddition of β-lactams.

The polymerization can be best interpreted by an anionic polyaddition mechanism. An essential condition for a smooth reaction is the constant presence of lactamate anions, which may be introduced directly as alkali metal lactamates or may be formed from the β-lactams at the beginning of the reaction. The β-lactam reacts with its anion to give ring opening. The anionic intermediate formed in this relatively slow initiation reaction is protonated by the lactam in the second, fast step. This step yields the dimeric lactam, with regeneration of the lactamate anion. The same

process is then repeated with the dimeric lactam, and the polymer chain is rapidly built up in this way.

Thus there are two steps involved in the incorporation of a lactam unit into the growing polymer chain:

a) Attachment of the lactam anion to the lactam ring with ring opening (arrows 1,3,5,7....).

b) Charge transfer from the chain to the monomeric lactam with regeneration of the lactamate anion (arrows 2,4,6,....).

The charge transfer, which is very fast, can be disregarded in the kinetic study of the course of the reaction. The rate of chain growth in the individual steps is determined by the attachment of the lactam anion. While the anion is attached to the original lactam in the initiation reaction, the chains subsequently grow by attachment of the anion to acylated lactam rings. These react several orders of magnitude faster than the free lactam. Consequently, the chains grow very rapidly, whereas their initiation is retarded.

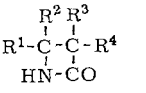
This inhibition of the initiation can be very easily eliminated by the addition of a small quantity of an acyllactam to the lactam used for the polymerization. The polymerization then proceeds almost ideally. The added acyllactam reacts very rapidly with the lactamate anions and the chains are initiated almost simultaneously. It is thus possible to obtain a relatively narrow molecular weight distribution. The number of chain initiations corresponds to the concentration of the acyllactam; thus the course of the polymerization is controlled by the chain initiation, and the molecular weight can be adjusted to the desired range.

The reaction course indicated also provides information about the end groups. If the polymer chain is initiated from the free lactam, the product contains amino end groups, which are detected with dinitrofluorobenzene in the manner described by *Zahn* and *Rathgeber*[13]. Similarly, acylamino end groups are formed if the polymerization is induced by acyllactams. The other end group is determined by the termination reactions. In the presence of small quantities of water, which is used to control the chain termination, the acyllactam group at the growing chain end is opened by a hydroxide ion, with formation of carboxyl groups.

Branching of the macromolecule could take place if an amide anion in the polymer chain reacted with the acyllactam group of a growing chain. However, our experimental findings showed no evidence of such branching processes.

As expected, the rate of chain growth depends on the number and nature of the substituents on the α and β carbon atoms of the lactam ring. According to *Hall*[14], polymerization of the five-membered ring lactam pyrrolidone is prevented even by the introduction of a single methyl group. However, the tendency toward ring opening is so strong in four-membered ring lactams that the anionic polyaddition with formation of high molecular weight poly-β-amides proceeds even when all the hydrogen atoms on the α and β carbon atoms are substituted, though the reaction rate decreases with increasing number of substituents (Table 2).

Table 2. Qualitative comparison of the polymerizabilities of substituted β-lactams as a function of the degree of substitution.
(1 = poor, 5 = good polymerizability).



R^1	R^2	R^3	R^4	Polymerizability
H	H	H	H	5
CH_3	H	H	H	4
CH_3	CH_3	H	H	3
CH_3	H	CH_3	H	*trans*: 4
				cis: 3
CH_3	CH_3	CH_3	H	2
CH_3	CH_3	CH_3	CH_3	1

Differences in the reactivities of the various β-lactams present no special difficulties in the preparation of poly-β-amides having uniform monomer units. The fast anionic polymerization offers sufficient latitude for adjustment of the parameters that influence the polymerization rate to suit the reactivity of the lactam. On the other hand, the differences in reactivity constitute a limitation in the preparation of poly-β-amides having different structural units since it is necessary to use components having comparable polymerization rates.

This condition is adequately satisfied by the very readily obtainable β-lactams having one or two substituents. Thus homogeneous copolymers having valuable properties can be prepared from β-butyrolactam and α-methyl-β-butyrolactam. Other combinations permit the preparation of readily soluble poly-β-amides. Despite the above-mentioned restriction, the wide range of β-lactams that can be obtained by the Graf synthesis offers great scope for variation in the preparation of polyamides containing β-amino acid structural units, as in the synthesis of polypeptides from α-amino acids *via* the Leuchs anhydride.

4.2. Molecular Weight

It has already been mentioned that the anionic polymerization permits the preparation of very high molecular weight poly-β-amides having linear structures and provides fairly accurate control of the degree of polymerization over a wide range. The range covered by the molecular weights can be illustrated by the case of the polyamide formed from β-methyl-β-butyrolactam (Fig. 1)[15].

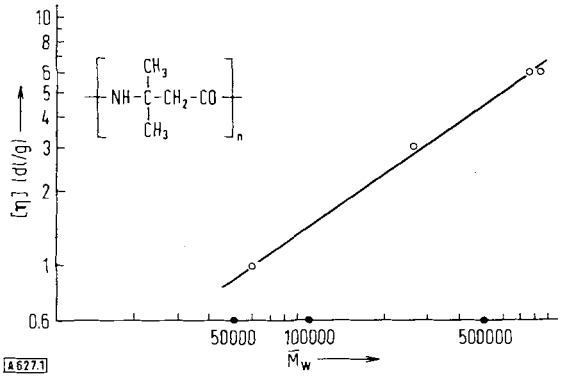


Fig. 1. Viscosity-molecular weight relationship from light-scattering measurements $[\eta] = 4.5 \times 10^{-4} \cdot \bar{M}_w^{0.7}$.

[13] *H. Zahn* and *P. Rathgeber*, Melliand Textilber. *34*, 749 (1953).
[14] *H. K. Hall*, J. Amer. chem. Soc. *80*, 6404 (1958).
[15] *E. Duch*, unpublished.

The measurements were carried out on polyamide samples whose intrinsic viscosities (dl/g in sulfuric acid) were 1 to 6. The molecular weights of these samples were found to be 60000 to about 750000. The high molecular weights are relatively easily obtainable. The lactams that recently became available from propylene, 2-butene, and butadiene gave poly-β-amides whose intrinsic viscosities of 8–10 dl/g indicate degrees of polymerization (P_w) of about 10000.

The parent substance β-propiolactam was also available for the first time for the synthesis of high molecular weight poly-β-alanine. The anionic polymerization of the propiolactam proceeds very rapidly, and conversion into poly-β-alanine is complete within a few minutes in dimethyl sulfoxide at room temperature. The intrinsic viscosity of the poly-β-alanine, which was obtained in a yield of 100 %, was 4–5, corresponding to molecular weights M_w of about 500000. This result confirmed our belief that the polymerization of lactams is also the best method for the preparation of high molecular weight poly-β-alanine.

5. Properties and Structure

The IR spectra of propiolactam and of the poly-β-alanine prepared from it (Fig. 2) show that the transition from the strained ring to the open-chain polymer results in a distinct displacement of the carbonyl stretching vibration toward longer wavelengths. The occurrence of the strong amide II band at 6.5 μm in poly-β-alanine indicates that the amide group changes from the *cis* to the *trans* configuration on opening of the ring and subsequent attachment to the macromolecule.

The properties of the poly-β-amides are mainly determined by the accumulation of the amide groups which form a tight crystal lattice as a result of hydrogen bonding. Some properties of a few of the poly-β-amides studied by us are shown in Table 3. The powder obtained from the polymerization and the films prepared from this powder give pronounced X-ray interferences, which indicate high crystallinity (see Fig. 3).

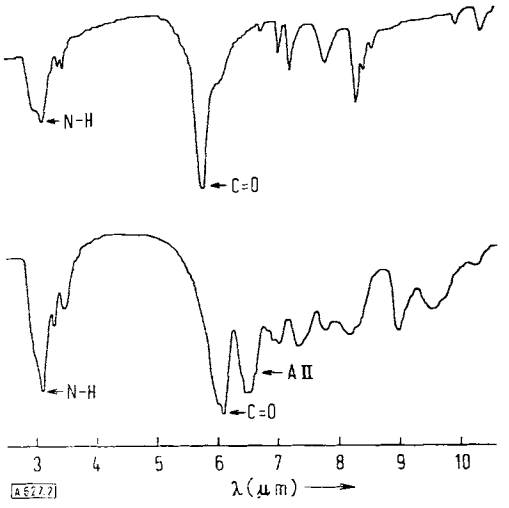


Fig. 2. IR spectra of propiolactam (top) and poly-β-alanine (bottom) in KBr. A II = amide II band.

A crystalline polyamide is obtained even from the tetramethylated monomer unit. On the other hand, bulky substituents such as a phenyl group or a propyl group together with a methyl group on the β-carbon atom lead to amorphous products.

It should be pointed out here that the melting points given are also decomposition points. They were determined by differential thermal analysis. The polymer chain is broken between the nitrogen and the β-carbon on melting of the crystal. The pyrolysis products are the amides and nitriles of the corresponding α,β-unsaturated carboxylic acids. The highly crystalline poly-β-amides are less soluble than the less crystalline polymers of this series. Hexamethylphosphoramide dissolves only a few poly-β-amides having methyl-substituted structural units. The polymers are completely dissolved by strong organic acids such as formic acid and dichloroacetic acid, and generally by sulfuric acid.

Two particularly interesting poly-β-amides have one methyl group on the α- and one on the β-carbon atom of the structural units. The carbon atoms are centers of unlike asymmetry, so that the structural unit occurs in two diastereoisomeric forms, and each of these as the racemate (see also Section 3). The poly-β-amides

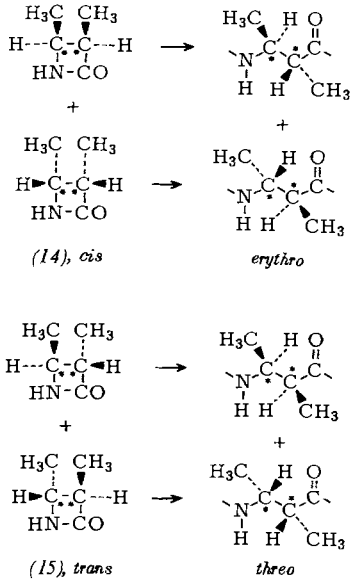
Table 3. Properties of some poly-β-amides.

Structural unit	Crystallinity	M.p. (°C) [a]	Solubility in HCO_2H	Solubility in HMPT [b]	Solubility in CH_3OH	Lattice spacings (Å)
$-NH-CH_2-CH_2-CO-$	+	340	+	–	–	d_1 4.67 d_3 3.76 d_2 4.02
$-NH-CH(CH_3)-CH_2-CO-$	+	330	+	–	–	d_1 5.27 d_3 4.37 d_2 4.74 d_4 3.35
$-NH-C(CH_3)_2-CH_2-CO-$	+	296	+	+	–	d_1 8.48 d_4 3.93 d_2 4.95 d_5 3.25 d_3 4.74 d_6 2.85
$-NH-CH(CH_3)-CH(CH_3)-CO-$						
erythro	+	405	–	–	–	d_1 6.32 d_3 3.34 d_2 4.50
threo	+	355	+	+	–	d_1 8.75 d_2 4.52
$-NH-C(CH_3)(C_3H_7)-CH_2-CO-$	–		+	+	+	

[a] Decomposition.

[b] Hexamethylphosphoramide.

built up from these *threo* and *erythro* units [16] have very different properties. The solubilities and decomposition points are given in Table 3, and the X-ray powder diagrams are shown in Figs. 3d and 3e.



The cyclic monomers were available in a very pure state both as the racemate of the *cis* form *(14)* and as the racemate of the *trans* form *(15)*. The configuration at the α- and β-carbon atoms is retained during ring opening and linking of the monomer units to form a chain. The zig-zag arrangement of the chain units is favored by the fact that the methyl groups can assume a staggered position instead of their former eclipsed position in the ring. In the *erythro* units, the methyl groups are in the *anti* position, while in the *threo* units they are in the *syn* position.

The polyamides consisting of these units differ considerably. *erythro*-Poly-β-amide is insoluble in all solvents suitable for polyamides (with the exception of concentrated sulfuric acid) whereas *threo*-poly-β-amide is readily soluble. Differential thermal analysis shows that the decomposition point of the *erythro* polymer is about 50 °C higher than that of the *threo* polymer. Since decomposition points determined by this method correspond roughly to the melting points of the crystallites, it may be concluded that the crystal lattice of the poly-β-amides formed from *erythro* units has a greater thermal stability.

The polyamides also differ in their X-ray powder diagrams (see Figs. 3d and 3e). The higher crystallinity of the *erythro*-polyamide (Fig. 3d) is shown by the sharpness of the reflections. Both polyamides give the strong outer reflection, which corresponds to a distance of 4.50 Å between the lattice planes. The difference in the crystal lattice is clear from the positions of the inner reflections. These correspond to interplane distances of 6.32 Å for the *erythro*-polyamide and 8.75 Å for the *threo*-polyamide.

[16] In agreement with the nomenclature report on steric arrangement in high polymers by *M. L. Huggins, G. Natta, M. Desreux*, and *H. Mark* [Makromolekulare Chem. *82*, 1 (1965)], we use the *threo-erythro* terminology for the two diastereoisomeric forms of the new fundamental structural unit.

The determination of the unit cell of the crystal lattice is not yet complete. Particularly in the case of *cis* lactams such as *(14)*, steric considerations point to selective linking of the units, and suggest the possibility of formation of diisotactic or disyndyotactic *erythro*-poly-β-amides. The elucidation of this problem will depend on the resolution of the *cis* lactams into their optical antipodes.

The crystal structure of the poly-β-amides is largely determined by the fundamental structural units used. The X-ray powder diagrams of the polymers are shown in Figure 3.

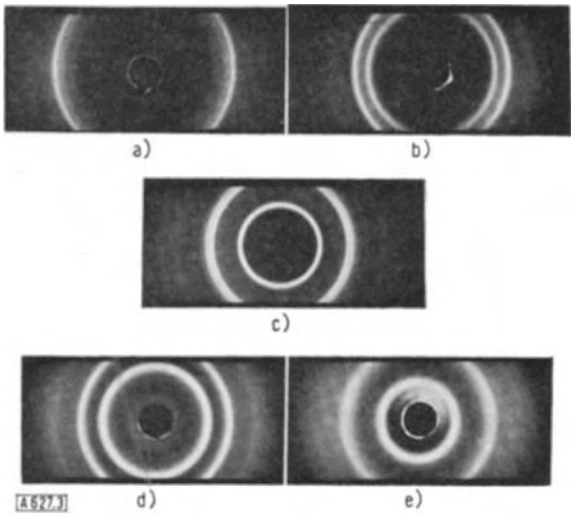


Fig. 3. X-ray powder diagrams of (a) poly-β-alanine, (b) poly-β-aminobutyric acid, (c) poly-β-valine, (d) poly-*erythro*-β-amino-α-methylbutyric acid, (e) poly-*threo*-β-amino-α-methylbutyric acid.

The polyamides having methyl-substituted structural units (Figs. 3b to 3e) are characterized by a strong outer reflection, the position of which varies only slightly. However, the inner reflection shows a wide variation of position. The polymer with the unsubstituted structural unit gives an entirely different diagram (Fig. 3a).

In the study of the lattice structure, we first considered poly-β-aminobutyric acid. Drawn films prepared from this polyamide could be used to determine the unit cell of the crystal lattice [17].

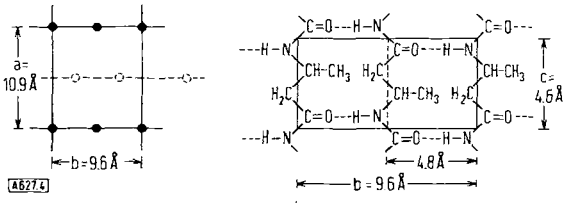


Fig. 4. Unit cell of poly-β-aminobutyric acid. The film was drawn parallel to the *c* axis.

The X-ray reflections of the drawn films lead to an orthorhombic unit cell having the dimensions given in Fig. 4. The identity period in the drawing direction, *i.e.* parallel to the *c* axis, was found to be 4.6 Å and so corresponds to the length of a β-amino acid structural unit in the almost extended polyamide chain. The IR spectrum of the film shows the perpendicular dichroism of the NH stretching vibration,

[17] *H. Scherer*, unpublished.

from which it must be concluded that the hydrogen bonds between adjacent chains are formed perpendicular to the drawing direction, *i.e.* parallel to the *b* axis in our model.

The interplane distances along the *a* and *b* axes of the lattice were determined from the equatorial reflections. The value of 4.8 Å is taken as the distance between chains linked by hydrogen bonds. This assignment is in complete agreement with the numerous investigations on polyamides and on fibroin. However, the distance between adjacent chains (4.8 Å) along the *b* axis cannot be the identity period in this direction. The orthorhombic lattice requires an antiparallel arrangement of adjacent chains, as shown in Figure 4. Thus the identity period is the distance from one chain to the next but one, and is equal to 9.6 Å.

The chains joined by hydrogen bonds form sheets. The arrangement of these sheets in the crystal lattice can be best illustrated by a section perpendicular to the drawing direction (see Fig. 4, left). In this diagram, the axes of the chain molecules appear as points. The hydrogen bonded sheets are arranged parallel to the *b* axis. The shortest distance between two identical sheets in the orthorhombic lattice was found from the X-ray reflections to be 10.9 Å.

As in fibroin, it must be assumed that a given sheet in poly-β-aminobutyric acid is identical only with the next but one, as indicated in the drawing. The unit cell then contains four β-amino acid units. The crystal density calculated on this basis agrees closely with the observed density of the film.

The unit cell of fibroin [18, 19] contains eight α-amino acid units. The main difference in the unit cells is that in fibroin identity along the polypeptide chain occurs only after a dipeptide unit 7.0 Å long, whereas in poly-β-aminobutyric acid identity occurs after one structural unit, *i.e.* after a distance of 4.6 Å.

6. Production of Filaments

The poly-β-amides are similar in structure to natural silk. The molecular weight can also be matched to that of fibroin (200000–300000) [20]. However, the problem of spinning filaments from the poly-β-amides, which are obtained in the form of powders, was not easy to solve. Melt spinning was impossible, since the melting points are high and lie in the decomposition range. The low solubility in suitable solvents makes dry spinning difficult. However, the observation that the poly-β-amides, with few exceptions, are readily soluble in formic acid or in a calcium isothiocyanate-methanol mixture led to the development of a spinning process similar to that used in industry for the production of rayon.

The spinning solutions contain 15–30 % of poly-β-amide. The precipitating bath consists of water, to which a salt is added in order to control the coagulation process. The filaments can be drawn by a factor of seven. Some of the poly-β-amides that are readily obtainable from the lactams were spun into filaments by this method and their suitability for the production of fibers was tested.

Table 4 shows the properties of filaments of two poly-β-amides, of natural silk, and of nylon 6. It is interesting to note that the filaments made from poly-β-aminobutyric acid, which are closest in structure to fibroin, are the nearest to natural silk in their properties.

Table 4. Comparison of filaments of poly-β-amides, natural silk, and nylon 6.

	Poly-β-valine	Poly-β-aminobutyric acid	Natural silk	Nylon 6
Crystallite m.p. (°C)	296	340	–	215
Density (g/cm³)	1.11	1.16	1.37	1.14
Breaking strength (g/den)	2–3	3.2–5.6	3.3–5.5	4.5–8.3
Elongation at break (%)	30–35	7–25	13–25	15–46
Moisture absorption (%)	4.5	8.6	9	4–4.5

Fibers and yarns are at present being prepared from poly-β-amides and made up into fabrics of a wide range of structures in order to test their practical application. Testing of these fabrics will show whether poly-β-amide fibers or yarns can compete successfully with conventional fibers.

I am grateful to Dr. H. Biener, Dr. E. Duch, Dr. E. Höroldt, Dr. H. Jensen, Dr. W. Rupp, Dr. H. Scherer, and Dr. E. Schmidt for their assistance and for valuable unpublished information.

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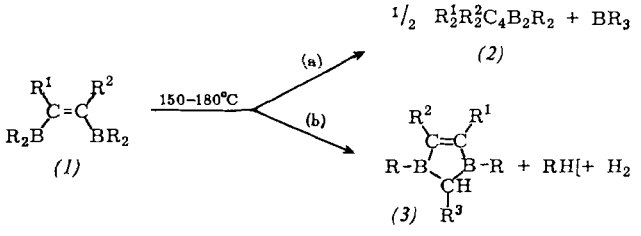
Formation of Boron Heterocycles from Vicinally Diborylated *cis*-Alkenes at High Temperatures

By *P. Binger* [*]

When vicinally diborylated *cis*-alkenes *(1)* [1] are heated, various boron heterocycles are formed, as in the pyrolysis of alkyl- and aralkylboranes [2].

Depending on the alkyl substituents on the carbon (R^1, R^2), *(1)* may disproportionate (path (a)) to give trialkylboranes

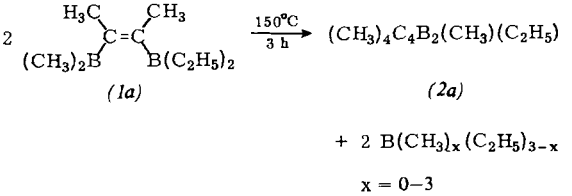


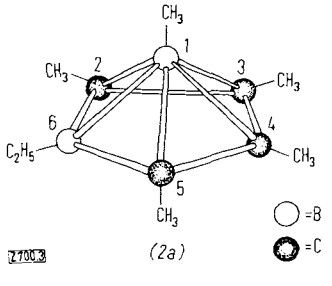
R	R^1	R^2	Temp. (°C)	Time (h)	Amount consumed (%)	(2) Yield (%)	(2) B.p. (°C/torr)	(3) Yield (%)	(3) B.p. (°C/torr)
CH_3	CH_3	CH_3	150	3	100	95	78/12	—	—
C_2H_5	C_2H_5	CH_3	160	5	80	55	123/12 [a]	35 ($R^3 = CH_3$)	92/12
C_3H_7	C_3H_7	CH_3	160	5	88	70	$59/10^{-3}$ [a]	15 ($R^3 = C_2H_5$)	$68/10^{-2}$
C_2H_5	C_2H_5	C_2H_5	160	5	60	1	$85/10^{-2}$	90 ($R^3 = CH_3$)	99/12

[a] Mixture of isomers.

and peralkylated 2,3,4,5-tetracarbahexaboranes(6) *(2)* [3], or it may react by path (b) to give peralkylated 1,3-diboracyclopent-4-enes *(3)* together with ethane ($R = C_2H_5$) or alkane, alkene, and hydrogen ($R > C_2H_5$, *e.g.* C_3H_7). Both reactions are irreversible.

Of the two possible isomeric tetracarbahexaboranes(6) that could be formed from the *B*-diethyl-*B'*-dimethyl-*C,C'*-dimethyl compound *(1a)* ($\nu_{C=C}$: 1555 cm^{-1}), the 1-methyl-6-ethyl compound *(2a)* (b.p. 93 °C/12 torr) is formed in 90% yield. Small quantities of the 1,6-dimethyl and 1,6-diethyl derivatives are also formed. No ring formation leading to *(3)* takes place.

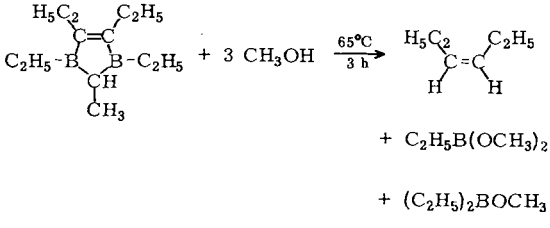




In the skeleton of *(2)*, the four C atoms and the two B atoms form a pentagonal pyramid with a boron atom at the apex [3]. The protons of the *B*-alkyl groups give ^1H–NMR signals whose τ values are characteristic of the position of the substituents: B(1)–CH_3, $\tau = 10.69$ (s); B(1)–C_2H_5:$\tau = 9.88$ (q,$J = 6.5$ Hz), $\tau = 9.36$ (t,$J = 6.5$ Hz); (B6)–CH_3:$\tau = 9.70$ (s); B(6)–C_2H_5:$\tau = 8.90$ (methylene and methyl protons give one signal). The IR and Raman spectra contain no absorption bands for C=C bonds.

The structure of *(3)* is found from the ^1H–NMR and IR spectra in conjunction with mass-spectrometric analysis; *e.g.* for 1,3,4,5-tetraethyl-2-methyl-1,3-diboracyclopent-4-ene: ^1H–NMR signals of the group $\diagdown\!\!\diagup CH-R^3$:$\tau = 8.30$ ($\diagdown\!\!\diagup CH-$, q,$J = 6.5$ Hz), $R^3 = CH_3$: $\tau = 8.80$ (d,$J = 6.5$ Hz); IR spectrum : $\nu_{C=C}$:1525 cm^{-1}; mass spectrum : molecular weight 190, with two boron atoms.

The compounds *(2)* and *(3)* differ considerably in their chemical behavior. In contrast to *(2)* [3], *(3)* is readily solvolyzed by water, alcohols, or carboxylic acids. Complete alcoholysis results in cleavage of both $BC_{alkenyl}$ bonds and of one $BC_{alkylidene}$ bond with formation of alkoxyalkylboranes and the same *cis*-alkenes as are obtained from *(1)* [1], *e.g.*:



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Chlorophyll-Water Interaction [1]

By *J. J. Katz* and *K. Ballschmiter* [*]

It has long been appreciated that chlorophyll and water have a special relationship [2–4], but the details of the interaction have remained unexplained. Recent IR [5] and NMR [6] investigations have shown that the central magnesium atom of chlorophyll has a coordination number that is always larger than 4, and is generally 5 [7]. In electron-donor solvents, chlorophyll occurs as a monomer with solvent molecules in an axial position. In nonpolar solvents, the coordination unsaturation of the magnesium is relieved either by interaction with nucleophiles [7] or by coordination of the ketone oxygen function of one molecule of chlorophyll with the

magnesium atom of another to form chlorophyll dimers. Water can act as a nucleophile and coordinate to the magnesium of chlorophyll, but the consequences of such an interaction depend on the concentration and on the type of nonpolar solvent used.

In the nonpolar solvents CCl_4, $CHCl_3$, or benzene, which are expected to be good solvation agents for the porphyrin ring, water acts as a nucleophile and disaggregates chlorophyll dimers (at concentrations of chlorophyll less than about 10^{-2} M) to Chl·H_2O or Chl·$2H_2O$. The extent to which disaggregation occurs is limited at higher chlorophyll concentrations because of the limited solubility of water in these solvents. In hydrocarbon solvents, such as cyclohexane, alkylcyclohexanes, dodecane, or hexadecane, which are generally poor solvating agents, but which could be expected to solvate strongly the phytyl chain of chlorophyll, the consequence of chlorophyll-water interaction below about 10^{-5} M is disaggregation; however, in more concentrated solutions chlorophyll-water micelles of colloidal dimensions, in which water coordinated to magnesium acts as the aggregating agent, are formed.

The IR spectra of chlorophyll *a* in the various nonpolar solvents are shown in Table 1. In all solvents the IR spectrum of dry chlorophyll characteristically shows an aggregation peak at 1650–1660 cm^{-1} as well as the free keto carbonyl at 1695 cm^{-1} [8]. Hydrated chlorophyll in CCl_4, $CHCl_3$, or benzene shows essentially the same spectrum with increased absorption at 1695 cm^{-1}, which is indicative of some disaggregation. In aliphatic solvents, however, a strong absorption peak at 1638 cm^{-1} is seen, whereas the absorption at 1695 cm^{-1} is very weak. We assign the peak at 1638 cm^{-1} to the Ring V ketone oxygen which is hydrogen-bonded to water coordinated to the central magnesium of another chlorophyll molecule: C=O···H–O(H)···Mg. Studies with models show that a water molecule coordinated to a magnesium atom can be so oriented as to form simultaneously a hydrogen bond to the ketone oxygen and to the methoxycarbonyl group of another chlorophyll molecule. The split ester peaks in the IR spectrum, as well as absorption maxima in the O–H stretching region, provide support for the feasibility of such an interaction. In pheophytin, the Mg-free chlorophyll derivative, only very slight changes in the IR spectrum are noted on the addition of water to a solution of the compound in an aliphatic hydrocarbon solvent. Obviously the H_2O-chlorophyll interactions discussed here require the presence of Mg.

Water interaction with chlorophyll in aliphatic solvents can thus, by repetition, build up aggregates in which the chlorophyll molecules are stacked parallel to one another with their phytyl chains immersed in the hydrocarbon solvent and with water molecules sandwiched between the rings. The formation of colloidal aggregates in hydrocarbon solvents is established by the results obtained from two independent lines of investigation: Neither dry chlorophyll in dry nonpolar solvents nor hydrated chlorophyll dissolved in CCl_4, or benzene, can be sedimented – even by continued ultracentrifugation. However, hydrated chlorophyll, dissolved in butylcyclohexane or hexadecane, is completely sedimented by ultracentrifugation at 130000 *g* for 30 minutes. In cyclohexane solution, sedimentation of hydrated chlorophyll at 130000 *g* occurs to only a limited extent – even after 14 hours of centrifugation – indicating smaller aggregate size in this solvent. X-ray diffraction of chlorophyll-water aggregates in hydrocarbon solvents reveals the presence of ordered arrays, whereas solutions of dry chlorophyll in hydrocarbon solvents show no X-ray reflections. A 5×10^{-3} M solution of hydrated chlorophyll in butylcyclohexane, dodecylcyclohexane, or hexadecane gives a sharp X-ray diffraction line corresponding to a 7.5 Å spacing. This distance is very close to that estimated from models for the Mg–Mg distance in two parallel chlorophyll molecules separated by a water molecule.

Earlier workers [3,4c] realized that there is a direct relationship between the visible absorption spectra and the extent of chlorophyll hydration. This can now be recognized explicitly as a correlation between λ_{max} (red) and the presence of (Chl–H_2O) aggregates. The red-shift exhibited by chlorophyll-water aggregates thus raises the question of possible relationships between (Chl–H_2O) micelles and the long-wavelength forms of chlorophyll known to occur in living plants.

Table 1. Infrared spectra in the region 1800–1600 cm^{-1} of dry and hydrated chlorophyll *a* in (A) CCl_4, $CHCl_3$, or benzene and (B) aliphatic or cycloaliphatic hydrocarbons. (Figures in cm^{-1}; vs = very strong; s = strong; m = medium; w = weak.)

State of Chlorophyll	Solvent Class	Propionic ester C=O	Methoxy-carbonyl C=O	H-bonded methoxy-carbonyl C=O [a]	Ketone C=O	Mg-coordinated ketone	H-bonded ketone [a]	Skeletal (C=C, C=N)
Dry	A	1735 (s)	1735 (s)		1698 (s)	1653 (s)		1608 (m)
	B	1737 (s)	1737 (s)		1700 (m)	1658 (s)		1608 (m)
Hydrated	A	1734 (s)	1734 (s)		1695 (s)	1652 (m)		1608 (m)
	B	1743 (s)[b]		1727 (m)	1695 (w)		1638 (vs)	1606 (m)
Dry	Film [c]	1735 (s)	1735 (s)		1690 (s)	1658 (s)		1608 (m)
Hydrated	Film [c]		1735 (s) [d]		1690 (w)		1638 (vs)	1604 (m)

[a] Three well defined peaks are seen in the O–H stretching region. A peak at 3590 cm^{-1} we assign to water coordinated to Mg: Mg···OH_2. A peak at 3460 cm^{-1}, to hydrogen-bonded methoxycarbonyl: $CH_3OC{=}O\cdots H{-}O(H)\cdots Mg$. A peak at 3280 cm^{-1}, to hydrogen-bonded ketone: C=O···H-O(H)···Mg. These assignments are entirely consistent with those made in the carbonyl region.

[b] The shift to higher frequency of the propionic ester C=O in chlorophyll-H_2O polymer suggest that this ester carbonyl function is subject to some small coordination interaction in chlorophyll dimer or chlorophyll dimer monohydrate.

[c] Dry film formed by evaporation from benzene; hydrated film formed by evaporation from cyclohexane.

[d] A broad band that includes all the ester contributions.

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[1] Based on work performed under the auspices of the U.S. Atomic Energy Commission.

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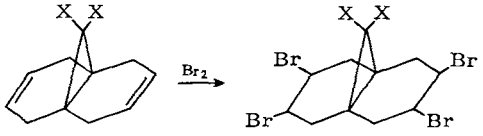
11,11-Dihalogeno-1,6-methano-[10]annulenes as Dihalogenocarbene Transfer Agents

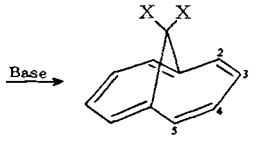
By *V. Rautenstrauch, H.-J. Scholl,* and *E. Vogel*[*]

Bridge-substituted 1,6-methano-[10]annulenes are of interest as potential generators of carbenes (thermal fragmentation to naphthalene and carbene) and as starting compounds for the preparation of benzocyclopropenes having substituents on the methylene carbon atom[1]. A carbene fragmentation of 1,6-methano-[10]annulenes[2] appears most likely to be possible when the carbene to be formed is stabilized by two halogen atoms. The present communication deals with the synthesis and thermal behavior of 11,11-difluoro-, 11,11-dichloro-, and 11,11-dibromo-1,6-methano-[10]annulene, *(3a)* to *(3c)*.



(1a), X = F
(1b), X = Cl
(1c), X = Br

(2a), X = F
(2b), X = Cl
(2c), X = Br



(3a), X = F
(3b), X = Cl
(3c), X = Br

These 11,11-dihalogeno-1,6-methano-[10]annulenes were obtained by bromination of the adducts *(1a)–(1c)* of dihalogenocarbenes[3] to the central double bond of 1,4,5,8-tetrahydronaphthalene and treatment of the resulting tetrabromides *(2a)–(2c)* (probably mixtures of stereoisomers) with bases.

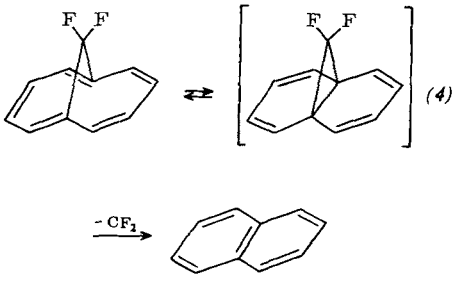
The tetrabromide *(2a)* could be smoothly dehydrobrominated by heating with methanolic potassium hydroxide; 11,11-difluoro-1,6-methano-[10]annulene *(3a)* was formed in 80% yield as a stable yellow compound having m.p. 122–123 °C. The structure of *(3a)* was established from the spectral data. The ^{1}H–NMR spectrum (CCl_4), as expected, contains an AA'BB' system at relatively low field strengths, centered at $\tau = 2.92$, ($\tau_{2,5} = 2.83$, $\tau_{3,4} = 3.02$; $J_{23} = 9.8$, $J_{34} = 8.9$, $J_{24} = -0.2$, and $J_{25} = 1.3$ Hz)[4], while the ^{19}F–NMR spectrum gives a signal at +126.2 ppm (CCl_3F as external reference)[5].

The UV spectrum [maxima at 253 ($\varepsilon = 64000$), 293 (5850), 380 (590), 389 (790), 398 (850), and 409 nm (535), in cyclohexane] is practically identical with the three-band spectrum of 1,6-methano-[10]annulene[6], except for the fine-structured longest-wavelength band, which has higher extinction coefficients for *(3a)*. Compound *(3a)* exhibits no tendency to enter into Diels-Alder reactions readily; this suggests that the energy threshold separating *(3a)* from the valence-isomeric norcaradiene form *(4)* is relatively high.

Dehydrobromination of *(2b)* gave 11,11-dichloro-1,6-methano-[10]annulene *(3b)* as yellow crystals having m.p. 104–107 °C (decomp.) in a yield of about 6% when 1,5-diazabicyclo[4.3.0]non-5-ene[7] (0 °C) was used as the base. The NMR spectrum ($CDCl_3$) of *(3b)* shows an only weakly resolved AA'BB' system at $\tau = 3.06$, which cannot be analyzed. The UV spectrum [maxima at 256 ($\varepsilon = 33900$), 280 (4720), and 388 nm (570), in cyclohexane] contains bands similar to those in the spectrum of *(3a)*, except that the extinction coefficients of the two short-wavelength bands are considerably lower. This decrease in the extinction coefficients may be due to a fast equilibrium of *(3b)* with an appreciable concentration of its norcaradiene form.

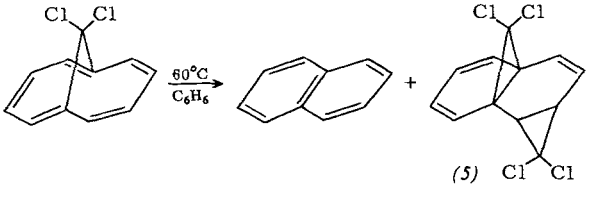
The dehydrobromination of *(2c)*, which was carried out in the same way as for *(2b)*, gave a low yield (2%) of an unstable yellow substance having m.p. 86–90 °C (decomp.), whose NMR spectrum (signal at $\tau = 3.25$ in $CDCl_3$) and UV spectrum [maxima at 259 ($\varepsilon = 23800$), 283 (5110), and 390 nm (450), in cyclohexane] indicates that it is *(3c)*.

On pyrolysis for a short time (450 °C/0.5 torr), 11,11-difluoro-1,6-methano-[10]annulene *(3a)* gave an almost quantitative yield of naphthalene, which was probably formed *via (4)*[8]. When *(3a)* was heated in an excess of cyclohexene at 250 °C (4 hours), 7,7-difluoronorcarane *(6)* was formed in 95% yield, based on reacted *(3a)*.



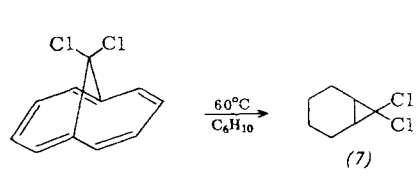
(4)

Owing to the unfavorable thermal behavior (partial decomposition and polymerization) of *(3b)*, the pyrolysis of this compound was carried out in dilute solution [approx. 0.1 M in *(3b)*] in benzene instead of in the gas phase. At 60 °C, the reaction was complete after 24 hours. The product consisted

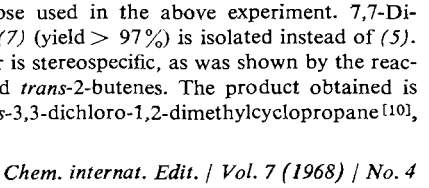


(5)

mainly of two substances (ratio 60:40), which were found to be naphthalene (main product) and an adduct of CCl_2 with *(3b)*. The product of the CCl_2 transfer, which is a colorless compound having m.p. 125–126 °C, probably has the norcaradiene structure *(5)*. The formation of *(5)* can be completely suppressed if the thermolysis of *(3b)* is carried out in benzene (again 0.1 M solution)[9] in the presence of a tenfold molar excess of cyclohexene and under otherwise identical



(6)



(7)

conditions to those used in the above experiment. 7,7-Dichloronorcarane *(7)* (yield > 97%) is isolated instead of *(5)*. The CCl_2 transfer is stereospecific, as was shown by the reaction with *cis-* and *trans*-2-butenes. The product obtained is pure *cis-* or *trans*-3,3-dichloro-1,2-dimethylcyclopropane[10],

respectively. Like *(3b)*, *(3c)* can transfer the bridge to cyclohexene in high yield (formation of 7,7-dibromonorcarane)[11].

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[1] *E. Vogel, S. Korte, W. Grimme*, and *H. Günther*, Angew. Chem. *80*, 279 (1968); Angew. Chem. internat. Edit. *7*, 289 (1968).

[2] On pyrolysis for a short time (500 °C/0.5 torr), 1,6-methano-[10]annulene gives an almost quantitative yield of benzocyclohepta-1,3,5-triene, the formation of which is explained by a Berson-Willcott rearrangement [*J. A. Berson* and *M. R. Willcott III*, J. Amer. chem. Soc. *88*, 2494 (1966)].

[3] Compound *(1a)* (m.p. 62–63 °C), which has not been described before, was obtained by reaction of 1,4,5,8-tetrahydronaphthalene with sodium chlorodifluoroacetate.

[4] The spectrum was analyzed by *W. Bremser*.

[5] We are grateful to *P. Junkes* for recording the ^{19}F–NMR spectrum.

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[8] For the formation of difluorocarbene by pyrolysis of *gem*-difluorocyclopropanes, see *B. Atkinson* and *D. McKeagan*, Chem. Commun. *1966*, 189; *J. M. Birchall, R. N. Haszeldine*, and *D. W. Roberts, ibid. 1967*, 287.

[9] Benzene had to be used as the reaction medium since *(3b)* is very sparingly soluble in cyclohexene.

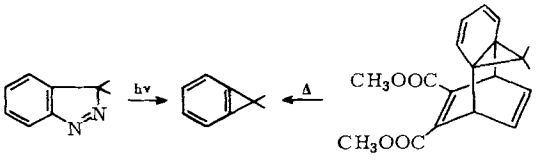
[10] It should be mentioned in this connection that the norcaradiene derivative 10,10-dichlorotricyclo[4.3.1.0]deca-2,4-diene can also transfer dichlorocarbene to olefins, though only at temperatures above 150 °C.

[11] The decomposition of a cycloheptatriene into benzene and a carbene has recently been reported by *A. P. Ter Borg, E. Razenberg*, and *H. Kloosterziel*, Recueil Trav. chim. Pays-Bas *85*, 774 (1966).

1,1-Difluorobenzocyclopropene

By *E. Vogel, S. Korte, W. Grimme*, and *H. Günther*[*]

Two methods are known at present for the preparation of benzocyclopropenes *(2)*. These are the photolysis of 3*H*-indazolines *(1)* and the pyrolysis of adducts of acetylenedicarboxylic ester with 1,6-methano-[10]annulenes *(3)*. While a number of 1,1-disubstituted benzocyclopropenes have been prepared by the first method[1], the parent compound itself has been synthesized by the second[2].

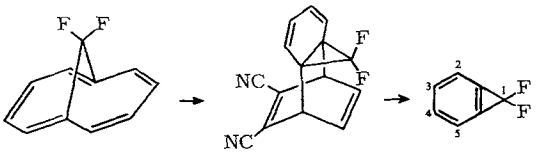


(1) *(2)* *(3)*

The availability of a large number of 1,6-methano-[10]-annulenes[2,3] with one or two substituents on the bridge led to a systematic study of the scope of the second process. Most of the bridge-substituted 1,6-methano-[10]annulenes examined so far (particularly 11-methyl-, 11-bromo-, and 11-cyano-1,6-methano-[10]annulene) gave Diels-Alder adducts of the type *(3)*, but the pyrolysis of these adducts did not lead to the desired benzocyclopropenes. The synthesis of 1,1-difluorobenzocyclopropene reported here shows that benzocyclopropenes substituted in the CH_2 group can also be obtained by this route.

11,11-Difluoro-1,6-methano-[10]annulene *(4)*[4] reacts with dicyanoacetylene at 100–110 °C (24 hours) to give a 1:1 adduct having m.p. 154 °C [yield 37%, based on reacted *(4)*]. On the basis of its spectral analogies with the 1,6-methano-[10]annulene-acetylenedicarboxylic ester adduct, the structure *(5)* is assigned to this product. The adduct *(5)* undergoes uniform and almost complete Alder-Rickert cleavage when passed through a pyrolysis tube heated at 380 °C in a high vacuum (approx. 10^{-4} torr). In addition to phthalodinitrile, there was produced a stable, colorless liquid having b.p. 33 °C/14 torr, $n_D^{20} = 1.4688$, which is the desired 1,1-difluorobenzocyclopropene *(6)*.

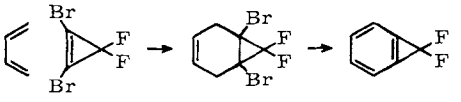
The main evidence for the structure *(6)* is provided by spectroscopic data. The UV spectrum [maxima at 242 (ε = 310), 246 (565), 252 (955), 258 (1230), and 264 nm (895) in cyclohexane] has the same shape as that of benzocyclopropene, but is displaced by about 13 nm toward shorter wavelengths. The ^1H–NMR spectrum (CCl_4) contains an AA'BB' system centered at $\tau = 2.46$, in which all the lines of the BB' part exhibit triplet splittings ($J_{H_2,F} = J_{H_5,F} = 3.4$ Hz) owing to long-range coupling with the fluorine atoms. In agreement with the ^1H–NMR spectrum, the ^{19}F–NMR spectrum[5] exhibits a triplet due to two magnetically equivalent F atoms at +80.4 ppm (CCl_3F as external reference), again with a splitting of 3.4 Hz. The equivalence of the fluorine atoms strongly suggests that the benzocyclopropene skeleton of *(6)* is planar. Analysis of the ^1H–NMR spectrum with the H,F coupling as a first order perturbation gave the values shown underneath formula *(6)* for chemical shifts and coupling constants[6]. The findings that the vicinal couplings differ appreciably in the sense $J_{23} > J_{34}$ and that J_{para}, contrary to the usual order, is greater than J_{meta} indicate that the Kekulé structure *(6)* is particularly important in the resonance hybrid of 1,1-difluorobenzocyclopropene[7]. The vicinal couplings in *(6)*, which are small compared with the *ortho* coupling in benzene (7.54 Hz)[8], evidently reflect a widening of the H–C–C angle[9], such as can be predicted for the fusion of a three-membered ring on a benzene ring. The formation of cycloheptane (85% of the hydrogenation product) on catalytic hydrogenation with platinum in glacial acetic acid (addition of sodium acetate) provides chemical evidence for the structure *(6)*.



(4) *(5)* *(6)*

$\tau_{2,5} = 2.52$, $\tau_{3,4} = 2.40$; $J_{23} = 6.7$ Hz, $J_{34} = 5.0$, $J_{24} = 0.9$, $J_{25} = 1.1$ Hz

The 1,6,7,7-tetrahalogenobicyclo[4.1.0]hept-3-enes, *e.g. (7)*, which according to *Tobey*[10] are relatively readily obtainable from dienes and tetrahalogenocyclopropenes, promise a simple route to 1,1-difluoro and possibly other 1,1-dihalogenobenzocyclopropenes. We found[11] in fact that the action of potassium hydroxide on *(7)* in triethylene glycol (at 80 °C and 14 torr) led to a liquid compound (yield approx. 40%), which was found to be identical with *(6)*.



(7)

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[1] *R. Anet* and *F. A. L. Anet*, J. Amer. chem. Soc. *86*, 525 (1964); *G. L. Closs*, Adv. alicyclic Chem. *1*, 64 (1966); *G. L. Closs, L. Riemenschneider-Kaplan*, and *V. I. Bendall*, J. Amer. chem. Soc. *89*, 3376 (1967).

[2] *E. Vogel, W. Grimme*, and *S. Korte*, Tetrahedron Letters *1965*, 3625.

[3] *E. Vogel* in: Aromaticity. Special Publ. No. 21, 113 (1967), Chemical Society, London.

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[5] We are grateful to *P. Junkes* for recording this spectrum.

[6] The assignment of the H,F coupling constants and of the resonance frequencies is based on the assumption that $J_{H_2,F} > J_{H_3,F}$.

[7] *H. Günther*, Tetrahedron Letters *1967*, 2967.

[8] *J. M. Read, R. E. Mayo*, and *J. H. Goldstein*, J. mol. Spectroscopy *22*, 419 (1967).

[9] *M. Karplus*, J. Amer. chem. Soc. *85*, 2870 (1963).

[10] *S. W. Tobey*, lecture to the Symposium International sur la Chimie des Petits Cycles et ses Applications, Louvain (Belgium) September 12–15, 1967; *D. C. F. Law* and *S. W. Tobey*, J. Amer. chem. Soc., in press. We thank Dr. *Tobey*, The Dow Chemical Company, Wayland, Massachusetts, for sending us a preprint of this article.

[11] According to experiments by *D. Schäpel*.

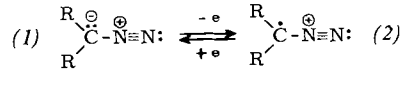
Electrochemical Oxidation of Diphenyldiazomethane[1]

By *W. Jugelt* and *F. Pragst*[*]

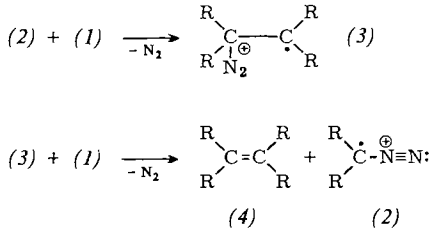
Few examples are at present known of free-radical reactions of aliphatic diazo compounds. The reaction of 9-diazofluorene with diaroyl peroxides is assumed to involve a free-radical intermediate *(2)*, R/R = fluorene residue[2]. The existence of such radical-cations *(2)*, R = C_6H_5, is demonstrated by the electrochemical oxidation of diphenyldiazomethane *(1)* which has been studied by the present authors. Diphenyldiazomethane is oxidized in a reversible diffusion-controlled one-electron process (20 °C, c = 0.05 to 0.5 mmole/l, ω = 34 to 118 sec^{-1}) at a rotating Pt disk electrode in 0.1 M $LiClO_4$/acetonitrile solution in the absence of oxygen at $E_{1/2}$ = +0.95 V (saturated calomel electrode)[3]. The reversibility of the redox process was demonstrated by means of a Kalousek switch[4] (switching frequency 12 Hz) at the rotating Pt electrode (ω = 63 sec^{-1}). The slope $dE/d[\log(i/i_d - i)]$ = 60 mV indicates a one-electron redox process. The cyclic current-voltage curve recorded at a stationary Pt electrode (rate of change of potential 400 mV/min) shows no current maximum in the cathodic branch corresponding to that in the anodic stage. It may therefore be assumed that the life of the radical-cations *(2)* formed as the primary oxidation products of *(1)* is relatively short, owing to subsequent irreversible reactions.

To study these secondary reactions, we followed the electrolysis of *(1)* under the same conditions at a constant potential (+0.95 V) at a rotating Pt electrode having a large area[5]. It was found that the quantitative decomposition of the diazo compound with liberation of N_2 requires only 15 to 4%, depending on concentration (c = 4 to 50 mmole/l), of the current required for a one-electron process. Tetraphenylethylene *(4)* is formed in 80% yield. The other electrolysis products were identified by thin layer chromatography as benzophenone *(6)*, benzopinacolone *(8)*, and benzohydrol *(9)*, R = C_6H_5 in each case. An electrochemically induced free-radical chain reaction of diphenyldiazomethane evidently takes place under these conditions.

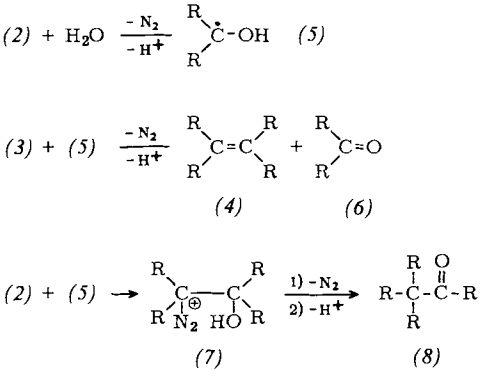
Initiation:



Propagation:

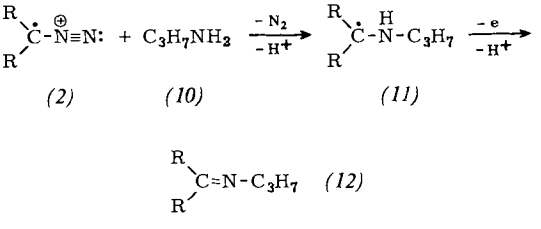


Termination:



Chain termination is caused by traces of water still present in the solution in spite of careful drying. Since the chain termination yields H^+ ions, the benzohydrol formed is probably the product of the acid-catalyzed hydrolysis of *(1)*.

The free-radical chain character of the electrochemically induced decomposition of diphenyldiazomethane is confirmed by the result of the electrolysis of this compound in the presence of an excess of *n*-propylamine *(10)*. A two-electron oxidation process can be detected coulometrically in this case. Benzophenone *n*-propylimide *(12)* was isolated as the reaction product.



The free-radical chain leading to *(4)* is obstructed under these conditions by the preferential reaction of the initially formed radical-cation *(2)* with *(10)*, which is the most nucleophilic reactant available, to give *(11)*. This free radical is then oxidized in a second step to *(12)*.

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[1] Part VII of the Structure and Reactivity of Aliphatic Diazo Compounds. Part V: *W. Jugelt* and *L. Berseck*, Tetrahedron Letters, in press.

[2] *H. Lind* and *E. Fahr*, Tetrahedron Letters *1966*, 4505.

[3] A second step of equal height, though not so well formed, is observed at +1.73 V (saturated calomel electrode).

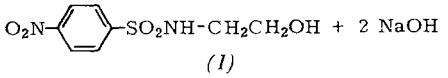
[4] *G. Schöber* and *G. Rehak*, Mh. Chem. *93*, 445 (1962).

[5] Experimental details will be given in a later publication.

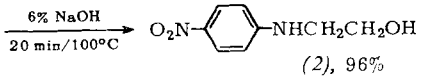
New Rearrangement of the Smiles Reaction Type

By *K. G. Kleb* [*]

N-(2-Hydroxyethyl)-4-nitrobenzenesulfonamide *(1)* reacts when heated with an excess of dilute sodium hydroxide solution to give 2-hydroxyethyl-4-nitrophenylamine *(2)*.



(1)



(2), 96%

Starting material	Rearrangement product M.p. (°C)	Yield (%)
4-O_2N–C_6H_4–SO_2–NH–CH_2–CH_2OH	110	96
4-O_2N–C_6H_4–SO_2–N(CH_3)–CH_2–CH_2OH	104	89
4-O_2N–C_6H_4–SO_2–N(CH_2–CH_2OH)$_2$	104–105	87
4-O_2N–C_6H_4–SO_2–N(C_6H_5)–CH_2–CH_2OH	106	90
4-O_2N–C_6H_4–SO_2–NH–CH_2–CH(CH_3)-OH	85–86	91
4-O_2N–C_6H_4–SO_2–NH–C(CH_3)$_2$–CH_2OH	123–124	95
2-O_2N–C_6H_4–SO_2–NH–CH_2–CH_2OH	75	8
4,5-Cl_2–2–O_2N–C_6H_2–SO_2–NH–CH_2–OH	143–144	60
2,4-(O_2N)$_2$–C_6H_3–SO_2–NH–CH_2–CH_2–OH	86	97
2-Benzothiazolyl-SO_2–NH–CH_2–CH_2OH	107	82

Derivatives with alkyl, cycloalkyl, or aryl residues on the C atoms or on the N atom of the 2-hydroxyethylamide group react in the same way. The yields are mostly very high, but the reaction time varies. Hydroxyalkylamides whose hydroxyl group is not in the β position or is sterically hindered do not react.

2-Hydroxyalkylamides of 3-nitrobenzenesulfonic acids also remain unchanged, whereas the derivatives of 2-nitrobenzenesulfonic acid react to form 2-hydroxyalkylamines. In this case, however, the yields are mostly considerably lower as a result of competing reactions. For example *N*-(2-hydroxyethyl)-*N*-methyl-2-nitrobenzenesulfonamide gives only a trace of amine when heated with an excess of dilute sodium hydroxide solution, whereas 2-methyl-3,4-dihydro-2*H*-5,1,2-benzooxathiazepine 1,1-dioxide (m.p. 118–119 °C) is formed in a yield of about 28 %.

N-(2-Hydroxyethyl)benzothiazole-2-sulfonamide and particularly *N*-(2-hydroxyethyl)-2,4-dinitrobenzenesulfonamide (m.p. 97 °C) are much more reactive. They rearrange under such mild conditions that the preparation of the pure sulfonamides with no rearrangement products requires great care.

The 2-hydroxyarylamides of 2- or 4-nitrobenzenesulfonic acid behave differently. Though they react in boiling dilute sodium hydroxide solution with elimination of the SO_2 group, the products formed are 2-aminoaryl ethers. For example, when *N*-(2-hydroxyphenyl)-4-nitrobenzenesulfonamide is heated for 2 hours in 6.5 % sodium hydroxide solution, 2-aminophenyl 4-nitrophenyl ether (m.p. 122 °C) is formed in 92 % yield.

It is only the more negatively substituted *N*-(2-hydroxyphenyl)-2,4-dinitrobenzenesulfonamide that reacts to give 2-hydroxyphenyl-2,4-dinitrophenylamine (m.p. 206 °C).

2-Aminoalkyl 4-nitrophenyl ethers cannot be obtained by the reaction of the corresponding starting compounds. They rearrange so readily into 2-hydroxyalkyl-4-nitrophenylamines that they cannot be prepared in the usual way [1].

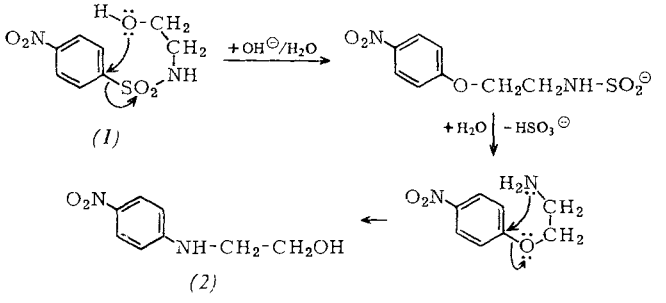
These findings show that the elimination of the SO_2 group takes place only if

1. the sulfonamide group is attached to an aromatic C atom having a strong partial positive charge and

2. there is a hydroxyl group in position 2 of an alkylamide or arylamide residue.

It may be concluded from the behavior of the 2-hydroxyphenylamides of 4- or 2-nitrobenzenesulfonic acids on the one hand and of the 2-aminoalkyl 4-nitrophenyl ethers on the other that the latter are intermediates in the reaction of the *N*-(2-hydroxyalkyl)-4-nitrobenzenesulfonamides, and that they cannot be detected only because their further reaction is faster than the rearrangement that leads to their formation.

We therefore believe that the SO_2 group is eliminated during a rearrangement in two intramolecular nucleophilic substitutions. The reaction therefore proceeds in the same manner as



(1)

(2)

the Smiles rearrangement [2] and the variants described by *Backer et al.* [3] and by *Caldwell* and *Schweiker* [4]. It is a special case, since the atoms are restored to their original order after the loss of one molecule of SO_2 by two rearrangements. The first step is also a new variant of the Smiles rearrangement.

This rearrangement may offer preparative advantages, since the starting materials are mostly readily obtainable and the operations simple to carry out. If the excess of alkali metal hydroxide is insufficient or if substances having a weakly alkaline reaction, such as sodium carbonate or ammonia, are used, side reactions take place on the nitro group as a result of the reducing action of the sulfite formed.

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[1] The compounds described by *A. Weddige*, J. prakt. Chem. (2) *24*, 247, 254 (1881), as 2-nitro- and 4-nitrophenoxyethylamine are really the rearrangement products 2-nitro- and 4-nitrophenyl-2-hydroxyethylamine (m.p. 75 and 110 °C) (see also [4]).

[2] Summary of the work of *S. Smiles*: *H. B. Watson*, Ann. Rep. Progr. Chem. *36*, 197 (1939).

[3] *H. J. Backer* and *S. K. Wadman*, Rec. Trav. chim. Pays-Bas *68*, 595 (1949).

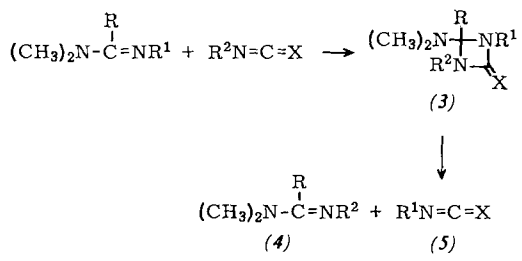
[4] *W. T. Caldwell* and *G. C. Schweiker*, J. Amer. chem. Soc. *74*, 5187 (1952).

Cycloaddition of Isocyanates and Isothiocyanates to Amidines and Guanidines

By *H. Ulrich, B. Tucker*, and *A. A. R. Sayigh* [*]

The reactivity of olefins in cycloadditions with heterocumulenes decreases in the order ketene aminal > enamine > olefin. The same relationship is to be expected for C=N double bonds, and we have confirmed this for the cycloadditions of isocyanates and isothiocyanates to amidines and guanidines.

Whereas azomethines react with isocyanates only at high temperatures [1], amidines and guanidines react with *p*-toluenesulfonyl isocyanate and 4-nitrophenyl isothiocyanate at room temperature. The 1:1 cycloadducts *(3)* can be isolated in some cases, but they often disproportionate even at room temperature to form *(4)* and *(5)*. The structures of the new



1:1 adducts *(3)* were established by elemental analysis, by fragmentation, and from spectroscopic data.

(3)

R	R^1	R^2	X	M.p. (°C)	Yield (%)
$(CH_3)_2N$	n-C_4H_9	4-$CH_3C_6H_4SO_2$	O	158–160	85.3
$(CH_3)_2N$	C_6H_5	4-$CH_3C_6H_4SO_2$	O	140–143	85

(4) *(5)*

R	R^2	M.p. (°C)	Yield (%)	R^1	X	B.p. (°C)	Yield (%)
H	4-CH_3–C_6H_4–SO_2	130–132	44	C_6H_5	O	162–163	86
$(CH_3)_2N$	4-CH_3–C_6H_4–SO_2	142–143	83.5	n-C_4H_9	O	[a]	84
$(CH_3)_2N$	4-CH_3–C_6H_4–SO_2	142–143	72	C_6H_5	O	162–163	85
$(CH_3)_2N$	4-O_2N–C_6H_4	80–82	69	n-C_4H_9	S	167	82.5

[a] Detected by titration with di-n-butylamine.

The significance of the novel exchange reaction lies in the easy transfer of the substituents R^1 and R^2. The reaction may therefore be used for the preparation of C=N double bond systems or of heterocumulenes.

Procedure:

7.88 g (0.04 mole) of p-toluenesulfonyl isocyanate is added dropwise to a solution of 6.89 g (0.04 mole) of N,N,N',N'-tetramethyl-N''-n-butylguanidine in 70 ml of benzene. The ensuing exothermic reaction yields 12.55 g (85.3%) of the 1:1 adduct *(3)*, R = $(CH_3)_2N$, R^1 = n-C_4H_9, R^2 = p-toluenesulfonyl, X = O, m.p. 158–160 °C, ν(C=O) 1639 cm^{-1}, NMR data: aryl-CH_3 protons: τ = 7.63; N–CH_3 protons: τ = 6.93 and 7.04; n-C_4H_9 protons: τ = 6.6 and 8.5–9.2; aryl protons: τ = 2.08 and 2.80; intensity ratio 3:12:9:4.

A solution of 9.2 g (0.025 mole) of the 1:1 adduct in 90 ml of o-dichlorobenzene is slowly distilled. 2.0 g (84%) of n-butyl isocyanate can be detected in the distillate by titration with di-n-butylamine. 5.6 g (83.5%) of N,N,N',N'-tetramethyl-N''-p-toluenesulfonylguanidine, m.p. 142–143 °C (lit. m.p. 143–145 °C[2]) can be obtained from the residue by digestion with ether.

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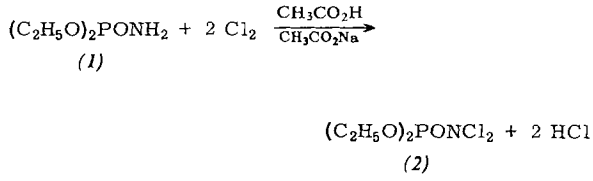
[1] *W. Merz*, German Pat. 1222042 (1966); Chem. Abstr. *65*, 13604 (1966).

[2] *A. Senning*, Acta chem. scand. *18*, 1958 (1965).

Synthesis of *O,O*-Diethyl *N,N*-Dichlorophosphoramidate and its Use for the Preparation of β-Chloro Amines from Olefins

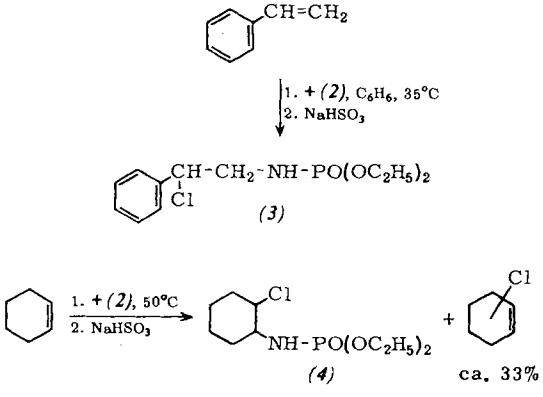
By *A. Zwierzak* and *A. Koziara*[*]

We have found that the chlorination of *O,O*-diethyl phosphoramidate *(1)* with gaseous chlorine at 15 to 20 °C in aqueous solution in the presence of acetate buffer (pH = 6.3) leads to the formation of *O,O*-diethyl *N,N*-dichlorophosphoramidate *(2)* in 85% yield. The reaction is strongly exothermic.



Compound *(2)* is a yellow, mobile liquid, which can be distilled without decomposition and is stable at room temperature, b.p. 56–57 °C/0.01 torr, n_D^{20} = 1.4620. The structure of the compound is deduced from elemental analysis, iodometric chlorine determination, and the IR spectrum [ν_{max} = 1288 cm^{-1} (P=O), 1268 cm^{-1} (P–O–C_2H_5)].

Like *N,N*-dichlorourethane[1], *(2)* readily adds to unsaturated hydrocarbons, such as styrene or cyclohexene, and forms *N*-chloro-*N*-(β-chloroalkyl)phosphoramidates, which can be readily reduced to the *N*-(β-chloroalkyl)phosphoramidates *(3)* and *(4)* by 20% aqueous sodium hydrogen sulfite

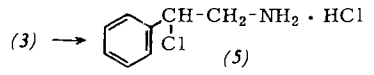


Compound *(3)* is a pale-yellow viscous oil, which was found by thin layer chromatography to be pure, b.p. = 135–136 °C/0.01 torr, n_D^{20} = 1.5097, yield 67%. IR (cm^{-1}): 3220 s (NH), 1245 s (P=O), 1170 m (P–O–C_2H_5), 1064 s, 1037 s (P–O–C as.)[2]. ^{1}H–NMR: broad singlet at τ = 2.66 (5H), triplet at τ = 5.03 (benzyl-H), J = 7.0 Hz, two quintets at τ = 6.01 and 6.05 (4H), two doublets at τ = 6.64 (2H), J_{H-CH} = 7.0 Hz, J_{H-NH} = 10.4 Hz, and a triplet at τ = 8.75 (6H), J = 6.8 Hz.

The compound *(4)* was purified by molecular distillation. It is a pale-orange viscous oil, which partly solidifies on cooling to give colorless crystals of *(4a)*; yield 7%. The yield of the noncrystallizing residue *(4b)* is 18%. *(4a)* has been identified as the pure *trans* isomer, and *(4b)* as a mixture of the *cis*- and *trans*-isomers. *(4a)*: m.p. 72–74 °C (from petroleum ether), IR (cm^{-1}): 3200 s (NH), 1250 s, 1237 s (P=O), 1168 w (P–O–C_2H_5), 1065 s, 1040 s (P–O–C as.), 739 m (C–Cl?). ^{1}H–NMR quintet at τ = 5.92 (4H), band complexes at τ = 6.6 to 7.6 (2H) and at τ = 7.5 to 8.8 (14H).

The structures of the addition products *(3)* and *(4)* were demonstrated by degradation reactions. Both compounds are

converted into the corresponding β-chloroamines *(5)* and *(6)* by the action of anhydrous hydrogen chloride in benzene at room temperature (24 hours)[3].



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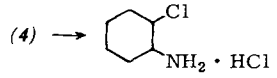

(6)

Compound *(5)* forms colorless crystals, m.p. 163–164 °C (from alcohol), yield 85 % (lit. m.p. 162–163 °C[4]).

The compound *(6a)* formed by degradation of *(4a)* is the hydrochloride of dl-*trans*-2-chlorocyclohexylamine. Colorless leaflets, m.p. 213 °C (from benzene/alcohol, 5:1), yield 50 %, IR (KBr): $\tilde{\nu}_{C-Cl}$ = 738 cm^{-1}, identical with a sample synthesized in accordance with[5].

The compound *(6b)* formed by degradation of *(4b)* is formulated as a mixture of *(6a)* and the hydrochloride of dl-*cis*-2-chlorocyclohexylamine. Colorless crystals, m.p. 183–189 °C (crude product), yield 59 %, IR(KBr): $\tilde{\nu}_{C-Cl}$ = 690 and 738 cm^{-1}. The corresponding values given in the literature are: m.p. (*cis*-isomer) 185–186 °C[6], IR (KBr): $\tilde{\nu}_{C-Cl}$ = 692 cm^{-1} (*cis*), 743 cm^{-1} (*trans*)[7].

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Tris(dimethylamino)boranetricarbonyltungsten

By *G. Schmid*, *H. Nöth*, and *J. Deberitz*[*]

Aminoboranes are potential π-donor ligands, though they behave toward iodine as amines[1]. On the other hand, the synthesis of hexamethylborazoletricarbonylchromium *(1)*[2] and of bis-(3,4-dimethyl-2,5-diphenylcyclo-1,3,4-triazadiborolyl)iron(II) *(2)*[3] shows that cyclic aminoborane systems are π donors, though X-ray structural analyses have not yet been carried out. Acyclic aminoboranes should thus also have this property.

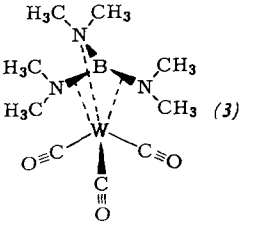
When tris(dimethylamino)borane, in analogy with[2], reacts with $(CH_3CN)_3W(CO)_3$ in dioxane for 8 hours at 80 °C or for 22 hours with frequent evacuation for short periods at 25 °C, yellow crystalline tris(dimethylamino)boranetricarbonyltungsten *(3)* is obtained in 5–10 % yield. The composition of *(3)* was verified by complete elemental analysis (with the exception of O). The crystals sublime at 30–40 °C/ 10^{-3}–10^{-4} torr; they are soluble in benzene and very sensitive to moisture. Decomposition takes place slowly at room temperature, and rapidly above 60 °C.

$$[(CH_3)_2N]_3B + (CH_3CN)_3W(CO)_3 \rightarrow [(CH_3)_2N]_3B{\cdot}W(CO)_3 + 3\ CH_3CN$$
(3)

The IR spectrum of *(3)* in *n*-pentane contains two sharp CO bands at 1930 (mw) and 1982 (s) cm^{-1}, showing that $B[N(CH_3)_2]_3$ is a stronger acceptor than hexamethylborazole. The UV spectrum in pentane consists of two broad strong bands at 28571 and 30581 cm^{-1}.

The ^1H–NMR spectrum in CCl_4 against $Si(CH_3)_4$ as the internal standard contains a single, sharp resonance line at −2.59 ppm, which is displaced by −0.09 ppm in relation to the signal of free $B[N(CH_3)_2]_3$. Thus the complex *(3)* contains magnetically equivalent N–CH_3 protons.

The ^{11}B–NMR signal of *(3)* against BF_3·ether as the external standard appears at −21.2 ppm and is displaced by +6.1 ppm in relation to the signal of $B[N(CH_3)_2]_3$. This change in the



(3)

chemical shift roughly corresponds to the difference between *(2)* and the free heterocycle[3], and is opposite in direction to the shifts of the ^{11}B–NMR signal in σ-donor complexes of aminoboranes. For example, the ^{11}B signal for $(CH_3)_2B$–N–$(CH_3)_2{\cdot}AlBr_3$ is found at −74 ppm[4], whereas that of the free aminoborane $(CH_3)_2BN(CH_3)_2$ lies at −44.6 ppm.

On the basis of these data, we postulate π-coordination of the tris(dimethylamino)borane in *(3)* with a relatively strong metal-boron interaction and $B[N(CH_3)_2]_3$ occupying three coordination sites (octahedral face).

Studies that are as yet incomplete indicate the existence of analogous complexes with other aminoboranes and other metals.

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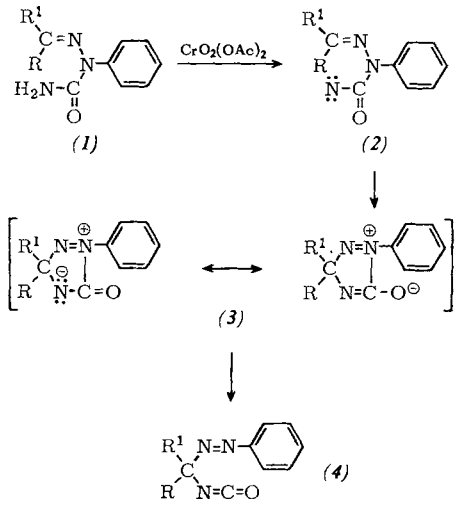
Formation of Phenylazomethyl Isocyanates on Oxidation of 2-Phenylsemicarbazones[1,2]

By *H. Schildknecht* and *G. Hatzmann*[*]

Chromyl acetate, $CrO_2(OAc)_2$[3], reacts with hydrazones of the type $R^1R^2C{=}N{-}NH{-}R^3$ with elimination of nitrogen and regeneration of the carbonyl compound from which the hydrazone is derived[4]. We found a different reaction in the oxidation of 2-phenylsemicarbazones *(1)*[5]. These are oxidized by chromyl acetate in chloroform to phenylazomethyl isocyanates *(4)*, the initially formed nitrene *(2)* presumably rearranging to the isocyanate *via* a five-membered ring *(3)*. Compound *(4)* is also formed on oxidation of *(1)* with lead tetraacetate.

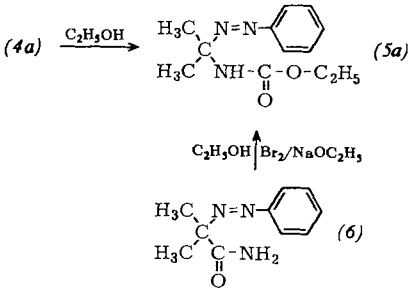
The structure of *(4)* was established by elemental analysis, from the IR spectrum [ν_{as}(N=C=O) = 2220 cm^{-1}; no NH band], and from the UV spectrum [λ_{max} in cyclohexane for



	R	R^1	B.p. (°C/torr)	Yield (%)
(4a)	CH_3	CH_3	128–30/18	66
(4b)	CH_3	C_2H_5	80–81/0.2	71
(4c)	$(CH_2)_5$		134–135/2 (m.p. 49–51 °C)	30

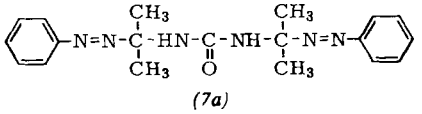
(4a): 268 nm (log ε = 4.05) and 385 nm (log ε = 2.18)], which agrees closely with the UV spectra of phenylazomethyl acetates[6] and of phenylazomethyl nitriles[7].

The reduction of *(4)* with lithium aluminum hydride again results in rearrangement, with formation of the original semicarbazone. The phenylazomethyl isocyanates react smoothly with amines to form the corresponding ureas. The addition of alcohols, on the other hand, proceeds only slowly and requires the presence of basic catalysts. *(4a)* reacts with ethanol in the presence of sodium ethoxide to give *(5a)*, b.p. 128–129 °C/0.4 torr, m.p. 53–54 °C, λ_{max} (cyclohexane): 268 nm (log ε = 3.95) and 387 nm (log ε = 2.19), IR: ν(NH) = 3350 cm^{-1} and ν(CO) = 1705 cm^{-1}.

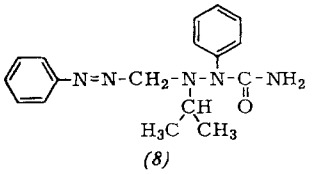


α-Phenylazoisobutyramide *(6)*[7] also gives *(5a)* on reaction with bromine and sodium ethoxide in ethanol, so that the structure of *(5a)* has also been verified by synthesis.

The reaction of *(4a)* in dioxane/water to form *(7a)*, m.p. 166–168 °C, IR: ν(NH) = 3340 cm^{-1} and ν(CO) = 1660 cm^{-1},



(7a)



(8)

also proceeds only very slowly in the absence of basic catalysts.

The analysis and the IR and UV spectra of *(7a)* indicate that it is identical with the compound obtained by *Whyburn* and *Bailey*[8] on oxidation of *(1a)* with permanganate, which these authors described as 1-isopropyl-1-phenylazomethyl-2-phenyl semicarbazide *(8)*. However, on the basis of the NMR spectrum, which contains only two singlets at τ = 3.70 (2H) and τ = 8.26 (12H) for two NH and four CH_3 groups, apart from a multiplet at τ = 2.20–2.80 (10H), the structure *(8)* must be abandoned in favor of *(7a)*. The UV spectrum in ethanol, λ_{max} = 263 nm (log ε = 4.35) and 396 nm (log ε = 2.52), in which the extinction values point to two phenylazo groups, is also in agreement with the structure *(7a)*.

Oxidation of (1):

A solution of 0.04 mole of chromyl acetate is prepared by reaction of equimolar quantities of chromium trioxide and acetic anhydride in 25 ml of anhydrous $CHCl_3$ while cooling with water (reaction time about 2 hours). The solution is added dropwise to an ice-cooled solution of 0.04 mole of the semicarbazone in 100 ml of anhydrous $CHCl_3$.The mixture is stirred for 30 min at room temperature and then hydrolyzed with 100 ml of 10 % Na_2SO_3 solution. The organic phase is washed with $NaHCO_3$ and the product is isolated by distillation.

The procedure for the oxidation of *(1)* with lead tetraacetate is similar to that described[6] for the oxidation of phenylhydrazones.

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Preparation and Properties of Tungsten Oxide Bromide, $WOBr_3$

By *J. Tillack* and *R. Kaiser*[*]

In the course of investigations on the reactions that take place in halogen lamps, we synthesized $WOBr_3$ – a compound which has not been described before.

Tungsten, tungsten trioxide, and bromine (molar ratio 2:1:4.5) in an evacuated sealed tube were introduced into a temperature gradient of 400 to approx. 40 °C in such a way that the W/WO_3 mixture was in the hot half and the bromine in the cold half of the slightly inclined tube. After about an hour, practically all the bromine had reacted to give higher tungsten bromides and oxide bromides; the contents of the tube then reacted in a temperature gradient of 450/400 °C to give $WOBr_3$:

$$2\,W + WO_3 + 4.5\,Br_2 = 3\,WOBr_3$$

A small excess of bromine (about 1 mg of bromine per ml of tube volume after complete reaction to form $WOBr_3$) prevented the formation of lower, nonvolatile bromides or

oxide bromides of tungsten, and at the same time permitted the purification of the crude product by chemical transport[1] in the same tube in a temperature gradient of *e.g.* 400/350 °C:

$$WOBr_3\,(s) + WBr_6\,(g) = WOBr_4\,(g) + WBr_5\,(g)$$

$WOBr_3$ is transported from the hot zone into the cold zone. After the transport, the gas phase (mainly WO_2Br_2 and $WOBr_4$) can be condensed in what was formerly the hotter half of the tube, and so separated from the transported $WOBr_3$. The product is freed from volatile compounds of hexavalent tungsten by heating (250 °C) under vacuum.

Owing to the reversibility of the reaction, tungsten and oxygen, or WO_2, can also react with bromine to give $WOBr_3$.

The procedure described here gave analytically pure $WOBr_3$ in the form of shiny blue-black needles 10–20 mm long, or clusters of needles, which are stable in air.

In the analysis of the product, 50–120 mg of $WOBr_3$ was heated for about 16 hours at 140 °C in an H-tube[2] with 1 volume of concentrated HNO_3 + 1 volume of H_2O: the tungsten was determined as WO_3 and the bromide as AgBr. When dry $WOBr_3$ is heated in a test tube, marked formation of WO_2Br_2 and slight formation of Br_2 are observed.

$WOBr_3$ is not appreciably attacked by concentrated hydrochloric acid, dilute or concentrated acetic acid, sodium hydroxide solution, or ammonia solution, either at room temperature or when heated. It reacts with boiling water within a few seconds to give an intensely blue solution and a dark, bulky precipitate, which has not been studied in detail. $WOBr_3$ reacts in a similar manner with ethanol (96 and 100 %), ethylene glycol monomethyl ether, and some electrolytes, such as $ZnSO_4$.

Weakly oxidizing solutions (3 % H_2O_2 in 2 N H_2SO_4, 2 N NaOH, or 2 N NH_3) have little effect on $WOBr_3$. On addition of hydrogen peroxide, however, clear colorless solutions are obtained after a short time. $WOBr_3$ is insoluble in organic solvents, such as acetone, ether, petroleum ether, chloroform, or dioxane.

The X-ray characterization of $WOBr_3$ is based on the following *d* values and estimated intensities (in parentheses) of the first reflections up to an angle of $\vartheta = 39.7°$.

8.26 (10); 7.76 (10); 5.15 (5); 4.98 (5); 3.59 (10); 3.43 (3); 2.87 (2); 2.81 (7); 2.73 (7); 2.61 (3); 2.25 (7); 2.22 (7); 2.11 (5); 1.94 (7); 1.90 (2); 1.78 (3); 1.61 (7); 1.59 (2); 1.46 (3); 1.42 (2); 1.24 (2); 1.22 (1).

The density of $WOBr_3$ as determined pycnometrically in toluene at 25.0 ± 0.1 °C is $D_{pyc,\,25\,°C} = 5.87$; $D_{X\text{-ray}} = 5.84$.

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Dirhenium Dihydratoheptoxide $Re_2O_7(OH_2)_2$ — New Type of Water Bonding in an Aquoxide[1]

By *H. Beyer*, *O. Glemser*, and *B. Krebs*[*]

Concentration of an aqueous solution of Re_2O_7 over P_2O_5 yields slightly yellow, hygroscopic crystals, which are referred to as "perrhenic acid" and formulated as $HReO_4$ (composition $Re_2O_7 \cdot H_2O$)[2,3]. Recrystallization from nitromethane gives single crystals[4], which are suitable for X-ray analysis. By such an analysis, we found that the compound corresponds to the composition $Re_2O_7 \cdot 2H_2O$, *i.e.* contains more water and exists as the molecule dirhenium dihydratoheptoxide $Re_2O_7(OH_2)_2$. It was shown in our first report[3] that, on the basis of its properties and a comparison of its simple IR spectrum with the complex spectrum of the polymeric Re_2O_7[5], "perrhenic acid" probably had a molecular structure.

$Re_2O_7(OH_2)_2$ crystallizes in the space group $P2_1/m\text{–}C_{2h}^2$. Lattice constants: $a = 8.82 \pm 0.02$ Å, $b = 8.89 \pm 0.02$ Å, $c = 5.03 \pm 0.01$ Å, $\beta = 112.0 \pm 0.3°$, $Z = 4$. The intensities were found from integrated Weissenberg and precession diagrams (measured photometrically, Weissenberg data corrected for absorption). Three-dimensional Patterson syntheses gave the positions of the rhenium atoms, and three-dimensional Fourier syntheses the positions of the oxygen atoms. Refinement by the method of least squares with isotropic temperature factors gave an *R* value of 4.6 % for the 1300 reflections observed. A final three-dimensional difference Fourier synthesis showed no maxima that could be considered as additional oxygen positions. The position parameters are given in the table. The figure shows a projection of the structure of $Re_2O_7(OH_2)_2$ parallel to [010].

Table 1. Position parameters of the atoms in $Re_2O_7(OH_2)_2$.

Atom	Multiplicity of equivalent positions	*x*	*y*	*z*
Re_1	2	0.8970	3/4	0.0356
Re_2	2	0.4454	3/4	−0.0146
O_1	2	0.654	3/4	0.011
O_2	2	0.303	3/4	−0.373
O_3	2	0.058	3/4	−0.091
O_4	4	0.934	0.903	0.266
O_5	4	0.418	0.908	0.164
$O_6(H_2O)$	4	0.778	0.905	−0.328

Since the positions of the protons could not be determined from the X-ray analysis, it was necessary to deduce the nature of the bonding of the water from the difference in the coordination of the oxygen atoms. Three formulations were considered: $Re_2O_5(OH)_4$, $Re_2O_6(OH)_2(OH_2)$, and $Re_2O_7(OH_2)_2$. The distance from rhenium to a terminal oxygen atom should be considerably smaller than the distance to an OH group or to an H_2O molecule. Only two terminal oxygen positions (O_6, O_6') per molecule had distances about 20 % greater from the octahedrally coordinated Re; it was therefore possible to decide conclusively in favor of the formulation $Re_2O_7(OH_2)_2$, which agrees with the IR spectrum and the ^1H–NMR broad-line spectrum[6].

Dirhenium dihydratoheptoxide $Re_2O_7(OH_2)_2$ is a remarkable compound. It is the first aquoxide in which coordinately bound water has been definitely detected, and the first metal aquoxide found to have a molecular structure in the solid state. The structure of the dinuclear hydratooxide is unusual. One rhenium atom is tetrahedrally surrounded by oxygen atoms, while the oxygens have a distorted octahedral arrangement around the second rhenium atom, the tetrahedral group being joined to the octahedral group by a common corner. The Re–O–Re angle is practically 180° — a rare situation. The ease of formation of the compound from Re_2O_7 is understandable from a comparison of the two structures. In Re_2O_7, one of the Re atoms is again surrounded by a tetrahedral arrangement of O atoms and the other is in a distorted octahedral environment, the two polyhedrons sharing a corner[7]. However, the resulting Re_2O_9 structural unit is linked to other units; consequently, Re_2O_7 is polymeric, in contrast to the molecular $Re_2O_7(OH_2)_2$. In the latter compound the molecules are joined to one another only by hydrogen bonds, the positions of which cannot yet be definitely established. One hydrogen bond could be

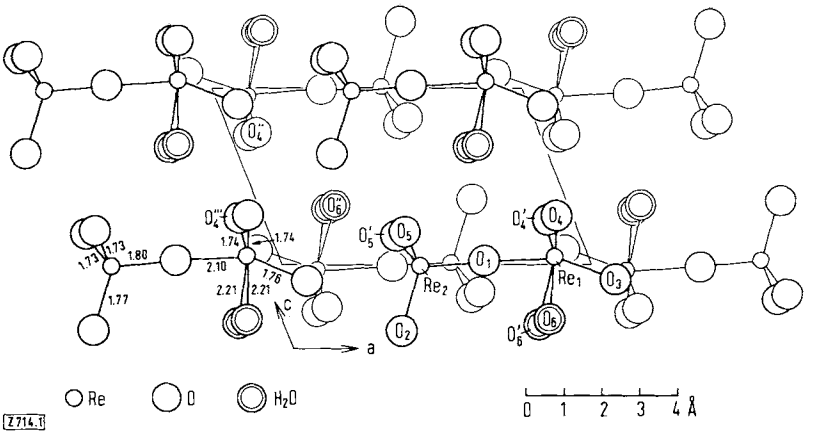

Fig. 1. Structure of $Re_2O_7(OH_2)_2$. Projection parallel to [010]. Atoms lying exactly in line are displaced slightly.

present between the atoms O_6'' and O_5' (cf. Fig. 1) and a second between O_6'' and O_4'', or between O_6'' and O_4'''. The hydrogen bonds are evidently retained in concentrated aqueous solutions of $Re_2O_7(OH_2)_2$, and this is the reason for the high viscosity of these solutions, as is the case with concentrated sulfuric and phosphoric acids. Tetrahedral ReO_4^- ions occur in dilute solution, and $ReO_3(OH)$ exists in the gaseous state [8].

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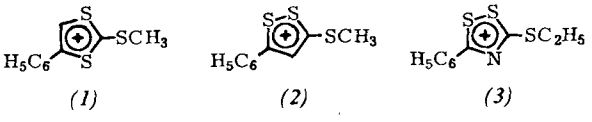
Heterofulvalenes and Azafulvenes

By *R. Gompper* and *R. Weiss* [*]

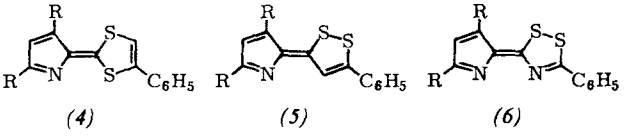
The synthesis of 3-(1,3-dithiolan-2-ylidene)indolium perchlorate from indole and 2-methylthio-1,3-dithiolanylium methyl sulfate [1] is the starting point for a simple route to the heterofulvalenes and azafulvenes [2], which have not yet been studied extensively.



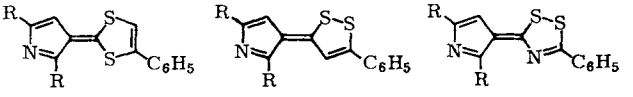
(1) *(2)* *(3)*

The reaction of dimethyl- or diphenylpyrroles with the methyl sulfates of *(1)* and *(2)* (which are prepared by heating the corresponding isotrithiones and trithiones with dimethyl sulfate) and with the fluoroborate of *(3)* (which is prepared from the corresponding azatrithione with triethyloxonium fluoroborate) proceeds at room temperature in glacial acetic acid within a few minutes (heating for 10 min is advisable in the case of the diphenylpyrroles) to give deeply colored solutions, from which crystalline perchlorates of the heterofulvalenes *(4)*–*(9)* are precipitated on addition of 70 % perchloric acid.

The free fulvalenes *(5)* and *(6)* crystallize from the solutions of the perchlorates in acetonitrile on addition of Hünig base. *(4a)* can be obtained from the perchlorate with Hünig base



(4) *(5)* *(6)*



(7) *(8)* *(9)*

(a), R = C_6H_5; *(b)*, R = CH_3

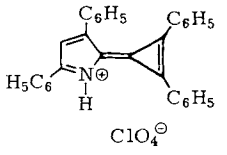
in ether. *(4b)*, *(7b)*, and *(8b)* can be stored for several hours in acetonitrile, whereas *(9b)* can be kept for only a few minutes.

Compound [a]	Yield (%)	M.p. (°C)	λ_{max} [b] (nm)	log ε	*p* [c]
(4a)		132	480	4.61	
(4a⁺)	67	241 [d]	500	4.83	
(4b)			416	4.55	0.51
(4b⁺)	89	240 [d]	432	4.52	0.51
(5a)		135	535	4.46	
(5a⁺)	40	220 [d]	517	4.59	
(5b)		130–132 [d]	482	3.93	0.50
(5b⁺)	88	256 [d]	476	4.21	0.49
(6a)		175	523	4.26	
(6a⁺)	51	245 [d]	515	4.41	
(6b)		119	468	4.13	0.50
(6b⁺)	40	245 [d]	462	4.35	0.50
(7b)			412	4.38	0.50
(7b⁺)	73	220 [d]	436	4.44	0.47
(8b)			580	3.96	0.49
(8b⁺)	45	255 [d]	468	4.23	0.49
(9b)					0.50
(9b⁺)	16	229 [d]	470	4.10	0.47

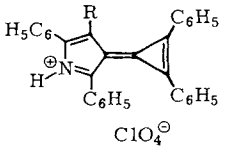
[a] (X^+) = perchlorates. [b] In acetonitrile. [c] = π-Bond order of the central C=C double bond. [d] = With decomposition.

When di- and triphenylpyrroles are heated with methylthiodiphenylcyclopropenylium perchlorate in glacial acetic acid or with dichlorodiphenylcyclopropene in acetonitrile, the

azatriafulvalenium salts *(10)*, m.p. 222 °C (dec.); $\lambda_{max}^{CH_3CN}$ = 390 nm, log ε = 4.70; $\nu_{C=C}$ = 1835 cm^{-1}, *(11a)*, m.p. 235 °C (dec.); $\lambda_{max}^{CH_3CN}$ = 372 nm, log ε = 4.18; $\nu_{C=C}$ = 1840 cm^{-1}, and *(11b)*, m.p. 205 °C (dec.); $\lambda_{max}^{CH_3CN}$ = 362 nm (shoulder), log ε = 4.09, $\nu_{C=C}$ = 1825 cm^{-1}, are obtained in yields of 79, 50, and 59% respectively. They are deprotonated to give the



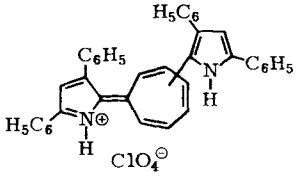
(10)



(11a), R = H
(11b), R = C_6H_5

azacalicenes *(10')* [$\lambda_{max}^{CH_3CN}$ = 384 nm, log ε = 4.63; $\nu_{C=C}$ = 1835 cm^{-1}], *(11a')* [unstable red oil], and *(11b')* [dark red solution]; *(10)* and *(11a)* by Hünig base in methylene chloride, *(11b)* by potassium *tert*-butoxide.

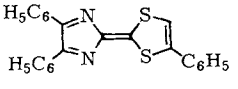
The action of tropylium perchlorate on 2,4-diphenylpyrrole under various conditions always gives a 1:2 adduct in a yield of about 15%. This adduct can be isolated as the perchlorate *(12)*, m.p. 282 °C (dec.); $\lambda_{max}^{CH_3CN}$ = 554 nm, log ε = 4.83. The free base is obtained from *(12)* with Hünig base (m.p. 279 °C; $\lambda_{max}^{CH_3CN}$ = 520 nm, log ε = 4.67). Compound *(12)* gives a red-violet anion with potassium *tert*-butoxide.



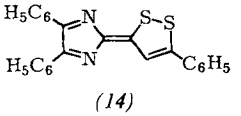
(12)

Benzoheterofulvalenes are obtained by reaction of pyrroles and indoles with the benzo-derivatives of the cations *(1)–(3)*.

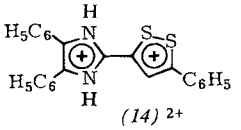
The Na salt of 4,5-diphenylimidazole, which is prepared by heating diphenylimidazole with NaH in benzene in the presence of a little diglyme, reacts surprisingly smoothly with *(1)* and *(2)* in boiling benzene to form the diazadithiafulvalenes *(13)* (red needles, m.p. 210 °C, yield 35%) and *(14)* (m.p. 205 °C; $\lambda_{max}^{CH_3CN}$ = 565 nm, log ε = 4.60; yield 49%). *(14)* forms a perchlorate [m.p. 280 °C (dec.); $\lambda_{max}^{CH_3CN}$ = 520 nm, log ε = 4.57]; reaction with an excess of perchloric



(13)



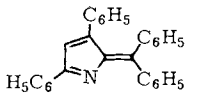
(14)



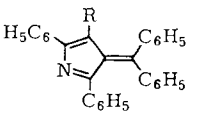
(14) $^{2+}$

acid gives the dication *(14)*$^{2+}$ ($\lambda_{max}^{CH_3CN-HClO_4}$ = 460 nm, log ε = 4.40). Compound *(13)* behaves in a similar manner.

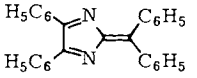
Di- and triphenylpyrroles react with benzophenone dichloride in acetonitrile at room temperature to give the azafulvenes *(15)* and *(16)*, which are isolated as the perchlorates and are deprotonated with Hünig base. In the presence of two equivalents of NaH, 4,5-diphenylimidazole reacts with benzophenone dichloride in boiling benzene to give the tetraphenyldiazafulvene *(17)*, which has already been synthesized by another route[3], and with 2-methylthio-1,3-dithiolanylium methyl sulfate to form the 6,6-dithiodiazafulvene *(18)*.



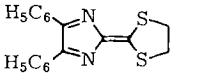
(15)



(16a), R = H
(16b), R = C_6H_5



(17)

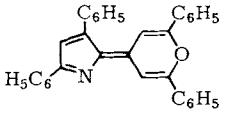


(18)

Compound [a]	Yield (%)	M.p. (°C)	λ_{max} [b] (nm)	log ε
(15)			380	4.20
(15+)	62	265 [c]	300–500 [d]	
(16a)		187	466	3.60
			347	4.12
(16a+)	80	226 [c]	550	3.76
			374	4.21
(16b)	55	208	300–450 [d]	*ca.* 4
(17)	30	174	410	4.52
(18)	30	235		

[a] (X^+) = perchlorate. [b] In acetonitrile. [c] With decomposition. [d] Broad band.

2,4-Diphenylpyrrole can be converted into the O analog *(19)* of a sesquifulvalene [m.p. 173 °C; $\lambda_{max}^{CH_3CN}$ = 490 nm, log ε = 4.64; yield 69%. Perchlorate: m.p. 306 °C (dec.); $\lambda_{max}^{CH_3CN}$ = 499 nm, log ε = 4.78] by heating in benzene with 4-methylthio-2,6-diphenylpyrylium perchlorate in the presence of one



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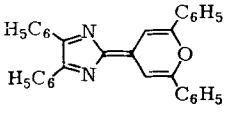

(20)

equivalent of NaH. *(20)* is obtained in the same way from 4,5-diphenylimidazole [m.p. = 227–228 °C; $\lambda_{max}^{CH_3CN}$ = 550, 518 nm. Perchlorate: m.p. 277 °C (dec.); $\lambda_{max}^{CH_3CN}$ = 507 nm. Dication: $\lambda_{max}^{CH_3CN-HClO_4}$ = 450 nm].

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[1] *R. Gompper* and *E. Kutter*, Chem. Ber. *98*, 1365 (1965).

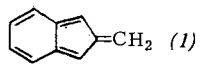
[2] Cf. *W. Rohr* and *H. A. Staab*, Angew. Chem. *77*, 1077 (1965); Angew. Chem. internat. Edit. *4*, 1073 (1965); *U. Mayer*, *H. Baumgärtel*, and *H. Zimmermann*, Angew. Chem. *78*, 303 (1966); Angew. Chem. internat. Edit. *5*, 311 (1966); Tetrahedron Letters *1966*, 5221; *H. Behringer* and *U. Türck*, Chem. Ber. *99*, 1815 (1966).

[3] *J. H. M. Hill*, J. org. Chemistry *32*, 3214 (1967).

Isobenzofulvenes

By *K. Hafner* and *W. Bauer*[*]

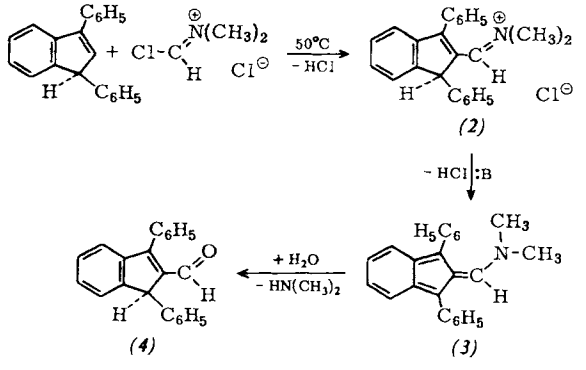
The hitherto unknown isobenzofulvenes (benzo[*c*]fulvenes) are of interest as being isosteric with isobenzofuran, isobenzothiophene, and isoindole, as well as with the still hypothetical nonafulvenes (cyclononatetraenefulvenes). Like fulvene, isobenzofulvene *(1)* should be stabilized by electron donors on the exocyclic C atom[1].



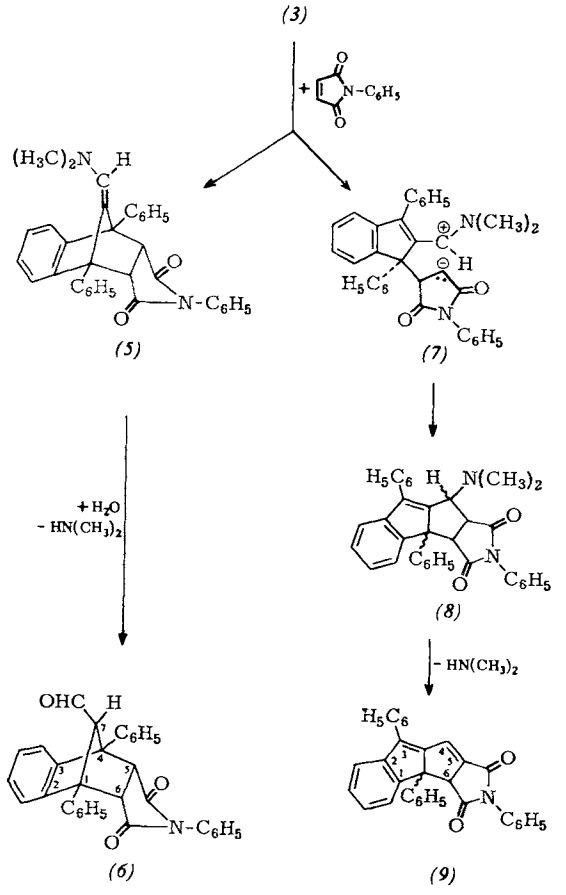
(1)

We have been able to confirm this assumption by the synthesis of *N,N*-dimethyl-*N*-(1,3-diphenyl-2-indenylidenemethyl)amine *(3)* [2].

1,3-Diphenylindene [3] reacts with chloromethylenedimethyliminium chloride in chloroform at 50 °C (about 8 days) to form *N,N*-dimethyl-*N*-(1,3-diphenyl-2-indenylmethylene)iminium chloride *(2)* in 83 % yield [light yellow crystals, dec. p. > 75 °C; UV spectrum in CH_2Cl_2: λ_{max} = 248 nm (ε = 9800), 270 (3200), 328 (11000), 379 (15400)]. The reaction of a suspension of *(2)* in ether/tetrahydrofuran (1:1) with diisopropylethylamine at −35 °C gives a deep blue solution. Removal of the solvent in a high vacuum gives *(3)* as dark blue, shiny prisms having m.p. 145–147 °C (from ether) [yield: 82 %; UV spectrum in tetrahydrofuran: λ_{max} = 250 nm (ε = 14900), 260 (14900), 339 (24800), 403 (26500), 593 (3540)]. The NMR spectrum (in $CDCl_3$ at 37 °C), which proves the structure of *(3)*, contains a singlet at τ = 2.01 (arising from the proton on the exocyclic C atom) and a multiplet centered at τ = 2.63 for the ten phenyl protons and the four protons of the fused benzene ring, as well as two singlets at τ = 6.89 and 7.36 for the two methyl groups of the tertiary amino group; in the NMR spectrum of *(3)* at 59 °C, the two signals combine to give one broad singlet at τ = 7.12.



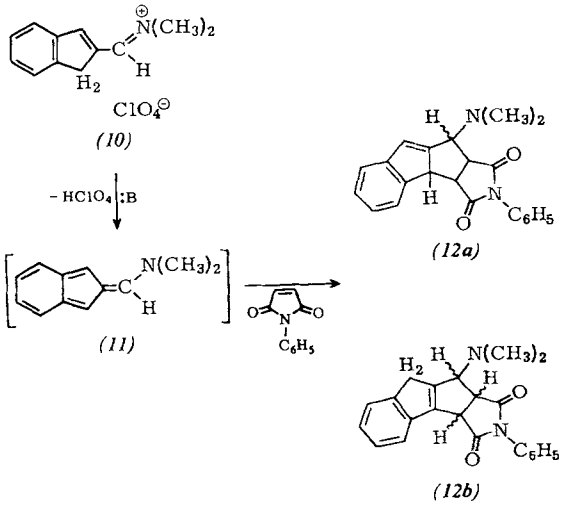
The mass spectrum of *(3)*, in addition to the molecular ion at *m/e* = 323, contains characteristic decomposition products at *m/e* = 246(M^+–C_6H_5),279(M^+–$N(CH_3)_2$), 308(M^+–CH_3) [4]. While *(3)* is stable by itself for a long time at room temperature in the absence of air, solutions of *(3)* in inert, aprotic solvents react rapidly with atmospheric oxygen to form a yellow resin; in the presence of water, *(3)* is hydrolyzed to 1,3-diphenylindene-2-carbaldehyde *(4)* [yield: 88 %; pale yellow prisms having m.p. 94–96 °C; UV spectrum in *n*-hexane: λ_{max} = 234 nm (ε = 18700), 239 (18500), 260 (8250), 265 (8100), 270 (7900), 307 (13500); NMR spectrum in $CDCl_3$: singlet at τ = 0.14 (CHO), multiplet centered at τ = 2.65 (aromatic protons), singlet at τ = 5.0 (H-1)]. Compound *(3)* combines with *N*-phenylmaleimide at 0 °C in ether/tetrahydrofuran (1:1) to form a green-yellow mixture, from which the products *(6)* [m.p. 238–240 °C; UV spectrum in dioxane: λ_{max} = 258 nm (ε = 1295), 264 (1015), 301 (75); NMR spectrum in $CDCl_3$: doublet at τ = 0.59 (*J* = 1.3 Hz) (CHO), multiplets centered at τ = 2.10 (four protons of the fused benzene ring) and at τ = 3.0 (15 aromatic protons of the three phenyl groups), singlet at τ = 5.39 (H-5, H-6), doublet at τ = 5.81 (*J* = 1.3 Hz) (H-7)] and *(9)* [m.p. 205–207 °C; UV spectrum in dioxane: λ_{max} = 222 nm (ε = 28400), 254 (22700), 375 (15800); NMR spectrum in $CDCl_3$: multiplet centered at τ = 2.47 (19 aromatic protons and H-4), doublet at τ = 6.0 (*J* = 2.6 Hz, allyl coupling, H-6)] formed by hydrolysis and by elimination of dimethylamine from the initially formed 1:1 adducts *(5)* and *(8)* could be separated by thin layer chromatography [silica gel PF_{254}, CCl_4-cyclohexane-isopropanol (30:30:1)].



The existing data are insufficient for a decision as to whether the compound *(6)* is the *exo* or the *endo* isomer. By analogy with the formation of corresponding Diels-Alder adducts of *N*-substituted isoindoles [5], the *endo* adduct *(5)* or its further reaction product *(6)* is probably formed first in the reaction of *(3)*.

The 1,3-cycloaddition to form *(8)* that accompanies the Diels-Alder reaction of *(3)* with *N*-phenylmaleimide probably proceeds by a two-step mechanism. A primary Michael addition with formation of the dipolar intermediate *(7)* is followed by the intramolecular cyclization of *(7)* to form the adduct *(8)*, which is stabilized by loss of dimethylamine to form *(9)*. A synchronous *cis* addition (1,3-dipolar cycloaddition) with formation of *(8)* [6] is incompatible with the Hoffmann-Woodward rules [7].

N,N-Dimethyl-*N*-(2-indenylmethylene)iminium perchlorate *(10)* [8] reacts with diisopropylethylamine in the same way as



the aldiminium salt *(2)*, with deprotonation. The expected *N,N*-dimethyl-*N*-(2-indenylidenemethyl)amine *(11)* has not yet been isolated as such, because of its low thermal stability.

Compound *(11)*, which is yellow-brown in solution (UV spectrum in CH_2Cl_2: λ_{max} = 364, 376 nm) reacts with *N*-phenylmaleimide at −40 °C to give a colorless 1:1 adduct having m.p. 215–216 °C. The UV spectrum (in *n*-hexane) [λ_{max} = 211 nm (ε = 28000), 217 (26000), 223 (23200), 258 (10100), 262 (9940), 267 (9000), 280 (3000), 286 (1100)] corresponds to that of an equimolar mixture of *N,N*-dimethyl-*N*-(2-indenylmethyl)amine and *N*-phenylsuccinimide, and so points to the formation of a 1,3 adduct having the constitution *(12a)* or *(12b)*; the NMR spectrum (in $CDCl_3$) of the adduct [multiplets centered at τ = 2.55 (9 H), 5.80 (3 H), 6.64 (2 H), and a singlet at τ = 7.68 (6 H)] is in agreement with a mixture of epimers of *(12b)*.

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[1] *K. Hafner, K. H. Häfner, C. König, M. Kreuder, G. Ploss, G. Schulz, E. Sturm,* and *K. H. Vöpel*, Angew. Chem. *75*, 35 (1963); Angew. Chem. internat. Edit. *2*, 123 (1963); *K. Hafner, K. H. Vöpel, G. Ploss,* and *C. König*, Liebigs Ann. Chem. *661*, 52 (1963); *K. Hafner, G. Schulz,* and *K. Wagner*, Liebigs Ann. Chem. *678*, 39 (1964); a quantum-chemical calculation of *(1)* has been carried out by *A. J. Sadlej*, Acta phys. Polon. *27*, 859 (1965).

[2] The compound *(3)* is based on 1,3-diphenyl-2*H*-indene, whose 2,2-dimethyl derivative was prepared by *K. Alder* and *M. Fremery*, Tetrahedron *14*, 190 (1961).

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[4] We are grateful to Dr. *D. Jung* for recording and discussing the NMR spectra, and to Dr. *N. Neuner-Jehle* for the mass-spectroscopic examination of *(3)*.

[5] *R. Kreher* and *J. Seubert*, Angew. Chem. *78*, 984 (1966); Angew. Chem. internat. Edit. *5*, 967 (1966).

[6] *R. Huisgen*, Angew. Chem. *75*, 742 (1963); Angew. Chem. internat. Edit. *2*, 633 (1963).

[7] *R. Hoffmann* and *R. B. Woodward*, J. Amer. chem. Soc. *87*, 4388 (1965), and earlier communications.

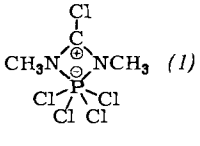
[8] *Z. Arnold*, Coll. czechoslov. chem. Commun. *30*, 2783 (1965); *(10)* can be isolated in a yield of about 50% as an intermediate in the Vilsmeier formylation of indene.

A Four-Membered Ring System Containing Hexacoordinated Phosphorus

By *H. P. Latscha* and *P. B. Hormuth*[*]

The reaction of *N,N'*-dimethylurea with phosphorus pentachloride (PCl_5)[1] in an inert solvent leads to the formation of a substance having the composition $C_3H_6Cl_5N_2P$. The compound is white, very sensitive to moisture, and melts at 129 °C after recrystallization from cyclohexane.

The ^1H–NMR spectrum in benzene against TMS as internal standard shows six equivalent methyl protons (δ = 2.67 ppm, J_{PH} = 20.8 Hz). The ^{31}P–NMR spectrum contains a signal at 202 ± 1 ppm (based on 85% H_3PO_4 as external standard), J_{PH} = 20 ± 1 Hz. This indicates a phosphorus atom having a coordination number of 6[2], and together with the elemental analysis, molecular weight, and IR spectrum, points to a 2,2,2,2,4-pentachloro-1,3-dimethyl-1,3-diaza-2-phosphonia^{VI}-cyclobutanide *(1)*.



(1)

Procedure:

1. For the preparation of *N,N'*-dimethylchloroformamidine hydrochloride see reference[1].

2. *N,N'*-Dimethylchloroformamidine hydrochloride is refluxed for five hours with PCl_5 (molar ratio 1:1) in CCl_4. The crude, slightly greenish product crystallizes out on concentration of the reaction solution. Recrystallization from anhydrous cyclohexane gives white crystals having m.p. 129 °C. The yield is almost quantitative.

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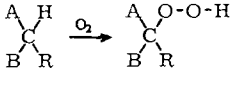
[1] *H. Ulrich* and *A. A. R. Sayigh*, Angew. Chem. *76*, 647 (1964); Angew. Chem. internat. Edit. *3*, 585 (1964).

[2] *H. P. Latscha*, Z. Naturforsch., in press.

Autoxidation of Dimedone Derivatives

By *H. Bredereck, R. Franz,* and *G. Bauer*[*]

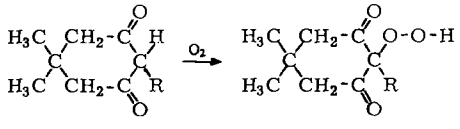
Hydroperoxides have until now been assumed to occur as intermediates in the initiation of the radical polymerization of vinyl monomers by means of CH-active compounds, atmospheric oxygen, Cu^{2+}, and Cl^-[1–3]. We have now



(1)

A and B = electron-withdrawing groups, R = H, alkyl

established their formation when dimedone derivatives are used as CH-active compounds. Dimedone hydroperoxides *(2)* were prepared for the first time by oxidation of dimedones with oxygen in benzene at room temperature.



(2)

(2), R =	Reaction time (h)	Crude yield (%)	M.p. (°C)
CH_3	12	40–50	55 (decomp.)
C_2H_5	12	35	81 (decomp.)
i-C_3H_7	12	40	116 (decomp.)
i-C_4H_9	15	30	90 (decomp.)
$C_6H_5CH_2$	2	70	119 (decomp.)

The hydroperoxides form colorless crystals that cannot be stored for long periods. They were identified by elemental analysis, iodometric titration, their reaction with lead tetraacetate, and their IR and NMR spectra.

The hydroperoxides that we have assumed to be formed during polymerization can decompose either thermally or on reaction with the cocatalysts Cu^{2+} and Cl^-[3,4]. For this reason we were able to isolate the hydroperoxides formed on autoxidation of dimedone derivatives only in the absence of these cocatalysts. In the case of benzyldimedone, however, we obtained the hydroperoxide also in the presence of Cu^{2+} and Cl^- because the extremely low solubility of the substance caused its immediate precipitation.

Procedure:

a) Reaction of the dimedone derivatives with R = CH_3, C_2H_5, i-C_3H_7, and i-C_4H_9: The dimedone derivatives (0.02 mole) are dissolved in benzene (50 ml) and shaken with oxygen at room temperature for 12–15 hours. The benzene is then distilled off in a rotary evaporator and the residue is purified by recrystallization from toluene or methanol.

b) Reaction of 2-benzyldimedone: 2-Benzyldimedone (0.03 mole) is suspended in benzene (50 ml) and, after addition of copper(II) acetylacetonate (1 mg) and lithium chloride (50mg), the solution is shaken with oxygen at room temperature for 2 hours. The starting material gradually dissolves and the hydroperoxide is obtained as a colorless flocculent precipitate that may be recrystallized from methanol.

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Tris(organometalo)phosphine-pentacarbonylchromium and -dicarbonylnitrosylcobalt

By *H. Schumann* and *O. Stelzer* [*]

The properties and reactions of organometal-substituted phosphines suggested that the "lone" pair of electrons on the phosphorus atoms is involved in bonding by way of a (p → d)π interaction between phosphorus and germanium, tin, or lead [1]. Tris(organometalo)phosphines should therefore show little, if any, tendency to function as σ-donors in transition metal complexes.

After having prepared organometalophosphinetricarbonylnickel(0) [2], we have now succeeded in synthesizing further compounds containing coordinatively tetravalent phosphorus. The tris(organometalo)phosphinedicarbonylnitrosylcobalt complexes *(1)* are obtained almost quantitatively when tricarbonylnitrosylcobalt is allowed to react with tris(trimethylsilyl)-, tris(trimethylgermanyl)-, or tris(trimethylstannyl)-phosphine in tetrahydrofuran at room temperature, with stirring, for 24 hours. They are ruby-red substances that are moderately soluble in benzene, tetrahydrofuran, and cyclohexane; they are diamagnetic and may be isolated in a high state of purity by sublimation at 80–100 °C (10^{-5} torr). Like the isosteric organometalophosphinetricarbonylnickel(0) complexes, they are stable toward atmospheric oxygen but by way of contrast are found to have a higher thermal stability than the former.

$$(CO)_3Co(NO) + [(CH_3)_3M]_3P \longrightarrow \begin{matrix} OC \\ OC \\ ON \end{matrix}\!\!>\!Co\!-\!P\!<\!\begin{matrix} M(CH_3)_3 \\ M(CH_3)_3 \\ M(CH_3)_3 \end{matrix} + CO$$

(M= Si, Ge, Sn) *(1)*

(1), M =	Decomp.p. (°C)	J [^{1}HCM^{31}P] (Hz)	νCO (cm^{-1})	νNO (cm^{-1})	νPM_3 (cm^{-1})	νCoP (cm^{-1})
Si	100	5.5	2024 1965	1742	413 389	450
Ge	132	5.3	2016 1960	1739	392 376	440
Sn	190	3.6	2008 1938	1718	352 345	438

If a solution of hexacarbonylchromium and tris(trimethylsilyl)-, tris(trimethylgermanyl)-, or tris(trimethylstannyl)-phosphine in tetrahydrofuran at room temperature is irradiated for 5 hours with UV light [3], carbon monoxide is evolved and the tris(organometalo)phosphinepentacarbonylchromium(0) complexes *(2)* are formed.

$$Cr(CO)_6 + [(CH_3)_3M]_3P \longrightarrow (CO)_5Cr\!\leftarrow\!P[M(CH_3)_3]_3 + CO$$

(M = Si, Ge, Sn) *(2)*

(2), M =	Decomp. p. (°C)	J[^{1}HCM^{31}P] (Hz)	νCO (cm^{-1})	νPM_3 (cm^{-1})	νCrP (cm^{-1})
Si	100	4.85	2058 1934 1901	424	474
Ge	150	4.7	2057 1934 1904	389	461
Sn	190	3.3	2053 1927 1898	347	458

On removal of the solvent in vacuum, yellow crystals are obtained which sublime at 60–100 °C (10^{-5} torr). With the exception of the silicon compound, they are stable toward atmospheric oxygen, and, like the analogous cobalt complexes, they have a relatively high thermal stability.

The coupling constants J[^{1}HCM^{31}P] of the complexes are in some cases considerably greater than those of the free organometalophosphines (M = Si: 4.62 Hz, Ge: 4.00 Hz, Sn: 1.95 Hz). The IR spectrum of the chromium compounds contains the three CO stretching vibrations required by C_{4v} symmetry; the vibrations are shifted only slightly toward shorter wavelengths with increasing atomic weight of M because the influence of the ligands is distributed over five CO groups [4]. The IR spectrum of the cobalt complexes *(1)* shows two CO stretching vibrations and one NO stretching vibration. As the phosphine ligands increase in size, the CO and the NO stretching vibrations are also displaced toward lower wavenumbers. In addition to the internal vibrations of the trimethylmetal groups, three further bands between 4000 and 280 cm^{-1} are to be seen in the IR spectrum of the Co complexes; we assign these to the $\nu_s PM_3$, $\nu_{as} PM_3$, and the νP–Co vibrations. The IR spectrum of the chromium compound contains two bands in this region, which correspond to the νPM_3 and the νP–Cr vibrations.

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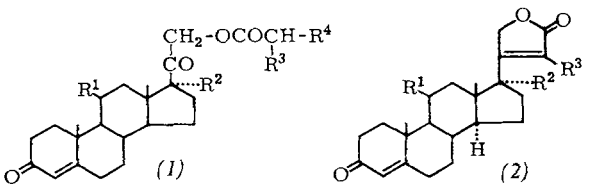
A New Cardenolide Synthesis

By *H.-G. Lehmann* and *R. Wiechert* [*]

When treated with alkali, 21-acyloxy-20-keto steroids *(1)* [1] undergo an intramolecular Wittig-Horner reaction to form cardenolides *(2)*.

Thus we were able to prepare 22-methyl-3-oxo-14α-carda-4,20(22)-dienolide *(2a)* (m.p. 243.5–245 °C, yield 51 %) by heating a mixture of 1-(3,20-dioxo-4-pregnen-21-yloxycarbonyl)ethyltriphenylphosphonium bromide *(1a)* with one equivalent of sodium hydride in dimethylsulfoxide, under



(a), $R^1 = R^2 = H$, $R^3 = CH_3$, $R^4 = P(C_6H_5)_3Br$
(b), $R^1 = R^2 = OH$, $R^3 = H$, $R^4 = P(C_6H_5)_3Br$
(c), $R^1 = R^3 = H$, $R^2 = OH$, $R^4 = PO(OC_2H_5)_2$

nitrogen, for four hours at 100 °C, pouring the mixture into acidified sodium chloride solution, filtration, chromatographic purification of the residue with hexane/acetone on silica gel, and recrystallization from ethyl acetate.

If a competing 17α-hydroxyl group is also present, it is advisable to use weaker bases. In such a case, we were able to isolate 11β,17-dihydroxy-3-oxo-14α-carda-4,20(22)-dienolide *(2b)* (m.p. 254–254.5 °C, yield 67 %) after refluxing (11β,17-dihydroxy-3,20-dioxo-4-pregnen-21-yloxycarbonylmethyl)triphenylphosphonium bromide *(1b)* with an excess of anhydrous potassium carbonate in *tert*-butanol for eight hours, working up, chromatographic purification, and recrystallization from ethanol.

On refluxing diethyl (17-hydroxy-3,20-dioxo-4-pregnen-21-yloxycarbonyl)methanephosphonate *(1c)* with an excess of potassium carbonate in *tert*-butanol for two hours, working up, and recrystallizing the product from ethyl acetate, we obtained 17-hydroxy-3-oxo-14α-carda-4,20(22)-dienolide *(2c)* (m.p. 267.5–270 °C, yield 51 %).

The UV spectrum of 17-hydroxy-3-oxo-5β,14α-card-20(22)-enolide, m.p. 240–242 °C, shows that the UV extinction coefficient $\varepsilon_{216} = 13\,300$ for the 17-hydroxy-20(22)-cardenolide system is lower than that for the corresponding 17-unsubstituted cardenolides [2]. The NMR signals for the 21-CH_2 group of the compound carrying no hydroxyl group on C-17 lie at 4.75 ppm (that of the olefinic proton on C-22 lies at 5.85 ppm), whereas the corresponding signals for 17-hydroxy-20(22)-cardenolides are to be found at 4.92 and 5.90 ppm (in $CDCl_3$ with $(CH_3)_4Si$ as internal standard).

The fact that this cyclization can also be applied to secondary ketol acylates was demonstrated by the reaction of *rac*-benzoin and 17β-hydroxy-3-methoxy-1,3,5(10)-estratrien-16-one.

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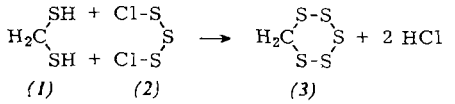
[1] The starting materials *(1)* can be obtained from 21-bromoacetoxy steroids either by converting them into the phosphonium bromides by reaction with triphenylphosphine in nitromethane or by converting them into the phosphonates by reaction with trialkyl phosphite.

[2] Cf. *N. Danieli, Y. Mazur*, and *F. Sondheimer*, Tetrahedron *23*, 715 (1967).

Synthesis of Pentathiane [1]

By *F. Fehér, B. Degen*, and *B. Söhngen* [*]

Tetrathiane (1,2,4,5-tetrathiacyclohexane) was first described a few years ago [2]; we have now succeeded in synthesizing pentathiane *(3)*. In contrast to cyclohexasulfur this compound is surprisingly stable and can be obtained relatively easily from methanedithiol *(1)* [3] and dichlorotrisulfane *(2)* [4] using the dilution technique.



(1) *(2)* *(3)*

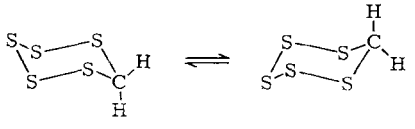
When strongly heated *(3)* is converted mainly into cyclomethyleneheptasulfane [5]. The twelve-membered ring compound 1,7-dimethylenecyclododecasulfur, which ought to be formed by a four-center reaction, could not be isolated.

Procedure:

Methanedithiol (0.1 mole) and dichlorotrisulfane (0.1 mole) are each dissolved separately in 100 ml of water-free ether. The two solutions are added at the same rate from dropping funnels to 3.5 l of water-free ether; the reaction mixture is continuously stirred during the addition, which is carried out at room temperature and over a period of 12 hours. The hydrochloric acid and insoluble polymeric products formed in the reaction are then removed from the reaction mixture, the former by passage of a stream of dry nitrogen and the latter by filtration. The filtrate is concentrated in a rotary evaporator until the appearance of a slight turbidity. Cooling of the concentrated liquor for 24 hours at −10 °C results in the precipitation of *ca.* 5.1 g (29 % yield) of a coarse crystalline product (m.p. 90–93 °C). This crude product can be purified by dissolving it, with stirring, in 1 liter of water-free methylene chloride, and working up of the resulting solution after decantation from insolubles, *i.e.* by concentration in a rotary evaporator and subsequent cooling at −10 °C. 3.5 g of pure *(3)* is obtained (pale yellow crystals, m.p. 95–96 °C).

The composition and structure of *(3)* are proved by elemental analysis, cryoscopic molecular weight determination in carbon disulfide, and by the IR spectrum (KBr disk, ν_{CH} 2950 2890; ν_{CS} 692; ν_{SS} 456, 473, 488 cm^{-1}). The mass spectrum of *(3)* shows the presence of the molecular ion at $m/e = 174$ and fragmentation ions of low intensity at $m/e = 156$, 141, 123, 127, 112, 110, 78, 76, 64, 46, and 45. The UV spectrum of *(3)*, in cyclohexane [$\lambda_{max} = 285$ nm ($\log \varepsilon = 3.12$), 244 nm ($\log \varepsilon = 3.65$)] is similar to that of cyclohexasulfur [6]. The NMR spectrum of an approx. 10 % solution in carbon disulfide recorded at 23 °C shows two doublets centered at $\delta_1 = 3.584$ and $\delta_1 = 5.373$ (referred to TMS).

Treatment as an AB system yields a coupling constant $J = 14.0$ Hz and a shift of the two nuclei towards each other of $\nu_0\delta = 160.4$ Hz. Results of investigations of the temperature dependence of the NMR spectrum suggest that the six-membered ring inverts at high temperatures:



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Preparation and Properties of Trifluorodithioacetic Acid

By *E. Lindner* and *H.-G. Karmann* [*]

Perfluorinated dithiocarboxylic acids were hitherto unknown. We have now succeeded in preparing trifluorodithioacetic acid *(3)* in fairly high yield by thiolysis of CF_3CN *(1)* with a mixture of liquid H_2S and HCl. The reaction proceeds in two stages and leads first, with evolution of a considerable

amount of heat, to trifluorothioacetamide *(2)*. On further thiolysis at 40 °C, compound *(2)* is converted into *(3)* within a period of two to three days.

$$\underset{(1)}{CF_3CN} + H_2S \xrightarrow[H_2S]{25\,^\circ C} \underset{(2)}{CF_3CSNH_2}$$

$$\underset{(2)}{CF_3CSNH_2} + H_2S + HCl \xrightarrow[H_2S]{40\,^\circ C} \underset{(3)}{CF_3CSSH} + NH_4Cl$$

The HCl present in the reaction mixture not only promotes the proton-catalyzed reaction but also serves to bind the NH_3 evolved as NH_4Cl, which being insoluble in liquid H_2S can then be readily removed.

Procedure:

CF_3CONH_2 (336 mmole) and P_4O_{10} (360 mmole) are mixed together and heated strongly. The reaction yields compound *(1)* which is collected in a cooled receiver (liquid nitrogen as coolant) and is subsequently distributed between three thick-walled tubes (each having a volume of *ca.* 75 ml). H_2S (four times the volume of *(1)*) is then condensed into the tubes, as well as 3–4 ml of HCl, and they are then sealed. In the course of the reaction that ensues when the tubes are allowed to warm to room temperature, compound *(2)* crystallizes out in the form of matted needles. Only when this stage has been reached are the tubes heated to a maximum of 40 °C, whereupon the vapor pressure of H_2S rises to 28.3 atm. Within 2–3 days, compound *(2)* is no longer visible and NH_4Cl precipitates out. The tubes are opened in an atmosphere of N_2. After evaporation of the unreacted H_2S and HCl and removal of the NH_4Cl by filtration, distillation in high vacuum (b.p. 25–30 °C/10^{-3} torr) yields the oxygen-sensitive acid *(3)* in 72 % yield (calculated with respect to CF_3CONH_2).

The composition and structure of *(3)* were established by elemental analysis and IR spectroscopic investigations (in CCl_4). The band at 2578 cm^{-1} (m) corresponds to the ν(S–H) stretching vibration, whereas the intense absorptions at 1299 (s), 1253 (vs), 1180 (vs), 1137 (s), 1115 (vs), and 1081 (m) cm^{-1} are to be attributed to the stretching vibrations of the CF_3 and the CS_2H groups. The spectrum of the deuterium compound CF_3CSSD, which is formed when *(3)* is shaken with D_2O, contains the ν(S–D) band at *ca.* 1870 cm^{-1}.

The highly viscous acid *(3)* is much more readily oxidized to the disulfide *(4)* by atmospheric oxygen than are non-fluorinated aliphatic dithio acids.

$$\underset{(3)}{2\,CF_3CSSH} + 1/2\,O_2 \rightarrow H_2O + \underset{(4)}{(CF_3CS)_2S_2}$$

The bis(trifluorothioacetyl) disulfide *(4)* is a light-yellow liquid that can be distilled in high vacuum at 80 °C/10^{-3} torr. The thermal instability of compound *(3)* is remarkable; decomposition of the acid with deposition of sulfur sets in at temperatures above 100 °C. It is readily soluble in the common organic solvents and also in alcohol when warmed (ester formation); however, it is completely insoluble in water.

If a solution of *(3)* in diethyl ether is slowly poured on to an aqueous solution of $Pb(NO_3)_2$, deep-yellow crystals of lead bis(trifluorodithioacetate) *(5)* are precipitated at the interface. When exposed to air, compound *(5)* decomposes within a few hours to a black substance (PbS).

$$\underset{(3)}{2\,CF_3CSSH} + Pb^{2+} \rightarrow \underset{(5)}{Pb(CF_3CSS)_2} + 2\,H^+$$

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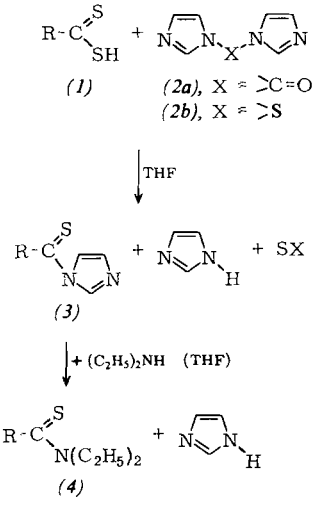
Synthesis of Thiocarboxamides by the Azolide Method

By *W. Walter* and *M. Radke* [*]

In connection with investigations on the preparative chemistry of azolides *Staab* synthesized various derivatives of thiocarbonic acids by way of *N,N'*-thiocarbonyldiimidazole [1]. The azolides have not hitherto been used for the synthesis of thioamides [2]. We have found that the reaction of dithiocarboxylic acids *(1)* with *N,N'*-carbonyldiimidazole *(2a)* or di-1-imidazolyl sulfide *(2b)* is suitable for the synthesis of the thioamides *(4)* of aromatic and aliphatic



carboxylic acids in one step without isolation of *(3)*. *N,N*-Diethylacetamide can, for example, be obtained in 28 % yield. In the reaction of *(2a)* with dithiobenzoic acid a number of by-products are formed which make the working up of the desired thioamide difficult; the reaction of *(2b)*, however, leads to the formation of pure *N,N*-diethylthiobenzamide in 49 % yield.

Birkhofer [3] prepared di-1-imidazolyl sulfide *(2b)* from *N*-trimethylsilylimidazole and SCl_2; we found that it could be prepared, in a state of purity satisfactory for the thioamide synthesis, by a method analogous to the Staab method [4].

Procedure:

a) Di-1-imidazolyl sulfide: A solution of 47.0 g (0.69 mole) imidazole in 500 ml anhydrous tetrahydrofuran (THF) is transferred to a 1-liter three-necked flask fitted with a KPG stirrer, a drying tube, and a 100 ml dropping funnel with pressure equalizer. 17.7 g (0.17 mole) of SCl_2, freshly distilled over phosphorus trichloride, is dissolved in 50 ml of anhydrous THF with vigorous stirring and then introduced dropwise into the flask over a period of 1/2 h. The mixture becomes slightly warm and turns yellow in color. After about 10 minutes a colorless precipitate separates out. After the addition of the SCl_2/THF solution is complete the mixture is stirred for a further 2 h. The precipitate is then filtered off by suction through a G4 sinter and the filtrate concentrated in a rotary evaporator at 50 °C (bath temperature) in the absence of moist air. The yellow crystalline di-1-imidazolyl sulfide which separates out is dried under oil-pump vacuum and stored under vacuum in a low-temperature cooling box. Yield 23.0 g (82 %), m.p. 80–85 °C (literature [3] m.p. 110–111 °C).

b) *N,N*-Diethylthiobenzamide: A solution of 5.4 g (35 mmole) of dithiobenzoic acid in 150 ml water-free ether and 100 ml anhydrous THF is transferred to a 500 ml three-necked flask fitted with a KPG stirrer, a drying tube, and a 50 ml dropping funnel with pressure equalizer. 6.6 g (40 mmole) of di-1-imidazolyl sulfide is added to the solution with stirring. The mixture becomes slightly warm and its

color changes from violet to light red. When all of the di-1-imidazolyl sulfide is in solution (after *ca.* 10 minutes), 45 ml anhydrous THF containing 4.3 ml (3.0 g; 41 mmole) of dry diethylamine is added dropwise to the mixture over a period of 30 minutes. The mixture is stirred for 1½ h and then concentrated in a rotary evaporator at 45 °C (bath temperature). The resulting red oil is dissolved in 100 ml $CHCl_3$, neutralized by washing twice with 100 ml 1 N H_2SO_4, and finally extracted with 100 ml portions of water until the aqueous extract is colorless. The organic phase is then concentrated in a rotary evaporator at 45 °C (bath temperature). A green oil is obtained which solidifies as greenish yellow crystals on cooling [crude yield 5.6 g (83 %)]. The crystals are dissolved in ethanol, insoluble sulfur is removed, and the solution is treated dropwise with water until a definite turbidity appears. On standing, diethylthiobenzamide crystallizes from the solution as greenish yellow needles [pure yield 1: 3.8 g (57 %)]. For further purification, an ethanolic solution of the product is boiled with activated charcoal for 15 minutes, filtered, and the filtrate treated with water. Chromatographically pure diethylthiobenzamide is obtained as pale yellow needles, m.p. 41–42 °C [pure yield 2: 3.3 g (49 %)].

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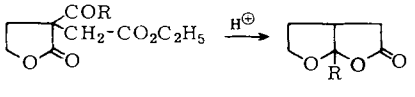
Synthesis of Hexahydrofuro[2,3-*b*]pyrrol-2-ones

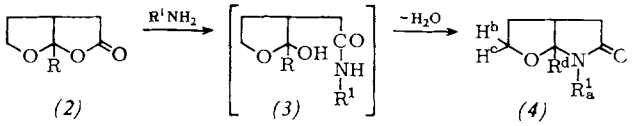
By *C. Lange*, *H. Wamhoff*, and *F. Korte* [*]

In a recent attempt to synthesize β-acyl-δ-lactones [1] from α-acyl-α-ethoxycarbonylmethyl-γ-lactones *(1)* we obtained, by a special type of acyllactone rearrangement [2], hexahydrofuro[2,3-*b*]furan-2-ones *(2)* [3].



(1) *(2)*

By virtue of their acetal-type structure these lactones can be converted into hexahydrofuro[2,3-*b*]pyrrol-2-ones *(4)* under comparatively mild conditions.

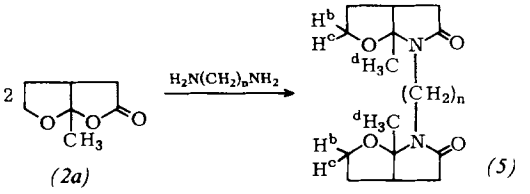


(2) *(3)* *(4)*

	R	R^1	Yield (%)	M.p. (°C) [B.p. (°C/0.01 torr)]
(4a)	CH_3	H	61	145–146
(4b)	C_5H_{11}	H	47	109
(4c)	CH_3	C_3H_7	63	[47–48]
(4d)	CH_3	C_4H_9	51	[59–60]
(4e)	CH_3	C_5H_{11}	67	[72–73]
(4f)	CH_3	C_8H_{17}	74	[92–93]
(4g)	CH_3	C_6H_5–CH_2	85	[100]

One must assume – similarly to the observations reported by *Barton* [4] in his investigation of the terpenoid bitter principle clerodin – the formation of the semiacetal amide *(3)* as an intermediate, which subsequently undergoes ring closure with loss of water.

Bifunctional amines react with two equivalents of lactone to form the 1,1′-alkylenebi(hexahydrofuro[2,3-*b*]pyrrol-2-ones) *(5a)* [*n* = 2, m.p. 160 °C, yield 46 %] and *(5b)* [*n* = 4, m.p. 155 °C, yield 41 %].



(2a) *(5)*

The following spectral data are found to be in agreement with the suggested structures: The IR spectrum (in $CHCl_3$) of *(4a)–(4g)* shows a carbonyl vibration at 1690–1700 cm^{-1}; the spectra of *(5a)* and *(5b)* show carbonyl bands at 1670 to 1675 cm^{-1}. In the NMR spectra (in $CDCl_3$; for TMS $\tau = 10$) most of the protons give rise to strongly coupled signals. In the spectra of *(4a)* and *(4b)* signals occur which can be ascribed to the lactam protons H^a at $\tau = 2.76$ and 3.23 resp. The signals assigned to the methyl protons H^d of *(4a)*, *(4c)–(4f)*, *(5a)*, and *(5b)* occur – similarly to the corresponding signals of *(2a)* [3,5] – between $\tau = 8.4$ and 8.5 whilst the methylene group H^b/H^c occurs as an AB part of an AB–MN spectrum, a complex group of signals between $\tau = 5.9$ and 6.5.

Synthesis of (4) and (5):

The lactone *(2)* is either boiled with a threefold excess of a primary amine in ethanol for 6 h or heated with liquid ammonia in an autoclave at 90–100 °C for 1 h. Bifunctional amines react with two equivalents of *(2a)*, at the temperature of boiling, within 20 h. Compounds *(4a)*, *(5a)*, and *(5b)* precipitate as solids whereas the other lactams are isolated as oils and are purified by distillation.

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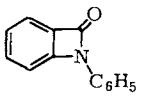
N-Phenylnaphtho[2,3-*b*]azetinone

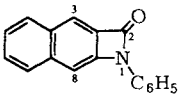
By *G. Ege* and *E. Beisiegel* [*]

The existence of *N*-phenylbenzoazetinone *(1)* in solution has been proved by trapping reactions [1] and by IR spectroscopy [2].

The formal similarity of the aceneazetinones *(1)* and *(2)* and the acenecyclobutadienes, of which the 1,2-diphenylnaphtho[*b*]cyclobutadiene has been prepared by *Cava et al.* [3], led



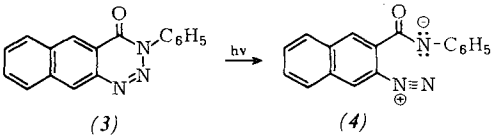
(1)



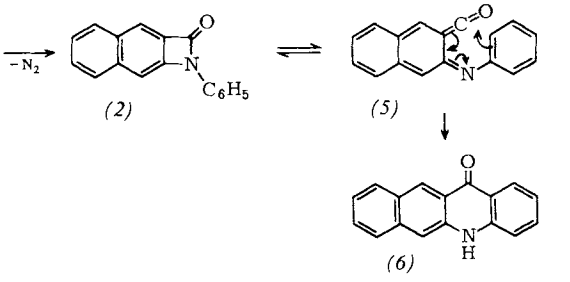
(2)

us to attempt the synthesis of *N*-phenylnaphtho[2,3-*b*]-azetinone *(2)*.

When a solution of 3-phenyl-3,4-dihydronaphtho[2,3-*d*]-1,2,3-triazin-4-one *(3)* [m.p. 226 °C, UV in CH_2Cl_2: 365 nm (ε = 6800); 348 nm (ε = 8500), 265 nm (ε = 44500), 246 nm (ε = 28300); IR (KBr): CO at 1700 cm^{-1}] in tetrahydrofuran is irradiated under a high-pressure mercury-vapor lamp (450 W, Hanovia) one equivalent of nitrogen is evolved with formation of *N*-phenylnaphtho[2,3-*b*]azetinone *(2)* and benzo[*d*]acridone *(6)*. After chromatographic working-up (silica gel, CH_2Cl_2) these compounds are isolated in yields of 92 % and 5 % respectively.



(3) (4)



(2) (5) (6)

Compound *(2)* is recrystallized from ether as golden-yellow rods, m.p. 155 °C, mol. wt. (osmometric) 245.8, (mass spectrometric) 245, UV (in CH_2Cl_2): 394 nm (ε = 2000), 276.5 nm (ε = 52000), 232 nm (ε = 36000). The β-lactam structure follows from the IR spectrum, in which a CO band appears at 1805 cm^{-1} in KBr (1815 cm^{-1} in CH_2Cl_2); it is remarkable that this band is shifted *ca.* 60 cm^{-1} to higher wavenumbers than is the corresponding CO band in the spectrum of 1,4-diphenyl-3-azetin-2-one[4]. The NMR spectrum of *(2)* shows a multiplet of aromatic protons between τ = 2.2 and 3.1 ($CDCl_3$); one proton, possibly the C-8 one, shows a greater upfield shift than the others and appears at τ = 3.07. In this region the spectrum of *(2)* resembles that of methyl 3-amino-2-naphthoate.

If compound *(2)* is boiled in methanol or heated in morpholine, the well known methyl 3-phenylamino-2-naphthoate or the morpholide, m.p. 155–156 °C, is obtained. The diazonium intermediate *(4)* probably occurs[5] during the formation of *(2)* from *(3)*; *(6)* is formed from *(2)* by valence isomerization to the non-isolable ketene *(5)*[6] and subsequent cyclization. We have obtained evidence for this reaction course by photolyzing compound *(2)*, from which we obtained *(6)*.

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[1] *G. Ege*, Angew. Chem. *77*, 723 (1965); Angew. Chem. internat. Edit. *4*, 699 (1965).

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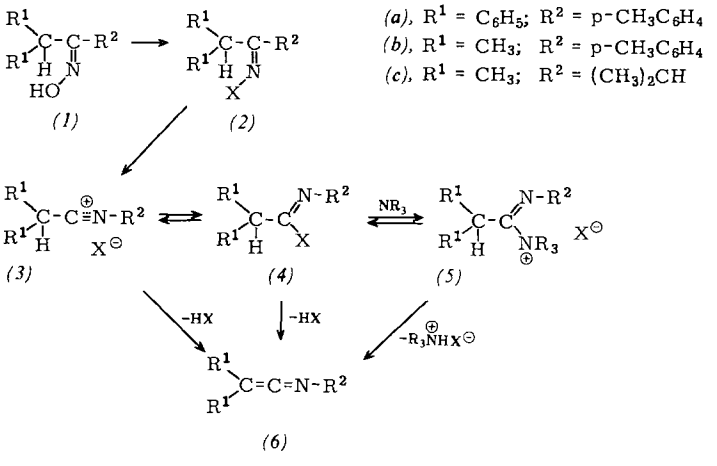
Preparation of Ketene Imines by a Beckmann Rearrangement

By *S. Hünig* and *W. Rehder*[*]

The Beckmann rearrangement of oximes *(1)* is initiated by conversion of the oximo hydroxyl function into a nucleofugal leaving group[1]. The intermediate *(2)* yields the nitrilium ion *(3)*[2], which was suspected some time ago[3] and which can exist in equilibrium with the imidic acid *(4)*. This imide *(4)* – and thus also compound *(3)* – can eliminate HX to form the ketene imine *(6)*, the existence of which is proved by its synthesis from the chloro imide *(4)*, X = Cl, with triethylamine in boiling toluene[4]. It is possible that compound *(5)* also plays a role[5].



Therefore all Beckmann rearrangements, which are carried out in aprotic solvents in the presence of a sufficiently strong, weakly nucleophilic base, should yield ketene imines *(6)*, which can be recognized by their intense IR absorption at *ca.* 2000 cm^{-1}[4].

These conditions apply, *e.g.*, for oxime sulfonates *(2)*, X = RSO_3[5,6]. Whereas esterification of the sterically hindered OH group in *(1a)–(1c)* proves difficult with benzenesulfonyl chloride, *(2a)–(2c)*, X = CH_3SO_2[8], are formed within 15 min when the reaction is carried out with methanesulfonyl chloride + triethylamine (even at −15 °C in toluene) owing to the formation of the intermediate sulfene[7]. On heating with an excess of triethylamine in toluene at 100 °C, the Beckmann rearrangement affords *(6)*. Thus *(1a)* yields a solution containing 95 % of *(6a)* within 20 min, *(1b)* gives a solution containing 83 % of *(6b)* after 90 min, and *(1c)* affords a solution containing 80–90 % of *(6c)* after 55 min. (The yields were determined by comparing the intensities of the IR bands of *(6a)* and *(6b)*[4] with standard solutions.) The hitherto unknown compound *(6c)* is one of the few completely aliphatic ketene imines[4b,9], Treatment of 3.3 mmoles of *(1a)* according to *Stevens*[10] affords *(6a)*, m.p. 79–80 °C, in 38 % yield.

As starting materials we used the pure R^1R^1CH-*syn*-oximes *(1)* whose constitutions were proved by Beckmann rearrangement to the corresponding toluidides and by the low frequency of the C–H signal in the NMR[11]. *(1a)*: m.p.

190–191 °C from methanol, δ = 6.25 ppm (singlet) in DMSO; *(1b)*: m.p. 96–97 °C from *n*-pentane[12], δ = 3.57 ppm (septet) in CCl_4.

These results are being published[13] because the reaction the sequence *(1)* → *(6)* has meanwhile been realized[15] by addition of triphenylphosphine dibromide, whose reaction with benzaldoxime was known[14].

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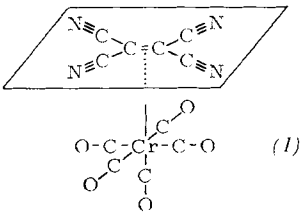
New Metal Complexes of Tetracyanoethylene

By *M. Herberhold*[*]

Treatment of $Ni(CO)_4$ with tetracyanoethylene (TCNE) leads, *via* a redox reaction[1,2], to the formation of the salt $Ni^{2+}(TCNE^-)_2$[1]. If the yellow solution of TCNE in benzene is irradiated in the presence of a hexacarbonylmetal $M(CO)_6$, replacement of a CO ligand takes place and the monosubstituted product $(TCNE)M(CO)_5$ (M = Cr, Mo, W) is formed. This photochemical substitution, by means of which the first TCNE complexes of the metals of the sixth sub-group could be synthesized, depends upon primary fission of CO from the metal carbonyl and stabilization of the light-sensitive TCNE complex by the aromatic solvent.

In the solid state, the intense blue-violet tetracyanoethylene-pentacarbonylchromium(0) *(1)* (decomp. at 102 °C with black coloration) is stable to air but somewhat sensitive to light. In solution it slowly decomposes, the decomposition being considerably accelerated on exposure to light; the intense green solutions in aromatic hydrocarbons are the most stable. Donor ligands [amines, CH_3CN, $P(C_6H_5)_3$] replace the TCNE of the complex.



(1)

The suggested structure *(1)*, with π-bonded TCNE as monoolefinic ligand, is based on the following findings:

1. The composition $(C_6N_4)Cr(CO)_5$ is established by elemental analysis and by mass spectrometry. The mass spectrum[3] shows the presence of the molecular ion (*m/e* = 320) and the fragment ions (*m/e* = 292, 264, 236, 208, and 180) which are expected to arise by stepwise loss of the CO ligands. The most abundant fragment ion is $Cr(C_6N_4)^+$ (*m/e* = 180). In the mass spectrometer, compound *(1)* decomposes to $Cr(CO)_6$ and TCNE.

2. The IR spectrum of *(1)* shows only one sharp C≡N stretching vibration at 2203 cm^{-1} (KBr), which is shifted toward lower wave numbers compared to the corresponding stretching vibration in the spectrum of TCNE[4] ($\nu C{\equiv}N$ = 2262 and 2222 cm^{-1}). This indicates the filling of antibonding orbitals in the cyano groups and is in accord with the occurrence of back-bonding from metal to ligand as has been established in other olefin-π-complexes. In the TCNE complexes $(PR_3)_2Pt(C_6N_4)$ ($\nu C{\equiv}N$ = 2222 cm^{-1})[5] and $[(P(C_6H_5)_3]_2Rh(CO)Cl(C_6N_4)$ ($\nu C{\equiv}N$ = 2230 cm^{-1})[6], once again only one strong $\nu C{\equiv}N$ absorption was observed. An unsymmetrical coordination of the ligand *via* the lone pair on the nitrogen atom or *via* the π system of a cyano group can therefore be ruled out.

3. The electronic spectrum of *(1)* is characterized by an intensive charge-transfer band ($\varepsilon \approx 1\times10^4$–$2\times10^4$ liter $mole^{-1}$ cm^{-1}), whose λ_{max} value depends strongly on the solvent. In the reflectance spectrum with LiF as standard white, a broad structureless maximum occurs at 760–820 nm; λ_{max} in the absorption spectrum occurs, depending upon the donor properties of the solvent, at 786 (mesitylene), 822 (toluene), 836 (benzene), 845 (nitrobenzene), 802 (acetonitrile), 878 (cyclohexane), or 900 nm (chloroform). The solvent molecules apparently envelope the π-bonded cyanoolefin, whose acceptor capacity for charge transfer from metal to the TCNE is thus varied.

A structure with π-bonded TCNE can also be assumed for the homologous blue-violet compounds $(TCNE)M(CO)_5$ (M = Mo, W). The analogous reaction of $C_5H_5Mn(CO)_3$ with TCNE leads to formation of a blue-green complex, whose ^1H-NMR spectrum (in [D_6]-acetone) contains a signal ascribable to the five-membered ring protons at about τ = 0.57 further downfield than the corresponding signal (at τ = 4.95) in the spectrum of $C_5H_5Mn(CO)_3$.

Procedure: $(TCNE)Cr(CO)_5$

0.550 g (0.0025 mole) of $Cr(CO)_6$ and 0.256 g (0.0020 mole) of TCNE are dissolved in 200 ml of benzene that is saturated with N_2 and irradiated with a high-pressure mercury-vapor lamp (Hanovia 450 W), which is housed in a water-cooled Jenaer glass jacket. When decomposition sets in and a darkening in the color of the green solution is observed (after *ca.* 4 hours), the mixture is fitered through a G3 sinter in a nitrogen atmosphere and the filtrate irradiated until the beginning of further decomposition (after *ca.* 2 hours). The clear green filtrate is then evaporated to dryness and the blue residue thus obtained is heated at 40–45 °C under vacuum until all the $Cr(CO)_6$ and TCNE has evaporated off (*ca.* 8 hours). The blue crude complex *(1)* (yield 0.08–0.10 g, 12.5–15.5 %) can be further purified by dissolution in

toulene at 50 °C followed by recrystallization with *n*-hexane at −95 °C. Small amounts of analytically pure complex, in the form of deep violet crystals, can be obtained by sublimation under vacuum at 45–50 °C; however, 95 % decomposition must be allowed for.

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[1] *O. W. Webster, W. Mahler*, and *R. E. Benson*, J. org. Chemistry *25*, 1470 (1960).

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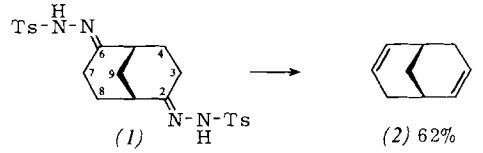
CONFERENCE REPORTS

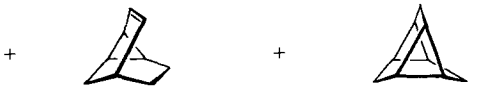
Asteranes

By *H. Musso* [*]

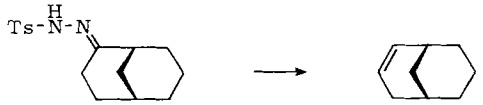
Decomposition of the bis(tosylhydrazone) *(1)* by sodium 2-hydroxyethoxide in ethylene glycol affords as main product the 2,6-diene *(2)*, as well as the tricyclic compound *(3)* and triasterane *(4)*; insertion to the 9-position or from the 2- to the 4-position in *(1)* was not observed [1]. However, in the analogous reaction of the monoketone derivative *(5)* *H. Klusacek* isolated tricyclo[4.3.0.0^{2,9}]nonane *(8)* as well as *(6)* and *(7)*; and *(8)* could be hydrogenated to bicyclo[3.3.1]-nonane and perhydroindane.



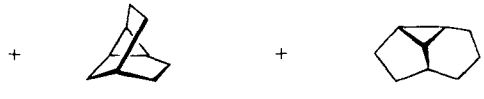
(1) *(2)* 62%



(3) 26% *(4)* 10%



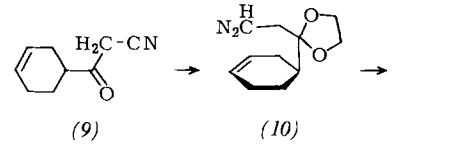
(5) *(6)* 81%



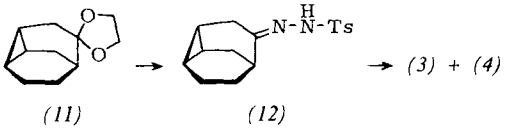
(7) 7.5% *(8)* 11.5%

A new synthesis of triasterane *(4)* starts with 3-cyclohexene-carboxylic ester, which is readily accessible by a diene reaction and condenses with acetonitrile to give *(9)*. Protection of the carbonyl group, hydride reduction of the nitrile to the amine, and cleavage of the alkylnitrosourea derived therefrom led to the diazo compound *(10)* which was decomposed by copper powder in cyclohexane to the protected tricyclic ketone *(11)* and two further products. The ketone obtainable from *(11)* afforded a tosylhydrazone *(12)* which with sodium 2-hydroxyethoxide in ethylene glycol again decomposed to a mixture (6:4) of *(3)* and *(4)* (*H. Klusacek*).

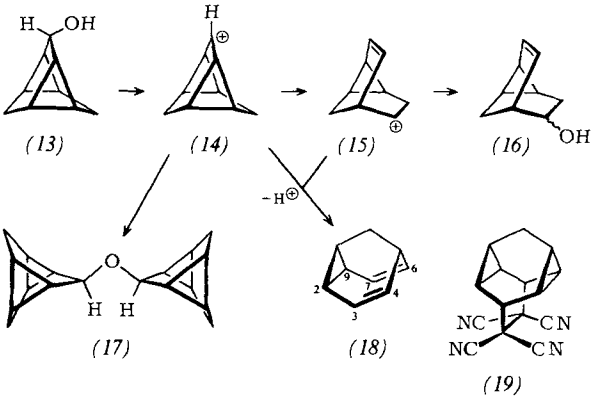
According to experiments by *U. Biethan* the alcohol *(13)* that is obtained from triasteranone on treatment with $LiAlH_4$ is rather unstable. In the crystalline state and in pentane over $Mg(ClO_4)_2$, *(13)* gives good yields of the ether *(17)*, and in water at 50 °C rearranges to the unsaturated alcohol *(16)*.



(9) *(10)*



(11) *(12)* → *(3)* + *(4)*



(13) *(14)* *(15)* *(16)*

(17) *(18)* *(19)*

In presence of strong bases the carbonium ion *(14)* → *(15)* loses a proton with formation of the diene *(18)* [2], which reacts with tetracyanoethylene in benzene at 20 °C to give the homo Diels-Alder adduct *(19)*. The NMR-spectrum indicates constitution *(19)* and unequivocally disproves structures which would be produced by addition at the 4,6- or 2,6-positions.

Lecture at Marl-Hüls (Germany), on November 8, 1967 [VB 124 IE]
German version: Angew. Chem. *80*, 290 (1968)

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[1] *H. Musso* and *U. Biethan*, Chem. Ber. *100*, 119 (1967).

[2] *U. Biethan*, *H. Klusacek*, and *H. Musso*, Angew. Chem. *79*, 152 (1967); Angew. Chem. internat. Edit. *6*, 176 (1967).

Kinetic Investigations with Solid Electrolytes

By *H. Rickert*[*]

Solid state galvanic cells have two properties that are important for kinetic studies: (1) reaction velocities can be measured in suitably constructed cells by means of the electric current and (2) the EMF of the cells provides thermodynamic information, particularly about chemical potentials or activities. The combination of velocity measurements with determination of thermodynamic parameters often permits analysis of kinetic processes. Four typical examples were discussed:

a) Diffusion of oxygen in solid and liquid metals.

b) Evaporation and condensation of sulfur, selenium, and iodine from and on to their solid metal compounds (including description of electrochemical Knudsen cells for study of the thermodynamics of vapors, *e.g.*, sulfur and selenium vapor).

c) Passage of Ag ions and electrons through the phase boundary Ag_{solid}/Ag_2S_{solid}.

d) The kinetics of formation of NiS_{solid} from Ni at 400 °C.

Lecture at Hannover (Germany), on November 23, 1967 [VB 125 IE]
German version: Angew. Chem. *80*, 292 (1968)

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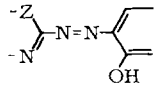
Heterocyclic Azo Dyes in Complex Chemistry and in Analytical Chemistry

By *L. Sommer*[*]

For many years azo dyes have been used as sensitive reagents in analytical chemistry (*e.g.*, for trace analysis and spectrophotometric determination of metals, also as indicators for metals in chelatometric titrations). N-Heterocyclic azo dyes



containing the characteristic donor grouping have won a special place. Dyes of the pyridine, thiazole, triazole, and tetrazole series normally form red or reddish-orange metal chelates, and derivatives of *p*-cresol, *p*-methoxyphenol, and chromotropic acid blue or green metal chelates which are more or less soluble in water. Metal ions with empty or with full or partly filled d-orbitals are particularly reactive. Analytically the most valuable reactions of heterocyclic dyes are those with ions of Cu^{II}, Zn, Cd, Sc, lanthanides, Ti^{IV}, V^{V}, Nb^{V}, Fe^{II}, Fe^{III}, Co^{II}, Ni^{II}, Pd^{II}, Ga, In, Tl^{III}, Pb^{II}, and UO_2^{2+}. No analytical importance attaches to the reactions of Be, Ca, Sr, Ba, Al, Sb^{III}, Cr^{III}, Mo^{VI}, or W^{VI} unless additional donor groups are present in the dye molecule.

Complex formation in solution has been studied for 4-(2-pyridylazo)resorcinol (PAR) and 4-(2-thiazolylazo)resorcinol (TAR) and compared with that of 1-(2-pyridylazo)-2-naphthol (PAN) and its thiazole analog (TAN).

PAR and TAR give protonated and "normal" 1:1 metal chelates over a broad pH range; at pH $\geqslant$ 5 in solutions containing an excess of reagent, 1:2 chelates are also formed, but only with difficulty and not always by Cu^{II} and not at all by uranyl.

Loss of the proton from the hydroxyl group on self-dissociation of the dye, and formation of a protonated metal chelate, must be taken into account when formulating the complex constants; so must the formation of hydroxychelates of In, Ga, and Tl^{III} in the hydrolysis range of these ions. The acidity of the *p*-hydroxyl proton is appreciably increased by formation of a stable protonated metal chelate as well as by presence in solution of an excess of metal ions of higher valence. PAN and TAN preferentially afford coordinately saturated metal chelates, which dissolve also in slightly polar solvents. Formation of 1:3 and 1:4 chelates of the lanthanides is an exception to the otherwise strictly maintained tridenticity.

The stability of metal chelates of N-heterocyclic azo dyes, as well as the tendency to complex formation of metal ions with this group of ligands, are with few exceptions directly proportional to the electronegativity of the metals (calculated with regard to their valence): $Pd^{II} > Cu^{II} > UO_2^{2+} > Fe^{II} > Ni^{II} \sim Co^{II} > Pb^{II} > Zn > Cd \sim Mn^{II}$; $Tl^{III} > Bi > Ga > Fe^{III} > In > Sc > Al >$ lanthanides $> Y > La$ The thiazole azo dyes are found to give chelates that are less stable than those obtained from pyridine azo dyes.

Coordination of the metals proceeds in two steps: the first involves bonding of the heterocyclic nitrogen, and the second is closure of the chelate ring by way of the *o*-hydroxyl oxygen and the azo nitrogen atom situated farthest from the heterocyclic nitrogen.

Lecture at Mainz (Germany), on November 23, 1967
and at Saarbrücken (Germany), on November 24, 1967 [VB 126 IE]
German version: Angew. Chem. *80*, 291 (1968)

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Chemisorption on Metal Films

By *G. Wedler*[*]

Changes in the physical properties of thin metal films on adsorption of gases can often be used for a study of the nature of the bonding between adsorbent and adsorbate. Since properties, such as the electrical conductivity and photoeffect, of evaporated films often differ markedly from those of the compact material, interpretation of adsorption effects requires a knowledge of the properties of films. We have studied Ni films of systematically varied thickness that were condensed at 77 °K in ultra-high vacuum at a rate of *ca.* 10 Å/min and then annealed at increasing temperatures. Electron-microscopical and X-ray-diffraction measurements show that the crystals are small plates and increase in size with increasing layer thickness and annealing temperature; the crystallites are arranged mostly with the {111}, and to a smaller extent with the {100}, faces parallel to the glass support[1]. The texture of the crystallites is dependent on the conditions of preparation. Because of the different coefficients of thermal expansion of the glass support and the metal film the annealed films are under a stress which leads to a decrease in the separation between the network planes that lie parallel to the support.

By applying Sondheimer theory to the dependence of electrical resistivity of the film on layer thickness the mean free path l_0 of the conduction electrons and the specific resistance ρ_0 can be determined for compact material that has the same volume density of impurity centers as the film. l_0, ρ_0, and analysis of the line profile of the X-ray reflections lead to the same conclusions about increase in the degree of order of the originally disordered films with increasing temperature.

Study of the dependence of the electron work function on layer thickness and temperature shows that for unannealed Ni films condensed at 77 °K the work function is the same, φ = 4.59 V, down to layer thicknesses of 40 Å. With rise in annealing temperature φ increases – more for thin than for thick films – so that films annealed at 373 °K give a constant work function of 4.95 V only at thicknesses of $>$ 200 Å.

When considering adsorption effects it is advisable either to study their dependence on the thickness of the metal films or

simultaneously to carry out other measurements that afford thermodynamic values.

Thus it is found, for instance, with the system Ni/CO that the increase in resistance observed as a consequence of adsorption cannot be explained by a change in the electron concentration or a decrease in the effective film thickness due to formation of a compound on the surface. However, if the fact is taken into consideration that a change in the number of free electrons must alter their mean free path, then the dependence of the increase in resistance on the film thickness, as measured, can be described correctly and quantitatively.

Information about the various species of an adsorbate occurring side by side in one system can be obtained by combining measurements of the electrical resistance, electron work function, and differential heats of adsorption and, if possible, studying their temperature dependence. Thus it can be shown that in the system Ni/H_2 at equilibrium pressures of $< 10^{-4}$ torr and 273 °K there is no molecularly adsorbed hydrogen (as there is at 77 °K) but that account must be taken of a second atomically sorbed species.

Lecture at Hamburg (Germany) on November 3, 1967 [VB 129 IE]
German version: Angew. Chem. *80*, 289 (1968)

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[1] Cf. *G. Wedler*, Angew. Chem. *78*, 827 (1966); Angew. Chem. internat. Edit. *5*, 848 (1966).

Rhenium(VII) Oxide and "Perrhenic Acid"

By *B. Krebs* [*]

The structure and coordination state of solid Re_2O_7 and of solid "perrhenic acid" have hitherto been unknown. Attempts to predict the constitution on the basis of spectral data and thermodynamic data did not lead to unambiguous results. The structure of both compounds has now been clarified in detail by X-ray structure analysis; this gave at the same time the composition of "perrhenic acid" that was not determined analytically in previous work. Both structures are characterized by unusual coordination relations. ReO_6 octahedrons and ReO_4 tetrahedrons, largely covalently bound, occur together.

Dirhenium heptoxide crystallizes in space group $P2_12_12_1$ (D_2^4) with $a = 12.508$, $b = 15.196$, $c = 5.448$ Å, $Z = 8$, and presents a new type of structure that has no direct relation to other oxide structures [1]. Chains of ReO_6 octahedrons, joined together at corners, are linked by corners to ReO_4 tetrahedrons in such a way that a polymeric double-layer lattice arises. The double layer can be described as an arrangement of rings comprising four polyhedrons linked at their corners (O–T–O–T) and in turn linked to one another by octahedrons. The separations in the tetrahedrons are between 1.68 and 1.81 Å, the terminal bonds being shorter than the bridge bonds in accord with their higher bonding order. The octahedrons are strongly distorted: Re is shifted from the center parallel to one of the three-fold octahedral axes (three Re–O distances between 2.06 and 2.16, the remaining three between 1.65 and 1.75 Å). Re_2O_7 thus constitutes a transition between the structure of the more strongly ionic oxides MoO_3 and WO_3 (distorted octahedral six-coordination) and the molecular structures of RuO_4 and OsO_4 (tetrahedral four-coordination). The mechanism of evaporation of the oxide with formation of Re_2O_7 molecules with tetrahedral coordination can be readily deduced from the structure.

Solid "perrhenic acid" (which can be recrystallized from organic solvents) has a molecular structure in which also distorted ReO_6 octahedrons occur alongside ReO_4 tetrahedrons (in the binuclear compound one octahedron is joined by a corner to one tetrahedron) [2]. The fact that two of the terminal Re–O bonds of the octahedron are very much longer (2.21 Å) than any of the others (octahedron, terminal 1.73–1.76 Å; bridge 2.10 and 1.80 Å; tetrahedron, terminal 1.73–1.77 Å) is in agreement with the broad-line ^1H–NMR spectrum and the IR spectrum in indicating that the compound is correctly formulated as dihydratoheptaoxidodirhenium $Re_2O_7(OH_2)_2$ with trebly linked oxygen in the H_2O.

Lecture at Göttingen (Germany) on December 14, 1967 [VB 132 IE]
German version: Angew. Chem. *80*, 291 (1968)

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[1] *B. Krebs, A. Müller*, and *H. Beyer*, Chem. Commun., in press.
[2] *H. Beyer, O. Glemser*, and *B. Krebs*, Angew. Chem. *80*, 286 (1968); Angew. Chem. internat. Edit. *7*, 295 (1968).

Preparative Chemistry of Chalcogenides

By *A. Rabenau* (Lecturer) and *H. Rau* [*]

If hydrogen sulfide is passed into an aqueous solution of a lead salt in the presence of free hydrohalogen acid, the first, precipitate is not black PbS but materials whose color changes from yellow *via* orange to red and finally *via* brown to black. The nature of these precipitates is an old problem of preparative chemistry. As early as 1836 *Hünefeld* [1] ascribed the composition $3\ PbS \cdot 2\ PbCl_2$ to a red precipitate obtained in this way from a solution containing hydrochloric acid. *Parmentier* [2] isolated from solutions containing hydrochloric or hydrobromic acid red precipitates which, according to analyses, should have formulas $PbS \cdot PbCl_2$ or $PbS \cdot PbBr_2$, respectively. *Lenher* [3] found $PbS \cdot 4PbI_2$. Since the low stability of the precipitates makes it impossible to separate preparatively the several phases constituting the mixture and X-ray control was not available at that time, the question of the existence of lead sulfide halides remained open.

On hydrothermal synthesis of PbS in concentrated hydrohalogen acids [4] we have isolated deep red single crystals of the composition $Pb_5S_2I_6$ *(1)* and $Pb_7S_2Br_{10}$ *(2)* [5]. Thermoanalytical and X-ray studies show that these are stable ternary phases in the pseudobinary systems $PbS–PbI_2$ and $PbS–PbBr_2$; they decompose peritectically at 418 *(1)* and 381 °C *(2)*, respectively. Analysis of the *d*-values of a compound "$PbS \cdot PbBr_2$" [6] showed that the preparation consisted of *(2)* and $PbBr_2$.

Experiments carried out on precipitates obtained from solutions containing hydrobromic acid showed that the precipitates consisted of PbS, *(2)*, and a still unidentified further phase in proportions that varied with the concentration of HBr.

No crystals other than $PbCl_2$ or PbS were observed during hydrothermal synthesis in concentrated hydrochloric acid. However, a ternary phase, Pb_4SCl_6, was found on rapid cooling of melts of the system $PbS–PbCl_2$; it was obtained in pure crystalline form on quenching a melt of this composition from 600 °C. This compound is metastable and decomposes into the binary components when kept at temperatures between 200 and 450 °C (eutectic).

Lecture at Hannover (Germany), on December 14, 1967 [VB 131 IE]
German version: Angew. Chem. *80*, 292 (1968)

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[1] *J. Hünefeld*, J. prakt. Chem. *7*, 27 (1836).
[2] *F. Parmentier*, C. R. hebd. Séances Acad. Sci. *114*, 298 (1892).
[3] *V. Lenher*, J. Amer. chem. Soc. *17*, 511 (1895).
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[5] *A. Rabenau, H. Rau*, and *G. Rosenstein*, Naturwissenschaften, *55*, 82 (1968).
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Biochemistry of Phosphatides Containing Vinyl Ethers (Plasmalogens)

By *Hildegard Debuch*[*]

Plasmalogens [2-acyl-1-(1-alkenyl)-*sn*-glycero-3-phosphoryl compounds[**]] occur, usually as choline or 2-aminoethyl esters, *in almost all animal cells and tissues*. By mild acid hydrolysis the aldehyde that is bound like a vinyl ether is liberated and a corresponding β-lysophosphatide is formed, whereas on mild alkaline hydrolysis a lysoplasmalogen is obtained. An "ether phosphatide" is obtained on catalytic hydrogenation. (Such compounds often occur in small amounts also in Nature.)

Plasmalogens are, specifically, components of the lipid mixtures that are obtained from myelin sheaths of nerve fibers (occurring there almost exclusively as 2-aminoethyl esters) and from the phosphatide fractions of heart muscle (here usually cholineplasmalogens). Correspondence in chain length and degree of hydrogenation can often be found when studying the α-groups of glycerophosphatides that are always derived from fatty acids, fatty aldehydes, or fatty alcohols. *In vitro* experiments with tissue homogenates or cell fractions from brain contributed little to the nature of biosynthesis of plasmalogens, so that *in vivo* experiments must be carried out to clarify such problems. Results to date do not provide unambiguous evidence whether the enol-ether-like linkage of the aldehyde in plasmalogens arises through oxidation of an ether group or through reduction of an ester linkage; in any case, ^{14}C-labeled aldehydes are not direct precursors of plasmalogens in the brain *in vivo*.

Lecture at Hamburg (Germany) on December 15, 1967 [VB 133 IE]
German version: Angew. Chem. *80*, 321 (1968)

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[**] "*sn*" denotes "stereospecific numbering"; for nomenclature see IUPAC Information Bull. *30*, 21 (1967).

Fluorides and Perfluoroorgano-substituted Compounds of I^{1+} and I^{3+}

By *M. Schmeisser*[*]

Iodine monofluoride is accessible in good yields as a pale gray solid of decomposition point 0 °C by reaction of iodine with the stoichiometric amount of fluorine, by reduction of iodine trifluoride with iodine in presence of traces of pyridine, and by metathetical reaction of iodine chloride with nitrosyl fluoride, in all cases in CCl_3F at temperatures from −40 to −50 °C:

$$I_2 + F_2 \rightarrow 2\,IF$$

$$I_2 + IF_3 \xrightarrow{C_5H_5N} 3\,IF$$

$$ICl + NOF \rightarrow IF + NOCl$$

Compounds $C_5H_5N{\cdot}I(O_2CR)$, where R = CF_3 or C_6F_5, are obtained by the action of iodine on silver salts of the corresponding perfluorocarboxylic acids in pyridine/benzene and can be considered as further derivatives of I^{1+}.

Pale yellow, solid iodine trifluoride, decomposition point −28 °C, is formed on treatment of iodine with an excess of fluorine at −45 °C in presence of catalytic amounts of IF_3 or pyridine and can be stabilized as 1:1 adducts with organic nitrogen bases. The compounds IF_2Cl, CF_3IF_2, $C_6F_5IF_2$, and IF_2NO_3, which can be considered as derivatives of IF_3, are formed on low-temperature fluorination of ICl, CF_3I, and C_6F_5I, or in the case of IF_2NO_3 by reaction of IF_2Cl with chlorine nitrate.

The covalently constituted iodine tris(perfluoroacylates)[1] $I(O_2CR)_3$, where R = CF_3, C_2F_5, C_3F_7, or C_6F_5, can be obtained in almost quantitative yields (a) by oxidation of iodine with fuming nitric acid in presence of the corresponding perfluorocarboxylic anhydride, (b) by treatment of iodine trichloride with silver perfluoroacylates, or (c) in the case of iodine tris(trifluoroacetate) by the action of peroxotrifluoroacetic acid and trifluoroacetic anhydride on elemental iodine; they can be isolated in pure form by fractional vacuum sublimation:

(a) $I_2 + 6\,HNO_3 + 6\,(CF_3CO)_2O \rightarrow 2\,I(O_2CCF_3)_3 + 6\,NO_2 + 6\,CF_3CO_2H$

(b) $ICl_3 + 3\,AgO_2CCF_3 \xrightarrow{(CF_3CO)_2O} I(O_2CCF_3)_3 + 3\,AgCl$

(c) $I_2 + 3\,CF_3CO_3H + 3\,(CF_3CO)_2O \xrightarrow[-15\,°C]{CCl_3F} 2\,I(O_2CCF_3)_3 + 3\,CF_3CO_2H$

When method (c) is used an intermediate, iodyl trifluoroacetate $IO_2(O_2CCF_3)$, can be isolated in 95 % yield.

Analogously to the preparation of iodine tris(perfluoroacylates) methods (a) and (c) can be used for preparation, also in almost quantitative yield, of pentafluorophenyliodine bis(perfluoroacylates) $C_6F_5I(O_2CR)_2$, where R = CF_3, C_2F_5, C_3F_7, or C_6F_5. Treating these compounds with $NaHCO_3$, leads to formation of dimeric pentafluoroiodosobenzene $(C_6F_5IO)_2$, as does hydrolysis of $C_6F_5IF_2$. This dimer reacts with perfluorocarboxylic anhydrides in the reverse reaction, regenerating the corresponding pentafluorophenyliodine bis(perfluoroacylates).

Lecture at Frankfurt/M. (Germany) on January 11, 1968 [VB 134 IE]
German version: Angew. Chem. *80*, 321 (1968)

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[1] *M. Schmeisser, K. Dahmen*, and *P. Sartori*, Chem. Ber. *100*, 1633 (1967).

Mechanism of Indirect Nuclear Spin Coupling

By *H. Dreeskamp*[*]

Scalar "indirect" spin coupling of nuclei of a molecule causes splitting of NMR signals owing to interaction of the magnetic field of the outer shell electrons and the magnetic dipole that is associated with the nuclear spin. The coupling constants J and their appropriate signs can be determined by analysis of the spectrum or by double resonance experiments and thus can be traced back to the coupling constant of directly bound C and H atoms. This constant is known to be positive (with the implication that a positive J denotes decrease in energy owing to antiparallel spin) from measurements on partially oriented molecules.

For tetramethyl derivatives and hydrides of elements of the fourth main group the normalized coupling constants J' (defined as the constants referred to a gyromagnetic ratio of + 1) of two nuclei linked by one bond have positive signs and are, within a good approximation, proportional to the product of the valence electron densities at the site of the coupling nuclei. It is thence concluded that the Fermi contact term makes a preponderant contribution to coupling of nucleus and electrons.

In a paper concerned with an MO approach to coupling constants calculated from peturbation energies and considering only the Fermi contact term, *Pople* and *Santry*[1] predict for J' a progression from positive values for the C–H and the C–C bond to negative values for the C–F and H–F bond. The analogous constants for Se and Te compounds confirm this theory, since J' for Se–C and Te–C is small

and negative but for Se–H is small and positive (each referred to data for compounds of the fourth main group). Finally, for hydrides of elements of the fourth main group, the geminal H–H coupling constant shows a progressive change from −12.4 Hz for CH_4 to +15.3 for SnH_4, which can be interpeted by a simple MO theory.

These examples can be used to show that values and absolute signs of coupling constants can, in principle, always be determined and that even relatively simple approximations yield useful interpretation of these data. Thus investigation of indirect nuclear spin coupling can enrich our conceptions of the electron shell of molecules.

Lecture at Berlin (Germany) on January 19, 1968 [VB 136 IE]
German version: Angew. Chem. *80*, 320 (1968)

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[1] *J. A. Pople* and *D. P. Santry*, Molecular Physics *8*, 1 (1964).

Abnormal Reaction in Alkylation of Silicon and Germanium Tetrahalides

By *J. Valade* [*]

It is known that alkylation of silicon and germanium tetrahalides by Grignard compounds can be used for preparation of C–Si and C–Ge bonds. Abnormal reactions (formation of H–Si or H–Ge bonds) have been occasionally noted. We have shown that for $SiHal_4$ and $GeHal_4$ these can become the main reactions.

The Grignard compound decomposes at 160 °C first into the unstable magnesium hydride which forms compounds having H–Si or H–Ge bonds ; on silicon two, but on Ge only one halogen atom is replaced by hydrogen. At 4 °C halogen-hydrogen exchange also occurs, but this differs from exchange at higher temperatures.

In the case of silicon the reaction at 4 °C proceeds through Cl_3SiH to yield R_2SiHCl. Ge^{IV}, however, is first converted into Ge^{II}, which is reoxidized to a germylated Grignard compound containing Ge^{IV}. The presence of this intermediate can be demonstrated best by hydrolysis.

Lecture at Giessen (Germany) on January 16, 1968 [VB 135 IE]
German version: Angew. Chem. *80*, 321 (1968)

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Adsorption Calorimetry

By *S. Černý* [*]

The bond dissociation energy is the measure of the strength of bonding of adsorbed particles to solid surfaces. Experimental determination of the bonding energy is, however, difficult and thus it is usually the adsorption energy, *i.e.*, the heat of adsorption, that is measured. Although the relation between bond energy and adsorption energy is close, it is not quite simple since the total energy effect consists, not only of the dissociation energies of the forming and breaking bonds, but also of the changes in degree of freedom of the system, and in particular, the final regrouping of the surface atoms of the adsorbent.

The value of the heat of adsorption and its dependence on occupation of the surface is extremely important for a study of chemisorption and heterogeneous catalysis. Nevertheless, there are few reliable data for heats of adsorption, on the one hand because the crystallographic state of the surface is usually inadequately defined and there is insufficient information about surface contamination, and on the other hand because of shortcomings in the measuring technique for the heat of adsorption itself.

Heats of adsorption can be measured indirectly or directly. Indirect methods utilize either equilibrium data (adsorption isosteres, retention times in gas chromatography) or kinetic data (thermal desorption, field emission microscopy). Direct, *i.e.*, calorimetric, determinations of heats of adsorption are carried out in calorimeters that operate adiabatically, isothermally, or diathermally; the first two of these types can be used only for powder adsorbents, but the diathermal calorimeter can be used also for films and threads.

For small temperature differences the heat transport (by conduction or radiation) between the calorimeter and the outer covering is described by Newton's law. The simple Tian formula is approximately valid for all diathermally operating calorimeters. If the explicit equation for the kinetics of the adsorption process is available, an expression can be set up for variation in the measured quantity with time. This expression affords the heat of adsorption and also provides a model of the calorimetric curves for use in an analog computer. Setting up the analog model provides valuable information about the role of individual parameters of the calorimeter and the kinetic parameters of the adsorption process.

Lecture at Hamburg (Germany) on November 17, 1967 [VB 130 IE]
German version: Angew. Chem. *80*, 290 (1968)

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SELECTED ABSTRACTS

Reactions of organocopper compounds with halogenoolefins have been studied by *J. Burdon, P. L. Coe, C. R. Marsh,* and *J. C. Tatlow.* Copper acetylides suspended in DMF or pyridine react readily with halogenoolefins at 40–100 °C to give ethynylolefins, *e.g.*

$$C_6H_5{-}C{\equiv}CCu + ICH{=}CHCl \longrightarrow C_6H_5{-}C{\equiv}C{-}CH{=}CHCl.$$

The yields are between 40 and 90%. The ease with which the halogens are replaced decreases in the order I > Br > Cl; fluorine is not replaced. Perfluoroalkyl iodides react when heated with halogenoolefins and copper bronze in pyridine or DMF to give perfluoroalkylolefins, *e.g.*

$$C_7F_{15}I + ICH{=}CHCl \xrightarrow[Cu]{} C_7F_{15}CH{=}CHCl.$$

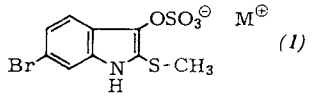
The reaction very probably proceeds *via* perfluoroalkylcopper compounds (yield 50–96%). / Chem. Commun. *1967*, 1259 / –Ma. [Rd 816 IE]

"Self assembly" of the fr-phage from the subunits of the coat protein and the phage RNA has been observed by *T. Hohn.* The isohedral protein coat of the fr-phage consists of more than 180 protein subunits having a sedimentation constant of 4 S. Since the shape of the coat can be achieved only with distortion of the surface arrangement of the subunits, the positions of the subunits are not equivalent. The subunits do not associate in 0.5 M tris-acetate buffer, even in the presence of the phage RNA. In 0.15 M tris-acetate buffer, on the other hand, about 80% of the material aggregates into particles

having a sedimentation constant of 70 S, which are practically indistinguishable from virulent phages under the electron microscope. (The sedimentation constants of the virulent phages is 79 S.) The subunits do not aggregate in the absence of the RNA, in contrast to the behavior of the tobacco mosaic virus, in which the coat protein subunits are arranged in equivalent positions. The yield of virulent phages in the self-assembly process is admittedly only 10^{-7} to 10^{-8}.

European J. Biochem. *2*, 152 (1967) / –Hö. [Rd 823 IE]

A precursor of antique purple, 6,6'-dibromoindigotin, has been isolated by *J. T. Baker* and *M. D. Sutherland* from a hypobranchial-gland extract from the Australian marine snail *Dicathais orbita* in the form of the Ag salt of a pale yellow-orange compound silver "tyrindoxyl" sulfate. The compound was identified as *(1)*, M = Ag. Enzymatic hydrolysis of the Na salt with aqueous gland extract followed by exposure to sunlight gave 6,6'-dibromoindigotin. When chromatograms of *(1)*, M = Na, were sprayed with 1N HCl and heated to 100 °C, the violet pigment was again formed.



(1)

Gland extracts from autolyzing snails gave a pale yellow-green precipitate of tyriverdin, $C_{36}H_{30}Br_4N_4O_5S_4$, which also gave 6,6'-dibromoindigotin, as well as dimethyl disulfide, on exposure to light. It is presumably a quinhydrone of *(1)* and a dehydro-*(1)*. / Tetrahedron Letters *1968*, 43 / –Ma. [Rd 815 IE]

Hydroxylammonium fluoride *(1)* has been prepared for the first time by *B. Frlec* and *H. H. Hyman*. Anhydrous HF was condensed on hydroxylammonium chloride in all Kel-F system, and the reaction was controlled by cooling with liquid nitrogen. When the reaction is complete, the system is slowly warmed to –78 °C. HCl vaporizes first, and the unreacted HF is then distilled off, the final stages being carried out under vacuum at room temperature. When the residual liquid $NH_2OH \cdot xHF$ (x = 1.6–2) is washed with anhydrous ethanol it forms crystalline, hygroscopic $(NH_3OH)F$ *(1)*. After drying under vacuum, *(1)* melts at 90 ± 3 °C (with decomposition; Kel-F capillary tubes). The thermal decomposition of *(1)* at 215 °C probably yields the following products.

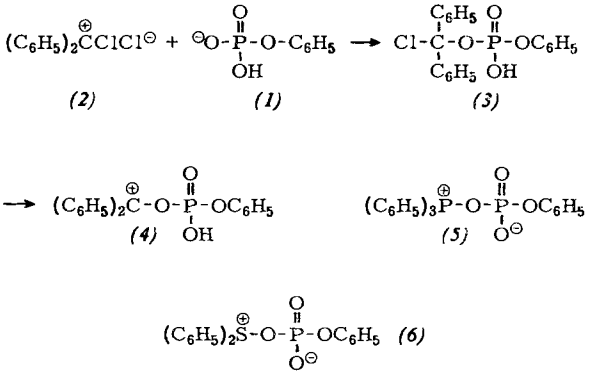
$$\underset{(1)}{3\,(NH_3OH)F} \xrightarrow{\Delta} NH_4F + 2\,HF + N_2 + 3\,H_2O$$

/ J. inorg. nuclear Chem. *29*, 2124 (1967) / –WG. [Rd 789 IE]

A new red modification of tin(II) oxide and the known red and black modifications were obtained in very pure states by *W. Kwestroo* and *P. H. G. M. Vromans*. The three modifications are prepared from 99.9999% tin, which is dissolved in pure hydrochloric acid. Concentrated ammonia is added to the freshly prepared $SnCl_2$ solutions. When the alkaline solution is heated 12–15 h at 70 °C, black tetragonal SnO is formed. In the preparation of the known red orthorhombic SnO, a little phosphorous acid is added to stabilize the product. To prepare the new red phosphorus-free tin oxide, sufficient NH_3 must first be added to raise the pH value to about 9. Concentrated hydrochloric acid is then added rapidly, in such a way that the temperature rises above 95 °C and the pH falls to a value of 4–5. The white precipitate changes within a few minutes into a red modification which is stable even in the absence of phosphite, and differs from the known red modification in its X-ray diagram as well as crystallographically. Its structure has not yet been established. / J. inorg. nuclear Chem. *29*, 2187 (1967) / –WG [Rd 790 IE]

The trimethylsilyl group can be used as a protective group for terminal alkynes in Grignard syntheses. *C. Eaborn*, *A. R. Thompson*, and *D. R. M. Walton* arrived at this conclusion while working with the phenylacetylene system, but believe that this method is also suitable for other alkynes. For example, *p*-bromophenylethynyltrimethylsilane can be readily prepared from *p*-bromophenylethynylmagnesium bromide and trimethylchlorosilane, and reacts with magnesium in THF to form the Grignard reagent $p\text{-}(CH_3)_3Si\text{–}C{\equiv}C\text{–}C_6H_4\text{–}MgBr$. Carboxylation yields the acid $p\text{-}(CH_3)_3Si\text{–}C{\equiv}C\text{–}C_6H_4\text{–}COOH$, and treatment with dilute alkali gives 4-ethynylbenzoic acid in an overall yield of 55%. / J. chem. Soc. (London) *C 1967*, 1364 / –DK. [Rd 791 IE]

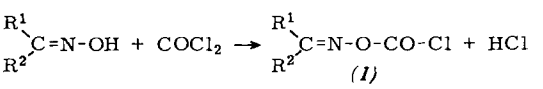
Phosphorylations involving carbonium, phosphonium, and sulfonium ions as intermediates have been described by *H. Kaye* and *Lord Todd*. Phenyl phosphate *(1)* reacts rapidly and quantitatively with dichlorodiphenylmethane *(2)* at 25 °C in a mixture of pyridine and a polar solvent such as nitrosomethane, DMF, or acetonitrile to form P^1,P^2-diphenyl pyrophosphate and benzophenone. In the presence of an excess of *n*-propanol and a very large excess of *(2)*, the reaction leads quantitatively to phenyl *n*-propyl phosphate. In the first step of the reaction, *(2)* probably reacts in the ionized form with *(1)* to form *(3)*, which is a phosphorylating agent of the P–X–Y–Z type. The carbonium ion *(4)* formed from *(3)* can then phosphorylate phenyl phosphate directly or after decomposition into monomeric phenyl metaphosphate, which is also a phosphorylating agent. The esterification of *n*-propanol probably proceeds *via* the pyrophosphate.



(2) *(1)* *(3)* *(4)* *(5)* *(6)*

Dichloromethylenetriphenylphosphorane (which can be prepared from triphenylphosphine and CCl_4) and diphenyl sulfide chloride react in a similar manner with phenyl phosphate to form the phosphorylating agents *(5)* and *(6)*. / J. chem. Soc. (London) *C 1967*, 1420 / –DK. [Rd 792 IE]

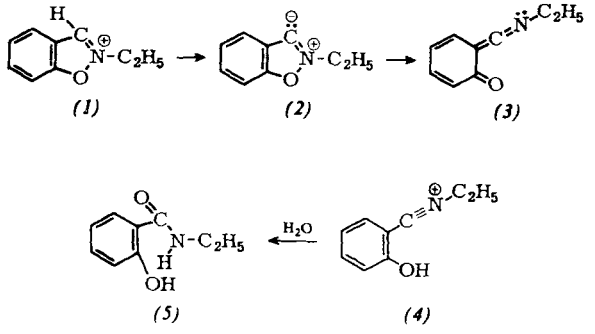
***O*-Chloroformyloximes,** a new and very reactive class of compounds, have been obtained by *A. Jumar*, *P. Held*, and *W. Schulze* by reaction of ketoximes with $COCl_2$. To avoid carbonate formation, the $COCl_2$ is preferably used in excess, and the reaction is carried out below 0 °C to obtain high yields. Examples: *(1)* $R^1 = R^2 = CH_3$, yield 88%, b.p. 50 to 53 °C/1.5 torr; $R^1 = CH_3$, $R^2 = C_6H_5$, yield 56% b.p. 58 °C/0.8 torr; $R^1 = CH_3$, $R^2 = C_6H_5$, yield 81%, m.p. 29–30 °C.



(1)

Chloroformyloximes are colorless, highly reactive substances. They react in the same way as carbonate ester chlorides with compounds containing reactive hydrogen (alcohols, thiols, amines). / Z. Chem. *7*, 344 (1967) / –DK. [Rd 793 IE]

The reaction of nucleophiles with *N*-ethylbenzoisoazolium cations *(1)* has been studied by *D. S. Kemp*. The first step is a base-catalyzed deprotonation to form *(2)*, and this is followed by a very fast *trans*-elimination:



(1) *(2)* *(3)*

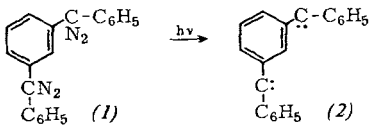
(5) *(4)*

The base finally adds to *(3)* or its conjugate acid *(4)* to form *N*-ethylsalicylamide *(5)*. Compounds *(3)* and *(4)* exhibit high selectivity toward bases. For example, high yields of *O*-acetyl-*N*-ethylsalicylamide are formed in aqueous acetate solution; this reaction thus provides a method for the *O*-acylation of salicylamides. / Tetrahedron *23*, 2001 (1967) / –Bu. [Rd 800 IE]

The stereochemistry of the electrolytic reduction of the C–Cl bond has been studied by *Barbara Czochralska*. In the reduction of optically active 2-chloro-2-phenylpropionic acid to α-phenylpropionic acid in 96% ethanol (mercury cathode, –1.4 V with respect to the Ag/AgCl electrode, 0.2 M CH_3COOH and 0.1 M $(C_2H_5)_4NCl$ as electrolytes), a product that had undergone inversion at the asymmetric C atom was obtained in 77–92% yield. The reaction may be assumed to proceed as follows: As in S_N2 substitution a carbanion with inverted configuration is formed in the rate-determining step *via* a complex involving five-coordinated carbon; the carbanion is then protonated by the solvent, with retention of configuration. / Chem. Physics Letters *1*, 239 (1967) / –Hz. [Rd 801 IE]

The molecular geometry of allyl alcohol has been studied by *A. Narasimha Murty* and *R. F. Curl jr.* on the basis of the microwave spectra of normal and of D- and ^{18}O-substituted allyl alcohol. Of the five conformations considered, that which best explains the spectra is one in which the ethylene group and the OH group are *gauche* with respect to each other, and the proton of the OH group is directed toward the ethylene bond. However, the postulated interaction between H and the π electrons is not strong enough to increase the O–H bond length appreciably (0.96 Å in alcohols, 0.97 Å in this compound). The dipole moment of allyl alcohol is 1.55± 0.04 D. / J. chem. Physics *46*, 4176 (1967) / –Hz. [Rd 802 IE]

A bis-carbene with a quintet ground state, according to *K. Itoh*, is formed by photolysis of 1,3-bis(α-diazobenzyl)benzene *(1)*. *(1)* can be incorporated into single crystals of benzophenone in a specific orientation. On photolysis of these crystals at 77 °K, one observes an ESR spectrum corresponding to a molecule having a spin quantum number S = 2 (quintet). This multiplicity had been predicted for the ground state of the expected photolysis product. Measurements at lower temperatures show that the observed ESR spectrum does in fact correspond to the ground state of *(2)*. *(2)* is very probably also formed on photolysis of *(1)* in liquids; however, the very complex ESR spectrum obtained in this case cannot yet be interpreted. / Chem. Physics Letters *1*, 235 (1967) / –Hz. [Rd 803 IE]



(1) *(2)*

Raman spectra of the tetraisothiocyanate complexes of the IIB metals in aqueous solution have been studied by *K. A. Taylor, T. V. Long II*, and *R. A. Plane*. The displacements of the C–S vibrational frequencies (700–800 cm^{-1}) in the complex in relation to those in the isothiocyanate ion show that the isothiocyanate ion is bound *via* nitrogen in the zinc complex and *via* sulfur in the mercury complex, while both types of linkage occur in the cadmium complex. This is also shown by the fact that cadmium complexes containing less than four isothiocyanate ligands give two C–S stretching frequencies, which merge into a single broad band in the case of the tetraisothiocyanate complex. The C–N frequencies (about 2100 cm^{-1}) are unaffected by *N*- or *S*-bonding of the isothiocyanate. / J. chem. Physics *47*, 138 (1967) / –Hz. [Rd 804 IE]

A free-radical flavoprotein containing flavin mononucleotide has been isolated and crystallized by *W. A. Bulen* from *Azobacter vinelandii*. The calculated molecular weight is 31200/mole of FMN; the protein contains one thiol group, but no iron or molybdenum. The free-radical nature of the anaerobically prepared flavoprotein was detected by paramagnetic resonance (EPR) measurements. The absorption maxima at 580 and 615 nm indicate a flavin semiquinone. This protein exhibits unusual behavior on oxidation and reduction. The anaerobically prepared protein, which is stable to atmospheric oxygen, is oxidized only in the presence of 50% saturated urea solution. The oxidized flavoprotein is reduced only very slowly and only to the semiquinone by dithionite; complete reduction is possible only in 75% saturated urea solution. This dependence of the stability of the free radical on the tertiary structure and the details of the EPR signal suggest the participation of a redox-active disulfide group. / J. biol. Chem. *242*, 3345 (1967) / –Scha. [Rd 805 IE]

A new reaction of nicotinamide adenine dinucleotide (NAD^+) has been discovered by *B. Zimmerman et al.* and by *B. M. Olivera* and *I. R. Lehman*. NAD^+ is required by an enzyme ("sealase") from *Escherichia coli* that converts hydrogen-bonded rings in the DNA of the λ-phage into covalently bonded rings. In this reaction, the ring closure takes place between a 5′-phosphoryl end and a 3′-hydroxyl end of the DNA by a 3′–5′-phosphodiester linkage. One NAD^+ is consumed per bond, the NAD^+ being broken down into adenosine 5′-monophosphate and nicotinamide mononucleotide. In the absence of DNA, the enzyme catalyzes an exchange between NAD^+ and NMN, but not between NAD^+ and 5′-AMP. The ring closure could therefore involve an adenylate enzyme as an intermediate (at the 5′ end of the DNA), which undergoes nucleophilic attack by the 3′-hydroxyl group of the opposite end. / Proc. nat. Acad. Sci. USA *57*, 1841, 1700 (1967) / –Scha. [Rd 806 IE]

Benzyl alcohol dehydrogenase, a new alcohol dehydrogenase (alcohol:NAD oxidoreductase; E.C. 1.1.1.1.), has been isolated by *M. Katagiri et al.* from a strain of *Pseudomonas* grown on toluene as the only source of carbon. The enzyme requires NAD^+ as an electron acceptor; $NADP^+$ cannot be used instead. The enzyme is stabilized by organic solvents. It is specific for primary, predominantly aromatic alcohols such as benzyl alcohol, saligenin, and furfuryl alcohol, but

not for aliphatic alcohols (methanol and ethanol are not affected). The enzyme is not inhibited by complexing agents or by monoiodoacetate and hydroxylamine, which are strong inhibitors of yeast and liver ADH respectively. It is inhibited by *p*-mercuribenzoate at a concentration of 1 μM. Since the benzyl alcohol dehydrogenase occurs only in bacteria grown on toluene or benzyl alcohol, it may be assumed that the occurrence of the enzyme is connected with the degradation of the toluene. / Biochim. biophysica Acta *139*, 173 (1967) / –Scha. [Rd 807 IE]

A simple ultramicro method for the quantitative determination of nitrogen in lipids and certain other compounds has been described by *G. H. Stone-Stanley*. It is possible to determine as little as 0.015 μg-atom of N. The samples are heated in 72% $HClO_4$, and after the addition of phenol, sodium pentacyanonitroferrate(II), alkaline phosphate buffer, and NaClO, the stable blue color at 635 nm is determined. No special purity requirements are imposed on the reagents apart from the water. / Biochem. J. *104*, 293, (1967) / –Scha. [Rd 808 IE]

A "Darwinian evolution experiment" has been carried out *in vitro* by *D. R. Mills, R. L. Peterson*, and *S. Spiegelman*. These authors used the enzyme "replicase" (RNA-dependent RNA polymerase), which is induced in *Escherichia coli* by the bacteriophages MS-2 and Qβ. This replicase requires the intact homologous RNA as a template and synthesizes identical RNA molecules, which can in turn be used as templates, and which are infectious. The system was subject to a selection pressure, *i.e.* the RNA was to be reproduced as rapidly as possible. The first molecules synthesized were accordingly removed soon after the start of the reaction and transferred to the next test tube to act as new templates. The rate of incorporation of ^{32}P–UTP into the RNA increased considerably in the course of the transfer, and after the 74th transfer, the molecules were being reproduced 15 times as rapidly as at the beginning. After only the 4th transfer the RNA had lost its infectious properties, and after the 74th transfer the molecule had been shortened by 83%. Since the replicase does not reproduce arbitrary fragments of the RNA, this process is a true "evolution" to an RNA that has a higher affinity for its enzyme, and which has lost all superfluous segments (which would have been necessary for the programming of an intact phage) in favor of those required for recognition and reproduction. / Proc. nat. Acad. Sci. USA *58*, 217 (1967) / –Scha. Rd 809 IE]

Three new α-amino acids of the type $R-O-CH_2-CH_2-CH(NH_2)-COOH$ (*O*-ethylhomoserine, *O*-propylhomoserine, and *O*-butylhomoserine) have been isolated by *T. Harada et al.* from culture media of *Corynebacterium ethanolaminophilum* when the media contained 1% of the corresponding alcohols (ethanol, *n*-propanol, and *n*-butanol). The amino acids were isolated by ion-exchange and paper chromatography and identified by elemental analysis and IR and NMR spectra. Comparison with synthetic material showed that the *O*-ethylhomoserine was the L isomer. The physiological role of these compounds is not yet known. / Biochem. biophysic. Res. Commun. *28*, 485 (1967) / –Scha. [Rd 810 IE]

The frequency-, temperature-, and concentration-dependent absorption of ultrasonic radiation by benzoic acid solutions was used by *L. Borucki* to determine the thermodynamic data given in the table for the association of benzoic acid (ν = 4 to 52 MHz; T = 15 to 55 °C). If it is assumed that the volume effect of the reaction can be disregarded, that the solutions behave ideally, that the dispersion of the speed of sound is negligible, that the absorption of sound is entirely due to the equilibrium $A+A \rightarrow A_2$, and that the monomers and dimers do not exist in isomeric forms, the reduced absorption coefficient is given by

$$\frac{\alpha}{\nu^2} = \frac{D\tau}{1+(2\pi\nu\tau)^2} + \left(\frac{\alpha}{\nu^2}\right)_S + bx$$

(x = mole fraction of sample; τ = relaxation time; b = -56×10^{-15} to 2.5×10^{-15} $cm^{-1} \cdot sec^2$; D = complicated expression involving the coefficient of cubic expansion and the static specific heat)

	c-C_6H_{12}	CCl_4	$CHCl_3$	C_6H_5Cl	$C_6H_5CH_3$
$\vec{k}_x$ (sec^{-1})	7.8×10^{10}	6.8×10^{10}	5.8×10^{10}	5.0×10^{10}	3.6×10^{10}
$\overleftarrow{k}_x$ (sec^{-1})	2.2×10^{5}	3.3×10^{5}	7.4×10^{6}	2.1×10^{6}	3.3×10^{6}
$\vec{\Delta H}^{\ddagger}$ (kcal·mol^{-1})	1.0	1.0	0.3	0.8	0.6
$\overleftarrow{\Delta H}^{\ddagger}$ (kcal·mol^{-1})	13.9	13.9	9.8	11.1	9.9
$\vec{\Delta S}^{\ddagger}$ (kcal·mol^{-1}·deg^{-1})	−5.2	−5.4	−8.1	−6.8	−8.0
$\overleftarrow{\Delta S}^{\ddagger}$ (kcal·mol^{-1}·deg^{-1})	13.6	14.4	6.7	8.6	5.4

$K_x = \vec{k}_x/\overleftarrow{k}_x$; $\Delta H = \overleftarrow{\Delta H}^{\ddagger} - \vec{\Delta H}^{\ddagger}$; $\Delta S = \overleftarrow{\Delta S}^{\ddagger} - \vec{\Delta S}^{\ddagger}$.

The diffusion of the molecules together ($A+A \rightarrow (A+A)$) is found to be rate-determining, rather than the subsequent dimerization ($(A+A) \rightarrow A_2$). In benzene the dimerization is disturbed by the formation of solvent complexes, or else several relaxation effects occur. The solvent dependence of the enthalpies and entropies of reaction is due to electrostatic effects. / Ber. Bunsenges. physik. Chem. *71*, 504 (1967) / –Jg. [Rd 811 IE]

A surface layer of Ag_2O_3 on silver catalysts used at 200 to 300 °C for the reaction ethylene + oxygen → ethylene oxide has been detected by electron optics (reflection and fine-range diffraction; replica method) and by X-ray analysis (Debye-Scherrer) by *M. Feller-Kniepmeier, H. G. Feller*, and *E. Titzenthaler*. Chemisorption models with formation of atomic oxygen and reactions *via* silver peroxide AgO_2 have been discussed. However, no AgO_2 or Ag_2O has been found. After removal from the carrier (Al_2O_3) by ultrasonic radiation, the fresh and the used catalysts exhibit characteristic differences, the former having caked, shapeless crystals, whereas the used catalyst frequently contains oriented, overgrown or pure Ag_2O_3 needles. The formation of Ag_2O_3 begins on the compact metal at 240 °C and can be detected up to 400 °C. An oriented arrangement of the crystallites in an oxidizing atmosphere is observed only in the presence of a component (*e.g.* ethylene) that makes transport reactions possible. Pure Ag_2O_3 without an Ag nucleus is catalytically inactive. / Ber. Bunsenges. physik. Chem. *71*, 606 (1967) / –Jg. [Rd 812 IE]

Crustacyanin, a chromoprotein from lobster shell, has been described by *H. Kühn* and the late *R. Kuhn*. The chromoprotein can be isolated from the shell with complexing agents on dissolution of the $CaCO_3$, and can be purified by precipitation with ammonium sulfate and ultracentrifugation. It is a blue (λ_{max} = 632 nm) protein having a molecular weight of 310000–320000 and containing 16 molecules of astaxanthin. The color depends on the quaternary structure of the protein, which can be (partially) reversibly resolved

into subunits. In neutral solutions of low ionic strength, β-crustacyanin (λ_{max} = 585 nm, molecular weight 38000, two molecules of astaxanthin) is formed. This can be split into two fragments (λ_{max} = 440, 482 nm, molecular weight 19000, each containing one molecule of astaxanthin) in 0.15% sodium dodecyl sulfate. It is only on further dissociation in 6–8 M urea in alkaline solution into fragments having a molecular weight of 7000–10000 that the pigment (λ_{max} = 400 nm) is separated in the form of aggregates containing protein. The intact crustacyanin molecule has an axial ratio of 1:10 (viscosity measurements). This together with the partial specific volume ($\bar{v}$ = 0.66 ml/g) leads to an estimated value of about 300 Å for the length of the molecule, which corresponds exactly to the length of eight astaxanthin molecules. / European J. Biochem. *2*, 349 (1967) / –Hö.

[Rd 827 IE]

A three-dimensional Fourier synthesis of human deoxyhemoglobin with 5.5 Å resolution has been completed by *H. Muirhead, J. M. Cox, L. Mazzarella,* and *M. F. Perutz.* The tertiary structure of the chains of human deoxyhemoglobin and of horse oxyhemoglobin is the same; however, there are appreciable differences in the quaternary structure. A preliminary structural analysis of horse deoxyhemoglobin showed that the differences between horse oxyhemoglobin and human deoxyhemoglobin are not species differences, but are the result of the incorporation of oxygen. The change in the quaternary structure on deoxygenation may be described as rotation of the subunits in the same direction through 9.4° (α chains) and 7.4° (β chains) about axes that converge outside the molecule in an acute angle above the two-fold axis of symmetry. This leads to loosening of the entire structure, and the distances between similar chains become greater. The interactions between the β chains are completely eliminated, since the distance between the β_1 amino group and the β_2 carboxyl group increases from 6 to 12 Å. The identity of the tertiary structures of horse oxyhemoglobin and human deoxyhemoglobin is shown by means of stereo pictures. / J. molecular Biol. *28*, 117 (1967) / –Hö. [Rd 824 IE]

An RNA synthesis in the direction 3′→5′ has been found by *D. H. L. Bishop, N. R. Pace,* and *S. Spiegelman* to occur alongside RNA synthesis in the known direction, *i.e.* from 5′ to 3′. The authors were able to elucidate the structure of the intermediates "HS" and "FS" (structures after *Hofschneider* and *Franklin* respectively) that can be detected during the reproduction of the RNA of the phage Qβ, and which can be separated by electrophoresis in polyacrylamide. The HS complex formed first consists of the RNA template and the attached incomplete ("negative") complementary chain. In the FS complex, the restarted positive chain is also bound to the negative chain. It was verified by the use of β,γ-labeled trinucleotides that the negative chain is synthesized in the "conventional" 5′→3′ direction, since all the newly incorporated nucleotides immediately lose their radioactivity because of the elimination of pyrophosphate. Only the nucleotide in the 5′ position (in this case GTP) retains its triphosphate. On the other hand, the last nucleotide incorporated into the new positive chain in the FS structure still has its triphosphate, *i.e.* the 3′-OH group of the entering nucleotide reacts with the 5′-triphosphate group of the existing chain. In this case, therefore, the synthesis takes place in the 3′→5′ direction. The synthesis of the new positive chain is started before the negative chain is complete. / Proc. nat. Acad. Aci. USA *58*, 1790 (1967) / –Hö. [Rd 828 IE]

Biologically active DNA has been synthesized *in vitro* by *A. Kornberg and M. Goulian.* The procedure used was as follows. DNA of the phage X 174 (annular) was incubated with φ X 174-induced *Escherichia coli* polymerase, polynucleotide ligase, and the four trinucleotides (TTP replaced by 5-bromo-UTP). The reaction product consists of double rings of the introduced ("positive") chain and the synthesized ("negative") chain containing bromine, these rings being wound round one another. They are treated with DNase until (statistical) opening of one ring per double ring had occurred. DNA containing bromine could then be separated from bromine-free DNA by density gradient centrifugation. The negative ring containing bromine, which was itself biologically active, was then used as a template for the synthesis of a new positive ring. The biological activity was detected by mixing the synthetic DNA with spheroblasts of *Escherichia coli,* in which the synthesis of new φ X 174 phages took place. The success of the experiment depended on the high purity of the polymerase (particularly removal of DNase) and the possibility of a reliable separation of the DNA introduced from that synthesized. This is the second case of an *in vitro* reproduction of biologically active hereditary matter (the other was the reproduction of phage RNA by *S. Spiegelman* two years ago), and the first case for DNA. / Proc. nat. Acad. Sci. USA *58*, 2321 (1967) / –Hö. [Rd 829 IE]

Methanol is oxidized in *Pseudomonas* by an unusual alcohol dehydrogenase. *C. Anthony* and *L. J. Zatman* have studied the C_1 metabolism of the bacterial strain that can grow on methanol as the only source of carbon and energy. The alcohol dehydrogenase was enriched by a factor of 10 (from *Pseudomonas sp.* M 27). It was found to behave homogeneously in the analytical centrifige ($S_{20,w}$ = 7.78 S) and on electrolysis on polyacrylamide. The molecular weight is 146000 (Archibald method). The spectrum of the enzyme shows maxima at 280 and 350 nm. The enzyme does not require nicotine adenine dinucleotide; nor is it a flavoprotein. *N*-Methylphenazonium methyl sulfate is used as the primary electron acceptor in the test. Denaturation results in the liberation of a low molecular weight substance exhibiting green fluorescence (fluorescence maximum 460 nm, excitation maxima 260 and 365 nm). On stepwise denaturation, the quantity of the material liberated is proportional to the loss of activity. It is assumed that a pteridine derivative acts as the prosthetic group. The enzyme molecule contains about 30 molecules of glucosamine. Ammonia or methylamine must be added for activation in the test. / Biochem. J. *140*, 953, 960 (1967) / –Hö. [Rd 825 IE]

The mode of action of the B_{12} coenzyme in the reduction of ribonucleotides has been studied by *R. H. Abeles* and *W. S. Beck.* 5,6-Dimethylbenzimidazolyl-5′-deoxyadenosylcobamide is required for the reduction of nucleoside triphosphates to deoxynucleoside triphosphates by thioredoxin or dihydrolipoic acid. When coenzyme B_{12} that is labeled with tritium in the 5′ position of the deoxyribose is used, one atom of tritium is given up to the water for each molecule of nucleotide reduced. If the reaction is allowed to take place with unlabeled coenzyme in water containing T_2O, tritium is incorporated into the coenzyme and is also attached to the 2′-deoxyribosyl carbon atom of the nucleotide. Thus coenzyme B_{12} acts as a hydrogen transfer agent in the synthesis of deoxyribonucleotides, as is also assumed for the methylmalonyl-CoA isomerization. / J. biol. Chemistry *242*, 3589 (1967) / –Hö. [Rd 826 IE]

Lehrbuch der Elektrochemie (Textbook of Electrochemistry). By *G. Kortüm*. Verlag Chemie GmbH, Weinheim/Bergstr. 1966. 4th Edit., xvi, 592 pp., illustrations and 72 tables, DM 52.–.

Originally written for science students in their later semesters, this book has acquired a very much wider circle of readers owing to the increasing importance of electrochemistry for many areas such as biochemistry, analysis, chemical kinetics, industrial processes, and new methods of generating electricity.

Basically, the book is devoted to the fundamental aspects. Only occasionally are indications of industrial use to be found in the text. The presentation of the principles covers much material. Thus the first 40 pages are reserved for the fundamental laws, and 45 pages are devoted to chemical thermodynamics. In the preliminary chapter on the preparation of pure substances the band model for the solid state is taken up anew, thereby laying the ground for the later treatment of electrode kinetics at semiconductor electrodes.

A third of the total number of pages is devoted solely to the theory of electrolytes. It contains a new section on concentrated solutions and molten salts (7 pages; the most recent papers cited there were published in 1962).

The phase boundary electrode/electrolyte occupies the main part of the book (five chapters). Analytical uses are here treated at reasonable length. The accounts of studies of the structure of the electrochemical double layer and of the types of polarization have been thoroughly revised. Numerous references to original papers make for easier access to the specialist literature in these fields.

The last of the 15 chapters has the title "Uses of electrochemical processes". Here are to be found very condensed but clear treatments of galvanic elements, of analysis, of the problems of electrodeposition, and of corrosion. Industrial electrochemical processes are not described, a fact that need not be deplored in this case, for an increased consideration of uses and industry in this book, which is directed to fundamental theories, would have destroyed the remarkable flexibility of the presentation and exceeded the limits of the treatment.

A chapter on photopotentials and electroluminescence in electrochemical systems could, however, have rounded off the picture of modern electrochemistry and should indeed find a place in this monograph.

It is not hard to prophecy that the fourth edition will confirm the view that *G. Kortüm*'s book is a standard work on electrochemistry, and is recognized as such beyond the boundaries of Germany. *F. v. Sturm* [NB 680 IE]

Physikalisch-chemisches Rechnen in Wissenschaft und Technik (Physicochemical Calculation in Science and Industry). By *H. Fromherz*. Verlag Chemie GmbH., Weinheim/Bergstr. 1966. 3rd Edit., xvi, 341 pp., 43 illustrations, DM 35.–.

On the assumption that the fundamental physicochemical laws can be learnt and mastered only by using them for relevant numerical examples, the author has collected 210 problems that are taken from actual practice or are met with daily by the physical chemist in his industrial work or in purely scientific work in the laboratory. In general, the present edition does not range beyond the limits of the second edition [*], but a number of formal details have been modified to meet recent international agreements.

Each of the 14 chapters is introduced by a preliminary statement of the important laws and the corresponding dimensions; but the main emphasis is always placed on setting and solving special problems. These exercises deal with problems of distillation technique, as well as others such as arise in connection with rocket propulsion, operation of a nuclear reactor, or medico-physiological work. Approximations are often used in solving the problems, since without approximations it is often impossible to make progress in practice. For example, the degree of dissociation is occasionally treated as identical with the conductivity coefficent, although these two concepts have somewhat different meanings; yet, in practice, treating the two numerical values as if they were equal often gives a better quantitative solution to an equilibrium problem than is obtained by the usual neglect or idealization of the degree of dissociation.

This book can certainly be recommended, not only to the beginner, but also to the expert, for it contains many hints on how to handle special problems more quickly.

Kl. Schäfer [NB 679 IE]

[*] Cf. Angew. Chem. *73*, 634 (1961).

Landolt-Börnstein, Zahlenwerte und Funktionen aus Naturwissenschaften und Technik (Landolt-Börnstein, Numerical Values and Functions from Science and Technology). Edited by *K.-H. Hellwege*. Gruppe II: Atom- und Molekularphysik. Band II. Magnetische Eigenschaften der Koordinations- and metallorganischen Verbindungen der Übergangselemente (Group II: Atomic and Molecular Physics. Vol. II: Magnetic Properties of Coordination and Organometallic Compounds of the Transition Elements). By *E. König*. Springer Verlag, Berlin-Heidelberg-NewYork 1966. xii, 578 pp., DM 232.–.

The present volume fully justifies the concept behind the "New Series" of Landolt-Börnstein, according to which a loosely connected series of rather small volumes on special areas is separated from the rigid arrangement into a few volumes covering wide fields. Research on magnetic properties, which has developed so rapidly, would have been very difficult to include clearly within the framework of the "Old Series". Specialized information on the magnetic properties of coordination and organometallic compounds of transition elements is collected in the volume under review.

The first part contains the results of measurements of magnetic susceptibility together with the temperature of measurement, the data being arranged according to the transition element concerned. The methods of determination and, for paramagnetic substances, the resulting magnetic moments and Θ values are also given. The arrangement thus corresponds with the established form of the *Foëx* and *Gorter* publication of 1957; the arrangement of literature references also corresponds to theirs. The references extend to 1965 but are not complete for the end of that year.

The tables are preceded by a brief introduction in which the fundamental equations for determination of magnetic moments from susceptibility values are given, together with diamagnetic corrections and also the calculation of moments with consideration given to the influence of ligand fields and the orbital momentum components. Ferro- and antiferromagnetic interaction are also briefly mentioned but ferrimagnetic interaction is not.

The most important and fundamental facts are skilfully extracted. Moreover, a comprehensive review of the literature makes it possible for the reader to obtain further information from more detailed works (for which purpose *Figgis* and *Lewis*' reviews seem particularly suitable). The tabular section (379 pages), which is supplemented by graphical presentation of magnetic measurements (29 pages), contains a few misprints (*e.g.* the reference for NbF_4 is to be found under A 65 Gi, not under 65 Gi), but these should not escape the critical user.

In the second Part the supplementary results of EPR measurements are again presented in a clear table (95 pages), the arrangement being the same as in the first part. Here too there is a short introduction, with references arranged according to specialist fields.

All in all, this is a reference book that will soon become essential to the expert. *W. Bronger* [NB 658 IE]

Einführung in die Liganden-Feldtheorie (Introduction to Ligand Field Theory). By *H. L. Schläfer* and *G. Gliemann*. Akademische Verlagsgesellschaft, Frankfurt 1967. 1st Edit., xiv, 522 p., 147 figures, DM 59.–.

The book is divided into two practically independent parts A and B, which approach the subject-matter from two different points of view.

The first part (and many readers will not go beyond it) starts with the problem "color and constitution" in complexes. Ligand and central atom absorption bands are distinguished empirically, and the important findings of the ligand field theory are likewise explained by reproductions of spectra and diagrams rather than by mathematical formulas. The reader is informed why the hexammine complex of divalent copper is deep blue, and is also told the answer to a number of other problems from the field of complex chemistry. Magnetic properties are also clearly explained, and a discussion of the important problem of the "kinetic stability" of complexes is included. Unfortunately, no theory of metal carbonyls and metal aromatic complexes is given, though the fundamentals underlying their comprehension are fully stated. A few lines of small print are all that is offered about the f electrons of the rare earths, and the interesting d^0 complexes of the type of the MnO_4^- ions have been left out.

While the second part of the book presupposes that the reader has but little knowledge of quantum chemistry, it is clear that it is designed for those who enjoy mathematical formalism. Presentation is in a clear, careful, systematic, and to some extent a pedantically detailed form. Before proceeding to the ligand field theory proper, the authors present a detailed description of the theory of free ions and group theory. The principal results are clearly tabulated.

The authors interpret the ligand field theory as an extension of the electrostatic theory, based on a classical article by *Bethe* (1929) and the evidently not very well known work of *Ilse* and *Hartmann* (1951). Justifiably, the molecular orbital theory of complexes is regarded as merely an extension and not as a true alternative.

Recent publications in this currently very active field are not considered in the discussion. The authors confine themselves to what is generally accepted, but give useful references to relevant literature.

The book can be recommended to a wide circle of readers, but above all to those interested in complex chemistry. A better coordination of Parts A and B might, perhaps, be achieved in a subsequent edition; Part B could, for instance, provide an explicit description of the derivation of the Tanabe-Sugano diagrams which form such an important item in Part A. A few blemishes in presentation could also be eliminated. *W. Kutzelnigg* [NB 703 IE]

Die Organische Chemie des Zinns (The Organic Chemistry of Tin). By *W. P. Neumann*. Ferdinand Enke Verlag, Stuttgart 1967. 1st Edit., xii, 232 pp., 4 illustrations and numerous tables, DM 69.–.

The chemistry of organotin compounds is one of the most important divisions of modern organometallic chemistry, because intensified research in this field and increased practical importance are bringing it more and more into prominence. The appearance of a monograph on the subject is therefore to be welcomed. Research on organotin compounds has been carried out by both organic and inorganic chemists, so that progress has profited from the experience of both groups of workers. Nevertheless, in spite of the common subject, the original papers usually bear the stamp of their origin both in the problem chosen and in the approach to its solution. This book is no exception in that it was obviously conceived and worked out by a true organic chemist, as the title also shows; it is to be taken literally.

The properties, methods of synthesis, and reactions of many organotin compounds are described in detail, reaction routes are interpreted mechanistically when possible, and relations between structure and reactivity are studied critically; further, points of practical interest, such as the numerous possibilities of industrial use, are treated at adequate length. On the other hand, other aspects are given only summary treatment, for instance, physicochemical and spectroscopic data (UV, IR, Raman, NMR, and Mössbauer spectra occupy a total of 3 pages), the complex-chemical behavior of organotin compounds, and the organotin derivatives of the transition metals. However, the original literature of these areas is well covered (930 references) and thus is at least made accessible from this course. The book therefore supplements the previous, smaller reviews of organotin chemistry, and may even replace them. The reviewer nevertheless considers the price rather high. *H. Schmidbaur* [NB 673 IE]

Kollagen (Collagen). By *G. Reich*. Verlag Theodor Steinkopff, Dresden 1966. xii, 308 pp., 61 illustrations, 85 tables, DM 48.80.

This book carries the modest-sounding sub-title "An Introduction to Methods, Results, and Problems of Collagen Research", but that is only a partial description of it. In fact, the book provides a good introduction into the varied aspects of our knowledge of this fibrous protein for those who are not specialists in collagen chemistry and also contains a wealth of references for the specialist. The appearance of this collation is particularly welcome because there has been considerable development of research on collagen in the past 10 to 15 years and the numerous recent original papers on chemical, medicinal, and technical aspects of the collagen field no longer suffice without considerable preknowledge; such knowledge has until now been difficult to obtain.

After an introduction into the construction of connective tissue, the structure and the physical and chemical properties of collagen are treated in great detail. Sections on general methods of protein chemistry are scattered throughout the text to help the beginner. The biological, biochemical, and medical aspects of collagen are intentionally treated rather more summarily; the detailed treatment returns with the production of leather and gelatin. The text is characterized by very conscientious coverage of the literature (1260 references). This has the natural result that very often the conclusions reached in the literature are described rather than the methods used or the experimental data, but this is to be welcomed in the interests of clarity and readability. The book will be a valuable help in literature searches for those who wish to delve deeply into the problems of collagen chemistry. Because the reviews that have appeared in the English language are outdated or concern mainly specialized sectional problems, this book may well gain a very wide audience.

H. Hörmann [NB 657 IE]

Comprehensive Biochemistry. Edited by *M. Florkin* and *E. H. Stotz*. Vol. 22. Bioenergetics. Elsevier Publishing Company, Amsterdam-London-New York 1967. 1st Edit., xi, 214 pp., 51 figures, Dfl. 35.–[1].

In intermediate metabolism, dissimilatory and synthetic energies are thermochemically coupled. The energy cycles

[1] Vol. 16, cf. Angew. Chem. *79*, 159 (1967); Angew. Chem. internat. Edit. *6*, 191 (1967).

and routes form the subject matter of volume 22 of this comprehensive handbook of biochemistry, which, so to speak, gives a chapter by chapter account of the foundations of a "submolecular biology". In the first chapter *A.* and *B. Pullman* describe the general ideas and methods of quantum biochemistry, which is concerned with the quantum mechanical investigation of the electronic structure of biologically important molecules. The achievements and predictions realizable by means of this theoretical treatment are illustrated by a number of examples. *B. Grabe*'s new interpretation of the "energy-rich bond" is, of course, not mentioned since only the literature up to the beginning of 1966 is referred to. Attempting to force such a rapidly developing science into a relatively slowly appearing compendium clearly has its limitations.

The mechanisms of energy transfer are dealt with by *Th. Förster* in a short section devoted to the problem of transfer of free energy between various cell components. A lucid account is given of the theoretical and the experimental approaches to the resolution of this problem which, of course, still rely largely on the use of models. Charge transfer complexes may be involved in conducting energy from one system to another in solution and in solids. The points touched on in the first chapter are discussed in more detail in the chapters written by *E. J. Bullock*. The latter also contain a tabular survey of the complex molecules of most biological substances, and in particular those of the flavins and the pyridine nucleotides. The excellently written and well thought out section by *P. Mitchell* is likely to prove of greatest interest to the biochemist. In 25 pages the principles of the chemo-osmotic ion translation through membranes are discussed. The four chapters blend well to give contemporary treatment of the subject. As the price might lead one to expect, printing and presentation are faultless.

L. Jaenicke [NB 721a IE]

Comprehensive Biochemistry. Edited by *M. Florkin* and *E. H. Stotz*. Vol. 28: Morphogenesis, Differentiation and Development. Elsevier Publishing Company, Amsterdam-London-New York 1967. 1st Edit., xii, 276 pp., Dfl. 42.50.

This volume of "Florkin-Stotz" demonstrates that embryology has at last outgrown its descriptive biology stage and is beginning to be understood on a molecular level as the chemical and physical parameters of the growing embryo become accessible to measurement. The contributors to this volume do not conceal the fact that the analytical treatment of these problems is tedious, and that a chemical understanding of the phenomenon of "life" is still far off. As on every occasion in the past, the editors have succeeded in finding experienced and skilled specialists to write about the selected topics. *A. Monroy* deals with oogenesis, in which an inert mature egg is fertilized and made to grow into a living organism by making the genetic information fixed in it capable of being identified. The information is contained in nucleic acids, the behavior of which during cell differentiation is described by *J. Brachet* in analogy to the better understood processes in bacteria. *E. Scarano* and *G. Augusti-Tocco* deal with chemical embryology in a most carefully compiled section which contains 416 references.

The biochemical processes and the metabolic pathway regulators acting by interaction of macromolecules during embryogenesis are modeled largely on reactions known to take place in the adult organism. An article by *T. Yamada*, which resembles more a review than a critical evaluation, discusses how the embryonic induction factors effect the formation of specific cell populations from undifferentiated prospective material.

The biochemical processes occurring during hormone-induced metamorphosis of amphibia are described by *R. Weber*. This widely embracing work provides interesting interpretations of long known but still uncertain processes which must operate in conjuction with "an attuned organism".

The analogous chapter on insect metamorphosis by *L. J. Gilbert* is an indication of the potential of insect biochemistry rather than just a compilation of data. This volume is stimulating in many respects although some of the aspects are treated subjectively. The bibliography includes very recent work; unfortunately, however, references to previous volumes are somewhat sparse. The neat arrangement of the work needs no reiteration. Like its predecessors, this volume has been printed on soft rough paper. The readability is therefore spoilt, not by glare, but rather by unsharp contours.

L. Jaenicke [NB 721b IE]

Cross Electrophoresis, its Principles and Applications. By *S. Nakamura*. Elsevier Publishing Co., Amsterdam-London-New York 1966. 1st Edit., ix, 194 pp., numerous illustrations and tables, Dfl. 47.50.

In 1953 *Grassmann* and *Hübner* showed that paper electrophoresis by the curtain principle is suitable for detection of complex formation or association by dyestuffs if the two components are applied in such a way that the paths taken by them on electrophoresis cross each other. This principle was applied by *Nakamura* to horizontal paper electrophoresis, extended to a two-dimensional technique, and tested on a series of interacting systems. Thus arose what is called "cross electrophoresis". However, a special case, in which the substances are applied to the strips in parallel streaks so that the faster-moving component passes over the slower (which reacts with it), is described by *Lang* as "Überwanderungselektrophorese" (overrunning electrophoresis).

The first 36 pages of this book are devoted to principles and apparatus, the next 23 pages to immunochemical use of the method. It seems to the reviewer that, particularly in immunological reactions, the usual carrier material (paper) might be replaced with advantage by agarose plates or acetate foil; then, similar results are to be expected to those obtained by *Ressler*'s or *Laurell*'s method in which the antibodies are equally distributed in the medium. Later sections of the book treat the behavior of trypsin inhibitors and the possibilities of studying enzyme-substrate complexes. 400 citations from the literature are given in this book, including more than 30 to work of the author.

For those who can and wish to apply this comparatively little-used technique to their own problems, this book is a safe guide, being written in clear language and well set out. Unfortunately the pictures obtained by means of cross electrophoresis have no aesthetic appeal!

B. Kickhöfen [NB 675 IE]

The Structure of Inorganic Radicals. By *P. W. Atkins* and *M. C. R. Symons*. Elsevier Publishing Corp., Amsterdam-London-New York 1967. 1st Edit., x, 280 pp., numerous illustrations and tables, bound, Dfl. 60.–.

Our knowledge of free radicals, their electronic states and bonding, has been greatly extended by the use of electron paramagnetic resonance (EPR). In this work, inorganic radicals have a special place because their composition is generally simple. Their electronic states are important for clarification of the electronic structure of analogous diamagnetic molecules which arise from these radicals by addition or removal of an electron. In the book under review, an attempt is made to collect the EPR results on inorganic radicals in a uniform framework, to consider them critically, and thus to make them accessible to a wider circle of readers.

The book begins with an introduction to the technique of EPR investigations and to the methods of preparation and matrix-isolation of radicals. This forms the basis for a gradually developing treatment of the types of radical: electrons in matrices and in solution; ions and atoms in matrices; and radical molecules containing two, three, four, or five atoms. A chapter in which generally valid conclusions

are drawn from the results already discussed closes the text of the main part of the book. Each chapter is introduced by a short description of its contents. Interpretation of the experimental results is highly critical. The literature is almost completely taken into account up to and including 1964.

Since the most important object of the book is to clarify the electronic structure of radicals, the authors' attempt to banish theoretical treatment of the results to a brief mathematical appendix must be criticized. This division has the result that many concepts and quantities are used in the main part although their definition is to be found only in the appendix. The reader thus needs some basic knowledge of quantum chemistry.

The book doubtless fills a noticeable gap and should thus be recommended to all who are concerned with the electronic structure of simple molecules and/or ESR measurements, and to every inorganic chemist. Printing and style are good, but in spite of many good points the price seems to be too high.

E. König [NB 677 IE]

Nuclear Magnetic Resonance for Organic Chemists. Edited by *D. W. Mathieson*. Academic Press Inc., London-New York 1967. 1st Edit., ix, 287 pp., numerous illustrations, tables, and spectra, 65 s/$ 10.50.

This book is a collection of lectures and practical exercises (with solutions) that formed a summer course held for chemists by the Royal Institute of Chemistry, London, in 1964.

The chapters are written by several authors but coordinate well with one another, and they present a cross-section of high-resolution nuclear resonance spectroscopy in which applications of the methods and analysis of the spectra, rather than theory, are placed in the foreground.

After a short introduction into the general principles of nuclear resonance spectroscopy (*N. Sheppard*), chemical shifts and spin-spin coupling are treated in detail and very clearly (*J. A. Elvidge*).

The next three sections treat the analysis of three-, four-, and multi-spin systems (*E. O. Bishop*), and the ABX spectral type is dealt with in detail (*C. N. Banwell*).

The first part ends with chapters on the dependence of coupling constants on stereochemical factors (*R. J. Abraham*) and a short account of the magnetic resonance of nuclei other than hydrogen that are of interest to organic chemists (*J. Feeney*).

The examples of spectral analysis comprise 22 very well chosen and in part very difficult problems (with solutions), which are discussed in detail and approached from the most varied directions.

In sum, the book provides a good survey of the problems and possibilities of nuclear resonance spectroscopy and can be highly recommended to organic chemists interested in structure determination.

H. Friebolin [NB 664 IE]

Introduction to Mass Spectrometry. Volume 3 of the series "Spectroscopy in Education". By *H. C. Hill*. Heyden & Son Ltd., London 1966. 1st Edit., xi, 135 pp., many illustrations, board 30 s or $ 4.50.

H. C. Hill is an experienced worker in the English heavy chemicals industry. In 135 pages he gives a concise survey of the mass spectrometry of organic compounds. Experimental technique, methods of introducing the sample into the ion source of the apparatus, and methods of recording the spectra are discussed with exclusive reference to the AEI apparatus (apparatus from a few other firms have a bare mention). The mechanism of formation of fragments of organic molecules in the electron-impact ion source is treated in detail, and this lays the foundation for the next section which is concerned with interpreting mass spectra for elucidation of the structure of organic compounds. The important rules for their interpretation are derived and illustrated by means of examples. 18 spectra of "unknown substances" are left for the reader to handle; unfortunately they are rather one-sidedly chosen – only one benzene derivative, no heterocyclic compound, the remainder all aliphatic or cycloaliphatic compounds.

The book can be recommended as an introduction; but anyone wishing to concern himself more deeply with methods and apparatus of mass spectrometry will soon have to turn to more detailed monographs. The title does not indicate that this book concerns only an introduction to the mass spectrometry of organic compounds and to the interpretation of spectra for structural analysis of such compounds; the many other uses of mass spectrometry are not mentioned.

H. Kienitz [NB 670 IE]

Analysis of Copper and its Alloys. By *W. T. Elwell* and *I. R. Scholes*. Pergamon Press, Oxford 1967. 1st Edit., xiii, 183 pp., 11 illustrations and 4 tables, 50 s.

This book sets out the various chemical procedures used for analysis of copper and its alloys. Methods are described for determination of 29 elements – Cu, Al, Sb, As, Be, Bi, B, Cd, C, Cr, Co, H, Fe, Pb, Mn, Hg, Ni, N, O, P, Se, Si, Ag, S, Te, Sn, Ti, Zn, and Zr (Hf); these are preceded by general considerations on sampling.

Each chapter begins with a survey of the methods available, indicating those which are at present most generally used, always with references to the original papers; and each chapter is divided according to the methods used for determination of the elements under consideration in respect of the concentration ranges of interest. The analytical procedures are formulated precisely and are provided with data concerning their applicability and – what is extremely relevant – usually also their accuracy. Not only gravimetric and titrimetric methods, but also photometric techniques and some instrumental methods (polarographic and atomic absorption spectrometric) methods are described. The chapter on the determination of non-metals – H, C, O, N, and S – must be singled out as particularly valuable.

The book is written by distinguished experts in the field, from the laboratories of Imperial Metal Industries, England. Only a few wishes remain unfulfilled: for instance, for photometric determination of some elements reagents are preferred that can no longer be regarded as the most effective, *e.g.* hydrogen peroxide for determination of Ti, or iodide for determination of Bi; on the other hand, occasionally reagents are preferred that – at least in our experience – have not been generally adopted, *e.g.* zinc dibenzyldithiocarbamate for photometric determination of Cu and *p*-nitrophenylazo-orcinol for that of Be. Finally, the importance of temperature in direct iodometric titration of Sn should have been more strongly emphasized.

Elwell-Scholes can be most warmly recommended to all who are interested in the analysis of copper.

G. Kraft [NB 669 IE]

Bile Salts. By *G. A. D. Haslewood*. Methuen & Co. Ltd., London 1967, xi, 116 pp., several illustrations and tables, 27s 6d.

This little book gives a good summary of the chemistry, biochemistry, and physiology of bile acids and their conjugates, without pretention to being an exhaustive monograph. It builds on older collective books, and thus 71 % of the references are to literature published after 1960. In addition, very many unpublished observations from the author's laboratory are reported – and the author is among the most knowledgeable workers in this field.

The chemical structure, physical properties, separation, determination, and biosynthesis of gallic acids and their derivatives, as well as their possible role in the organism, are described, often too briefly but yet in suitable form. A special chapter is devoted to the distribution of the various bile acids; this is the only chapter where complete coverage is attempted and it forms a basis for a discussion of the importance of bile acids in evolution in the animal world. This part is without doubt the most valuable contribution and should ensure a wide readership for *Haslewood*'s little book, particularly among biologists and all others who are interested in the history of the development of animals.

G. Snatzke [NB 659 IE]

Gas Phase Reaction Rate Theory. By *H. S. Johnston.* From the series: Modern Concepts in Chemistry. The Ronald Press Company, New York 1966. 1st Edit., ix, 362 pp., numerous illustrations and tables, $ 10.–.

H. S. Johnston is the author of many papers on reaction kinetics. In the introductory chapter of this book he separates the concept of elementary chemical reactions from that of physical and physicochemical reactions. The principles of quantum mechanics and of classical and statistical mechanics that are important for gas-phase reactions are enunciated in six further chapters. In this part, particular attention is paid to the one-dimensional tunnel effect, the description of molecules by normal coordinates and of equilibria by the distribution functions of classical and wave-mechanical statistics. Then follows the main portion of the book, with chapters on impact velocities, bimolecular atom-transfer reactions, activation energies, preexponential factors of bimolecular atom transfer, the kinetic isotope effect, three-body collision reactions with particular attention to recombination of iodine atoms, the theory of complex reactions, and finally a summary.

The individual chapters are of a high standard and are written with the set purpose of demonstrating the theoretical principles underlying the rates of gas-phase reactions. Carefully selected experimental results obtained by modern methods are compared with the conclusions drawn from theory. As customary in books by American authors, the reader is presented with problems on which he can test his understanding of the subject. The excellent exposition is intended primarily for the physical chemist and is likely to rouse the enthusiasm of the reader for the old, but still very topical, field of gas-phase reaction kinetics. *H. Wolff* [NB 666 IE]

Treatise on Adhesion and Adhesives. Edited by *R. L. Patrick.* Vol. 1: Theory. Marcel Dekker Inc., New York 1967. 1st Edit., xi, 476 pp., numerous illustrations and tables, bound $ 21.75.

Following *De Bruyne* and *Houwink*'s monograph "Adhesion and Adhesives" of 1951, there now appears a three-volume "Treatise on Adhesion and Adhesives". The first volume, concerned with the theory of adhesion, has already been published.

Since intensive work in this field (particularly from a technological point of view) began only after 1950, a comprehensive treatment of recent views on problems of adhesion and their physicochemical basis was urgently needed.

The present volume contains contributions, some in excellent form, from nine authors who report mainly the results of work in their own special fields. It seems unavoidable that this should lead to some overlap of content and to overemphasis of some problems.

After a relatively short introduction by *R. L. Patrick, R. J. Good* gives a short summary of current knowledge of intermolecular interactions in the boundary region. Detail has intentionally been omitted, since it can be obtained from comprehensive monographs. *R. R. Stromberg* deals with adsorption of high polymers from solution on to solid surfaces. Because high polymers undergo marked changes in conformation during the adsorption process, there is as yet no satisfactory theoretical treatment for this subject, particularly as regards changes in entropy. For instance, the temperature-dependence of adsorption of polymers is not yet fully understood.

The relation between the structure of the adhesive and its adhesive behavior is reported by *I. R. Huntsberger.* The problem of wetting receives detailed discussion, the well-known papers by *Zisman* being reported. In contrast to some other researchers, the author is of the opinion that electrostatic interaction is of negligible importance for adhesives. Problems of adhesives that are of a mechanical or industrial nature (elongation, strain, fracture) are treated by *T. Alfrey Jr., D. H. Kaelble, G. R. Irwin,* and *J. L. Gardon.* Clear separation of theory from empiricism is not always achieved in these articles, as indeed is the case generally with problems that lead to formulas containing many parameters. The four contributions assume specialist knowledge of theoretical mechanics. It would be welcomed if in later editions some references were included in the article by *T. Alfrey Jr.*, so as to help the non-physicist with this field.

Finally there is an informative and comprehensive account of the chemistry of surfaces by *F. M. Fowkes*, who treats the most important problems from a thermodynamic and molecular-theoretical point of view.

To summarize, it may be said that this book will appeal equally to the chemist and to the technologist and engineer. It is to be hoped that the two further volumes of the "Treatise on Adhesion and Adhesives" will appear soon.

G. Peschel [NB 674 IE]

The Solid-Gas Interface. Edited by *E.A.Flood.* Marcel Dekker Inc., New York 1967. Vol. I, 1st Edit., 514 pp., numerous illustrations, bound $ 21.75.

The editor has set himself the task of providing, in cooperation with recognized experts, a two-volume work giving a survey of phenomena occurring at the gas/solid interface insofar as these are to be ascribed to physical adsorption and its consequences. Experimental results and theory are both considered.

In the first volume, which has now appeared, it is mainly the principles and their theoretical description that are treated. The second volume is to report recent experimental methods and results.

After an historical introduction by *H.Taylor, E. A. Flood* treats adsorption from the point of view of Gibbs and Polanyi thermodynamics. The Langmuir theory and the BET theory are described by *S. Brunauer, L. E. Copeland,* and *D. L. Kantro*; derivation of the adsorption isotherm and testing of its applicability form the main part of this section.

E. L. Pace is concerned with experimental investigations of thermodynamic values for the adsorption phase, such as heat of adsorption, heat capacity, and entropy of the adsorbent. A survey of the heats of adsorption measured by various schools is provided by *J. M. Holmes,* and *A. C. Zettlemoyer* and *K. S. Narayan* discuss heats of wetting and their relation to adsorption.

Van der Waals forces arising at the solid/gas interface, and chemical binding forces, are treated by *A. D. Crowell*; questions of surface energy and surface tension of crystalline solids are discussed by *G. C. Benson* and *K. S. Yun. W. J. Dunning* considers the structure of the surface and its importance for adsorption.

W. A. Steele studies mobile and localized monolayer adsorption, as well as multilayer adsorption, from the standpoint of statistical mechanics, and *J. M. Honig,* in a highly specialized article, places entropy at the focus of his considerations.

D. L. Kantro, *S. Brunauer*, and *L. E. Copeland* discuss determination of surface area by the BET method; *H. E. Farnsworth* reports on possible ways of preparing atomically "pure" solid surfaces and on tests of their "purity".

A section by *J. B. Hobson* is devoted to physical adsorption at extremely low pressures; a section by *S. Ross* is concerned with the influence of heterogeneity of the surface on adsorption. Finally, *G. D. Halsey* gives a summarizing, critical survey of the contributions in volume I of "The Solid-Gas Interface".

The particular advantage of this book over others lies in the facts that physical adsorption is discussed in it from such different standpoints and that, for once, the variety of factors that influence physical adsorption is recorded. The extensive references to the literature at the end of each chapter also deserve mention. It is to be hoped that the second volume will also contain such a wealth of information.

G. Wedler [NB 683 IE]

The Chemistry of Lignin. By *I. A. Pearl*. Edward Arnold (Publishers) Ltd., London 1967. Marcel Dekker, Inc., New York. 1st Edit., xi, 339 pp., 24 figures, $15.75.

Since the appearance of the last comprehensive review of lignin chemistry by *F. E. Brauns* and *D. A. Brauns* in 1960 our knowledge of the structure of lignin has become much more precise. The new book by *I. A. Pearl* offers a clear, concise, and readable survey of the present state of lignin chemistry, and is intended for chemists, biologists, and plant physiologists.

In the chapter on methods of isolation, the greatest amount of space is devoted to the lignin-sulfonic acids obtained from sulfite waste liquor. Today's most valuable lignin preparation — Björkman lignin — is discussed very briefly, in contrast to Klason and hydrochloric acid lignin, and no method of preparing it is given. In the chapter on structure, the presently postulated structure of lignin would be more soundly based if the classification were arranged in terms of structural units; moreover, it is superfluous to give eleven alternative proposed structures for spruce lignin. Considerable confusion is caused by the detailed and repeatedly cited formulation scheme of *Forss* and *Fremer* (pp. 124–127 and 162–169) which not only differs markedly from all other proposed structures, but also ignores the postulates of many groups of workers concerning the nature and number of the structural types present in lignin.

In two further chapters the biosynthesis of the monomeric lignin precursors (*p*-hydroxycinnamyl alcohols) and the chemical reactions of lignin during technical processing (sulfite and sulfate pulping and bleaching) are dealt with in detail. Chapter 6 deals with the chemical reactions of lignin and is restricted to a brief selection of the reactions that are most important in regard to the structure and use of the material. The following chapters give an account of the physical properties, the biological and thermal decomposition, and the bonding of lignin in the plant. A clearly written chapter displaying an impressive knowledge of the subject and describing the utilization of technical lignins in terms of their chemistry and economic aspects concludes the book. Some minor flaws are to be found: α-α linkages (γ-γ according to IUPAC) are retained (p. 71), though the evidence adduced would suggest 1,2-diarylpropane bonds. On p. 127 the fact that pinoresinol units have been clearly detected in natural lignin is ignored. A twelfth structural scheme (p. 157) for spruce lignin proposed by *F. E. Brauns* in 1962 was allegedly based on NMR evidence obtained by *McCarthy* in 1964. It would be desirable if more emphasis were placed on results and their evaluation concerning the structure of lignin (*e.g.* UV, Δε, IR and NMR spectra).

The bibliography includes all material published up to the end of 1965 with few exceptions; some of the literature cited is otherwise not readily accessible. All in all, the reader is offered a survey based on expert knowledge and a thorough approach to the subject. At the same time, the book deserves commendation for its clarity and concentration on the essentual features of lignin chemistry. *H. Nimz* [NB 714 IE]

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Cycloadditions – Definition, Classification, and Characterization

BY R. HUISGEN[*]

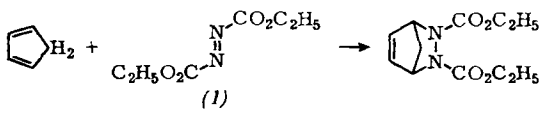
Dedicated to Professor A. Steinhofer on the occasion of his 60th birthday

The growing volume of publications on cycloadditions indicates that this general type of reaction merits a place beside the better-known substitutions, eliminations, and additions. The world of phenomena does not provide us with definition and classification principles. These are created by the scientist and are not free from arbitrariness. A terminology[1] is suggested for cycloadditions. These reactions do not all proceed by the same mechanism. Since ideas about reaction mechanism can change with the introduction of new criteria, it is shortsighted to base definitions and classifications on mechanism alone. Consequently, the definition of cycloadditions will not be restricted simply to multi-center processes with a cyclic electron shift.

1. Definition

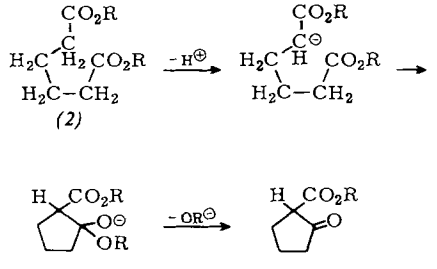
It is much easier to agree on which reactions are definitely cycloadditions than on the criteria to be applied in borderline cases. On the other hand, the term loses its value if the definition is too all-encompassing. In cases of doubt, usefulness should take precedence over absolute consistency.

The reaction of cyclopentadiene with diethyl azodicarboxylate *(1)*[3] led *Diels* and *Alder* to develop the reaction scheme which bears their names. In this cycloaddition, the total number of bonds remains unchanged, but the number of σ bonds increases at the expense of the number of π bonds.



(1)

Rule 1. Cycloadditions are ring closures in which the number of σ bonds increases.



(2)

The Dieckmann condensation[4] of adipates *(2)* constitutes a ring closure, with elimination of alcohol in the overall reaction. Though the cyclization step agrees with Rule 1, it should not be regarded as a cycloaddition. It is simply an intramolecular ester condensation.

The final product *(3)* in the next example again is not equivalent to the sum of the components. The synthesis of piperidines from amines and pentamethylene dibromide consists of two alkylation steps, the second of which is also a ring closure. The intramolecular S_N2 reaction is, however, not a cycloaddition.

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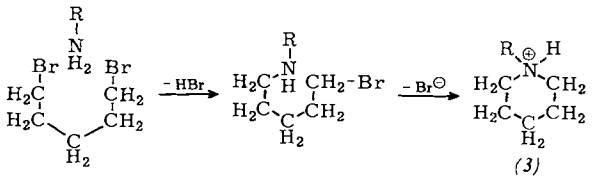
[1] The rules developed earlier in a handbook article [2] are expounded here and illustrated by examples.

[2] *R.Huisgen, R.Grashey,* and *J.Sauer* in *S. Patai*: The Chemistry of Alkenes. Interscience, New York 1964, p. 739.

[3] *O. Diels, J. H. Blom,* and *W. Koll,* Liebigs Ann. Chem. *443,* 242 (1925); *O. Diels* and *K. Alder, ibid. 450,* 237 (1926).

[4] *W. Dieckmann,* Ber. dtsch. chem. Ges. *27,* 102 (1894).

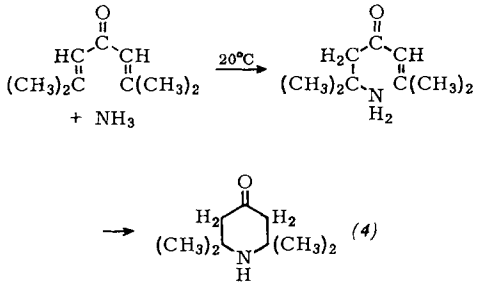


(3)

Rule 2. Cycloadditions are not associated with the elimination of small molecules or ions. The cycloadduct corresponds to the sum of the components.

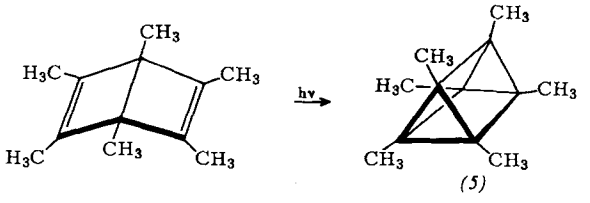
"Cycloadditions are chemical transformations giving at least one product having at least two new bonds as constituents of a new ring". This recent definition [5], which does not forbid the elimination of small molecules, is inadequate in our opinion [6], since the above reaction would then be a cycloaddition when the starting material was 1,5-dibromopentane, but not if the 5-bromopentylamine was isolated and then converted into *(3)*.

In the formation of tetramethyl-4-piperidone *(4)* from phorone and ammonia [7], though the final product corresponds to the sum of the components, the reaction is better classified as the addition of an amine to electrophilic double bonds. The reaction, which proceeds in several steps, involves the cleavage of NH bonds.



(4)

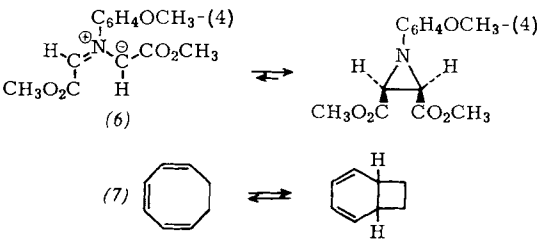
Rule 3. Cycloadditions do not involve the cleavage of σ bonds.



(5)

As in substitutions, the reacting groups in cycloadditions may be parts of the same molecule. A current example of this is the photochemical formation of hexamethylprismane *(5)* from the Dewar benzene derivative [8].

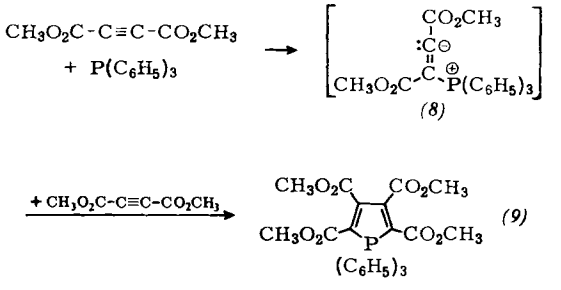
Electrocyclic reactions [9] cannot be denied recognition as cycloadditions, even when they are transannular. In this case one new σ bond is formed at the expense of



(6) *(7)*

a π bond. Examples of such reactions are the conrotatory closure of the aziridine ring from the azomethine ylide *(6)* [10] and the disrotatory valence isomerization of 1,3,5-cyclooctatriene *(7)* [11].

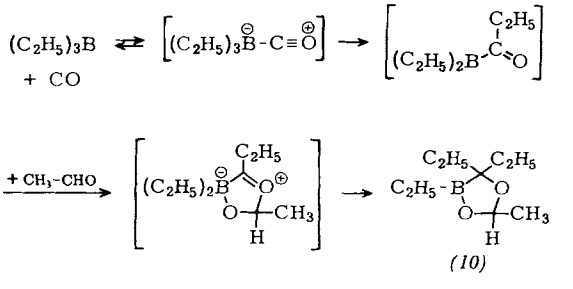
Rule 4. Cycloadditions can be intramolecular if one molecule contains the necessary functional groups.



(8) *(9)*

More than two components may also come together to form a ring.

Reactions of this type probably always involve several steps. Triphenylphosphine combines with two molecules of dimethyl acetylenedicarboxylate to form the unstable phosphole derivative *(9)* [12]. Though the 1:1 intermediate zwitterion *(8)* cannot be isolated, it can be intercepted with carbon dioxide [13].



(10)

The synthesis of a 1,4,2-dioxaborolane *(10)* from triethylborane, carbon monoxide, and acetaldehyde [14] actually involves three intermediates that cannot be isolated. From the existence of the boranecarbonyl, it is probable that the trialkylborane first reacts with the CO; the subsequent migration of an ethyl group again

[5] *J. E. Baldwin*, J. org. Chemistry *32*, 2438 (1967).

[6] The reason for this liberal definition was probably that in a series of small papers entitled "Cycloadditions", the American author dealt with a reaction that did not comply with Rule 2, which was already widely accepted at that time.

[7] *J. Guareschi*, Ber. dtsch. chem. Ges. *28*, Ref. S. 160 (1895).

[8] *W. Schäfer, R. Criegee, R. Askani*, and *H. Grüner*, Angew. Chem. *79*, 54 (1967); Angew. Chem. internat. Edit. *6*, 78 (1967).

[9] Definition: *R. B. Woodward* and *R. Hoffmann*, J. Amer. chem. Soc. *87*, 395 (1965).

[10] *R. Huisgen, W. Scheer*, and *H. Huber*, J. Amer. chem. Soc. *89*, 1753 (1967).

[11] *A. C. Cope, A. C. Haven, F. L. Ramp*, and *E. R. Trumbull*, J. Amer. chem. Soc. *74*, 4867 (1952).

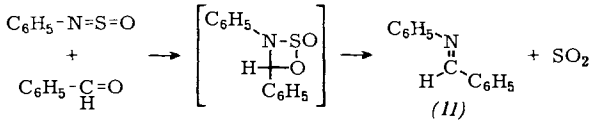
[12] *J. B. Hendrickson, E. R. Spenger*, and *J. J. Sims*, Tetrahedron *19*, 707 (1963).

[13] *A. W. Johnson* and *J. C. Tebby*, J. chem. Soc. (London) *1961*, 2126.

[14] *M. E. D. Hillman*, J. Amer. chem. Soc. *85*, 1626 (1963).

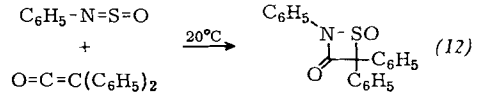
has nothing to do with the cycloaddition. The unstable primary product of the cycloaddition to acetaldehyde is stabilized by a further migration of an alkyl group.

Rule 5. When more than two components combine, only the reaction step leading to the ring is a cycloaddition.



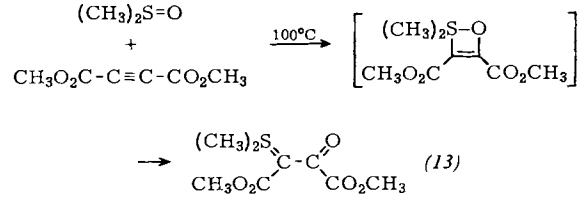
(11)

The ring of the primary cycloadduct may be rapidly opened or fragmented. When *N*-sulfinylaniline is heated with benzaldehyde, benzylideneaniline *(11)* and sulfur dioxide are formed [15]. Other four-membered cycloadducts of *N*-sulfinylaniline, *e.g.* the 1,2-thiazetidin-3-one derivative *(12)* obtained with diphenylketene [16], can be isolated.



(12)

The addition of dimethyl sulfoxide to esters of acetylenedicarboxylic acid [17] can be plausibly explained by a 2 + 2 cycloaddition followed by ring opening to form *(13)*. Similar four-membered rings (1,2-oxaphosphetanes) could also occur as intermediates in the Wittig olefination of carbonyl compounds [18].



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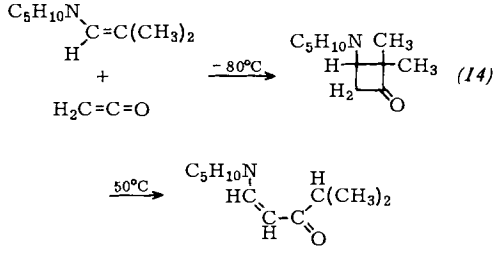
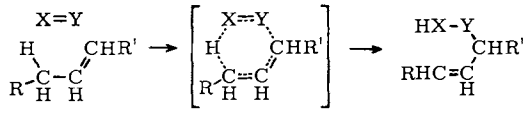


(14)

A better-established case is the intermediate cycloadduct in the β-acylation of enamines with ketenes. In the example given, *i.e.* the reaction of 1-piperidinoisobutene with ketene, the cyclobutanone derivative *(14)*, though thermally unstable, can be isolated [19]. The tendency toward ring opening is completely absent in 3-piperidino-2,2,4,4-tetramethylcyclobutanone, which is formed from the above-mentioned enamine and dimethylketene [20].

However, it is recommended that the term cycloaddition should be avoided when the reaction simply involves a cyclic transition state, as is the case in "ene reactions". These are allylic substitutions by a compound X=Y with an obligatory double bond shift; they are also contrary to Rule 3.



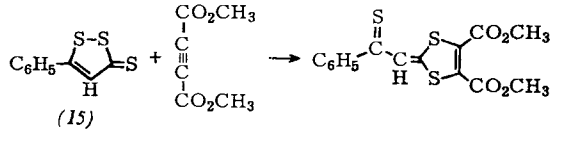
The reactant X=Y may be *e.g.* maleic anhydride [21], formaldehyde [22], or an ester of azodicarboxylic acid [23]. These ene reactions are undeniably related in mechanism to the Diels-Alder addition. However, cyclic activation configurations are postulated for so many reactions that though they might greatly enrich the range of cycloadditions, the enrichment would be uncontrolled and of doubtful value. The cycloadduct must have a finite life.

Rule 6. The products of the cycloaddition need not be stable or isolable, but the cycloadducts must occur at least as intermediates.

2. Classification

Cycloadditions are best classified on the basis of the number of new σ bonds. The resulting classes may be subdivided according to the size of the ring and the number of ring members contributed by each component.

Probably the only difficulty in the application of the first criterion is presented by simultaneous or subsequent ring opening.



(15)

In the reaction of 5-phenyl-3*H*-1,2-dithiole-3-thione *(15)* with dimethyl acetylenedicarboxylate [24], the net gain is one σ bond. The 1,3-dithiole ring formed obviously contains two new σ bonds, but the old ring is opened with the loss of one σ bond. The reaction is logically a cycloaddition with formation of two new σ bonds. The same situation arises in the cycloaddition

[15] *G. Kresze* and *R. Albrecht*, Angew. Chem. *74*, 781 (1962); Angew. Chem. internat. Edit. *1*, 595 (1962).

[16] *H. Beecken* and *F. Korte*, Tetrahedron *18*, 1527 (1962).

[17] *E. Winterfeldt*, Chem. Ber. *98*, 1581 (1965).

[18] A stable cycloadduct of a methylene phosphorane with hexafluoroacetone has very recently been described: *G. H. Birum* and *C. N. Matthews*, J. org. Chemistry *32*, 3554 (1967).

[19] *G. Opitz* and *F. Zimmermann*, Liebigs Ann. Chem. *662*, 178 (1963).

[20] *R. H. Hasek* and *J. C. Martin*, J. org. Chemistry *28*, 1469 (1963).

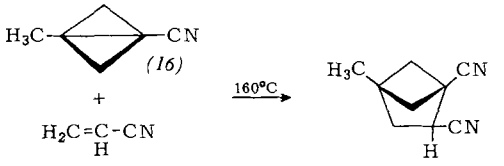
[21] *K. Alder*, *H. Söll*, and *H. Söll*, Liebigs Ann. Chem. *565*, 73 (1949).

[22] *R. T. Arnold* and *J. F. Dowdall*, J. Amer. chem. Soc. *70*, 2590 (1948).

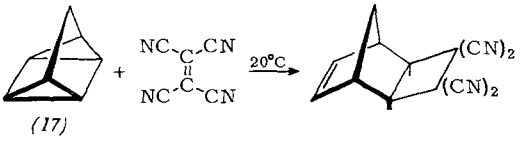
[23] *R. Huisgen* and *H. Pohl*, Chem. Ber. *93*, 527 (1960).

[24] *H. Behringer* and *R. Wiedenmann*, Tetrahedron Letters *1965*, 3705; *D. B. J. Easton* and *D. Leaver*, Chem. Commun. *1965*, 585.

of 1-cyano-3-methylbicyclo[1.1.0]butane *(16)* with acrylonitrile [25]. In this case there is no doubt about the simultaneity of the intra-annular loss of one σ bond (though not a "true" one) and the formation of two σ bonds to the unsaturated nitrile.



In the cycloaddition of quadricyclane *(17)* with tetracyanoethylene [26], the number of rings decreases from four to three. It is possible, however, to single out the cycloaddition step from the more complicated overall process. The ring to be considered is the new four-membered ring; thus two new σ bonds are formed.



(17)

Unification of the notation is desirable in the application of the ring-size criterion. The terminology "1,4-1′,2′ cycloaddition" is clumsy, as well as confusing, because *e.g.* hexa-2,4-diene adds in the 2,5 positions. A simpler and clearer name for this process, which yields a five-membered ring, is 3+2 cycloaddition. In this notation, the formation of a cyclic sulfone from butadiene and sulfur dioxide is a 4+1 cycloaddition.

Further subdivision may be based on method or on mechanism. Thus the photochemical 2+2 cycloadditions, which can in turn be grouped into singlet and triplet processes, can be distinguished in this way from *e.g.* the thermal dimerization of the polyfluoroalkenes or the cycloaddition of ketenes to olefins. Views on the mechanism of the "true" Diels-Alder reaction are so firmly established [27] that this name is not given to any 4+2 cycloaddition that deviates from this mechanism in any important criterion.

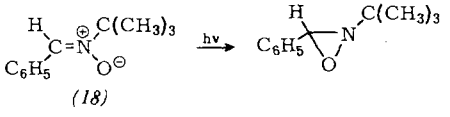
The distinction between one-step multi-center reactions and two-step processes, which relates to the energy profile of cycloadditions, is significant. This distinction is often the object of current investigations, but should not be used as a criterion, *e.g.* by regarding only one-step reactions as "true" cycloadditions. The Woodward-Hoffmann rules [28] predict the possibility of one-step processes on the basis of the conservation of orbital symmetry.

A few examples will now be given to illustrate the suggested classification system.

This group includes the wealth of electrocyclic reactions [9].

Three-membered Rings

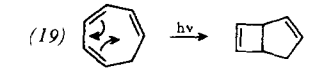
The equilibrium between azomethine ylides and aziridine derivatives was mentioned in Section 1 [compound *(6)*] [10]. A photochemical example is the conversion of the nitrone *(18)* into the oxaziridine [29].



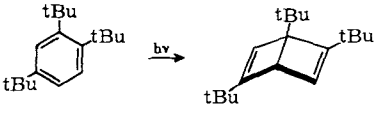
(18)

Four-membered Rings

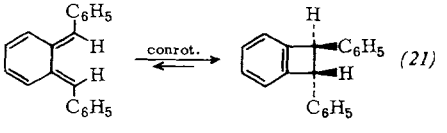
1,3-Dienes are converted into cyclobutenes on irradiation (for 1,3-butadiene, see [30]). Cycloheptatriene *(19)* [31], tropolone γ-methyl ether [32], and similar compounds react as 1,3-dienes, since this photocyclization in ring systems can only be disrotatory.



Even the benzene system behaves as a diene, as is shown by the photochemical formation of Dewar benzene derivatives *(20)* [33].



An example of the thermal conrotation is provided by the equilibrium established between *trans*-1,2-diphenyl 1,2-dihydrocyclobutabenzene *(21)* with *trans,trans*-5,6-bis(benzylidene)-1,3-cyclohexadiene [34].



(21)

Five-membered Rings

2-Acyl-5-phenyltetrazoles spontaneously lose nitrogen; the resulting *N*-acylnitrilimines are immediately transformed into 2,5-disubstituted 1,3,4-oxadiazoles *(22)* [35]. Many 1,5-cyclizations follow this scheme.

[25] *A. Cairncross* and *E. P. Blanchard*, J. Amer. chem. Soc. *88*, 496 (1966).

[26] *C. D. Smith*, J. Amer. chem. Soc. *88*, 4273 (1966); cf. *H. Prinzbach* and *J. Rivier*, Angew. Chem. *79*, 1102 (1967); Angew. Chem. internat. Edit. *6*, 1069 (1967).

[27] *J. Sauer*, Angew. Chem. *79*, 76 (1967); Angew. Chem. internat. Edit. *6*, 16 (1967).

[28] Review: *R. B. Woodward*, Chem. Soc. (London), Spec. Publ. *21*, 217 (1967).

[29] *J. S. Splitter* and *M. Calvin*, J. org. Chemistry *23*, 651 (1958).

[30] *R. Srinivasan*, J. Amer. chem. Soc. *85*, 4045 (1963).

[31] *W. G. Dauben* and *R. L. Cargill*, Tetrahedron *12*, 186 (1961).

[32] *O. L. Chapman* and *D. J. Pasto*, J. Amer. chem. Soc. *82*, 3642 (1960).

[33] *E. E. van Tamelen* and *S. P. Pappas*, J. Amer. chem. Soc. *84*, 3789 (1962).

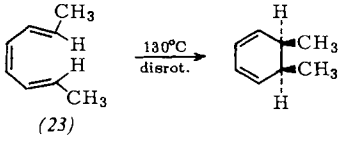
[34] *R. Huisgen* and *H. Seidl*, Tetrahedron Letters *1964*, 3381.

[35] *R. Huisgen*, *J. Sauer*, *H. J. Sturm*, and *J. H. Markgraf*, Chem. Ber. *93*, 2106 (1960).

(22)

Six-membered Rings

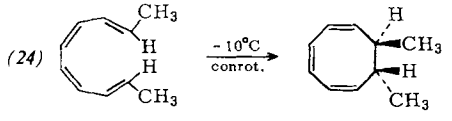
Compounds such as *(23)* containing the 1,3,5-hexatriene system give cyclohexadienes when heated (disrotatory)[36] or when exposed to light (conrotatory)[28]. The valence tautomerism of oxepin with benzene oxide[37] is an intracyclic example of such a change.



(23)

Eight-membered Rings

all-*cis*-Octatetraene changes spontaneously into 1,3,5-cyclooctatriene[38]. The cyclization of *trans,cis,cis, trans*-2,4,6,8-decatetraene *(24)* at −10 °C (this is a surprisingly ready formation of an eight-membered ring) reveals the steric course of this reaction[39].



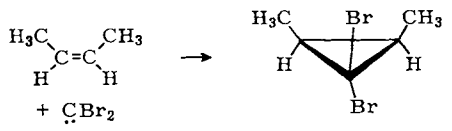
(24)

2.2. Two New σ Bonds

The cycloadditions of the greatest preparative importance belong to this group, which is estimated to include 90 % of the known cycloadditions. Thus the small number of examples given is no reflection on the importance of this class.

2 + 1 → 3

The component that provides the single ring member must be both electrophilic and nucleophilic. This requirement is satisfied by carbenes, azenes, the oxygen atom, and halogen cations. The addition of dibromocarbene to *cis*- and *trans*-butene[40] illustrates the *cis*-stereospecificity of the reaction.



[36] *E. Vogel, W. Grimme,* and *E. Dinné,* Tetrahedron Letters *1965,* 391; *E. N. Marvell, G. Caple,* and *B. Schatz, ibid. 1965,* 385.

[37] Review: *E. Vogel* and *H. Günther,* Angew. Chem. *79,* 429 (1967); Angew. Chem. internat. Edit. *6,* 385 (1967).

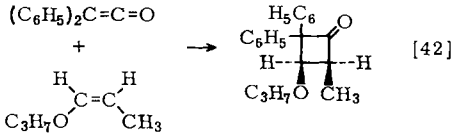
[38] *W. Ziegenbein,* Chem. Ber. *98,* 1427 (1965).

[39] *R. Huisgen, A. Dahmen,* and *H. Huber,* J. Amer. chem. Soc. *89,* 7130 (1967).

[40] *W. v. E. Doering* and *P. La Flamme,* J. Amer. chem. Soc. *78,* 5447 (1956).

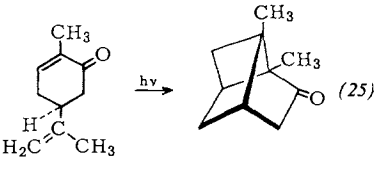
2 + 2 → 4

This group includes the thermal dimerizations of fluorinated olefins and of allenes and ketenes, as well as their additions to ordinary or conjugated olefins[41]. There is no uniformity of mechanism in this group.



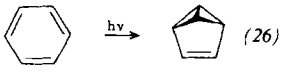
[42]

A reaction type of not minor importance is the photochemical dimerization of α,β-unsaturated carbonyl compounds or their addition to ordinary alkenes and alkynes or aromatic compounds[43]. An example of an intramolecular photoisomerization[44] is the formation of carvonecamphor *(25)*[45].



(25)

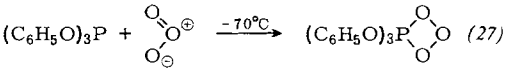
Irradiation of benzene yields benzvalene *(26)*[46]. In this interesting variant, the two new σ bonds are used for the formation of the bicyclo[1.1.0]butane system.



(26)

3 + 1 → 4

This scheme is very rarely encountered. A 1:1 adduct *(27)* of triphenyl phosphite and ozone exhibits the ^{31}P resonance of pentacovalent phosphorus[47].



(27)

3 + 2 → 5

The 1,3-dipolar cycloaddition is a one-step multi-center process[48]. According to work carried out in the past eight years, its versatility in the synthesis of heterocycles[49] is comparable to that of the Diels-Alder reaction in the formation of carbocyclic systems. The

[41] Review: *J. D. Roberts* and *C. M. Sharts,* Org. Reactions *12,* 1 (1962).

[42] *R. Huisgen, L. Feiler,* and *G. Binsch,* Angew. Chem. *76,* 892 (1964); Angew. Chem. internat. Edit. *3,* 753 (1964).

[43] Review: *R. Steinmetz,* Fortschr. chem. Forschung *7,* 445 (1967).

[44] *W. L. Dilling,* Chem. Reviews *66,* 373 (1966).

[45] *G. Ciamician* and *P. Silber,* Ber. dtsch. chem. Ges. *41,* 1928 (1908).

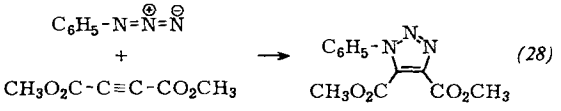
[46] *K. E. Wilzbach, J. S. Ritscher,* and *L. Kaplan,* J. Amer. chem. Soc. *89,* 1031 (1967).

[47] *Q. E. Thompson,* J. Amer. chem. Soc. *83,* 845 (1961).

[48] Kinetics and mechanism: *R. Huisgen,* Angew. Chem. *75,* 742 (1963); Angew. Chem. internat. Edit. *2,* 633 (1963).

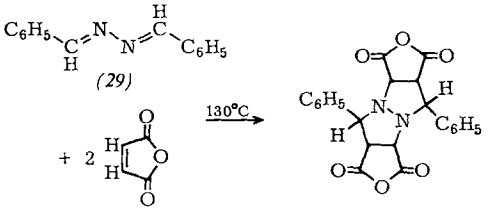
[49] Review: *R. Huisgen,* Angew. Chem. *75,* 604 (1963); Angew. Chem. internat. Edit. *2,* 565 (1963).

example of the formation of the triazole *(28)* [50] should serve to remind us that this type of reaction was known before the turn of the century.



(28)

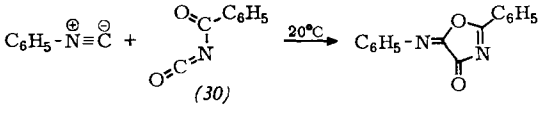
We encountered a reaction of a deviating charge type in Section 1 in the formation of *(10)* from trialkylborane, CO, and acetaldehyde [14]. Another example is the "criss-cross addition" of two molecules of maleic anhydride to benzalazine *(29)* [51].



(29)

4 + 1 → 5

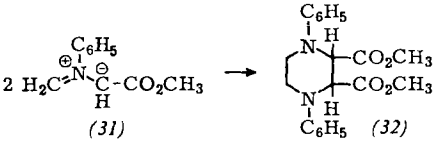
The best-known reaction of this type is the formation of cyclic sulfones from 1,3-dienes and sulfur dioxide [52]. The reaction of acyl isocyanates such as *(30)* with isonitriles [53] also belongs to this group.



(30)

3 + 3 → 6

Some 1,3-dipoles achieve stability by dimerization. The azomethine ylide *(31)* that exists in equilibrium with the ester of 1-phenylaziridine-2-carboxylic acid at 180 °C undergoes a head-to-head addition to form the piperazine derivative *(32)* [54].

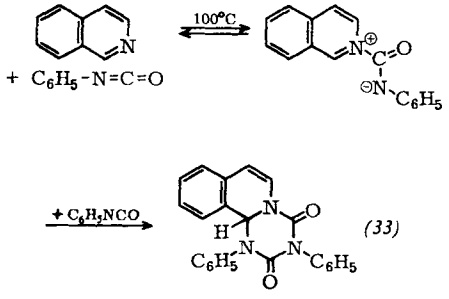


(31) *(32)*

4 + 2 → 6

The Diels-Alder reaction is the most extensively studied of all cycloadditions, and the literature has been summarized in numerous reviews and books [55]. Like many cycloadditions, the one-step multi-center process is particularly fast when one of the components is electron-rich and the other electron-deficient. The combination of electron-rich 1,3-dienes with electron-deficient dienophiles, the original type, has been supplemented recently by additions "with inverse electron requirements" [27].

A second principle of appreciable scope that leads to six-membered rings is the 1,4-dipolar cycloaddition, which, unlike the Diels-Alder addition, is a two-step process [56].

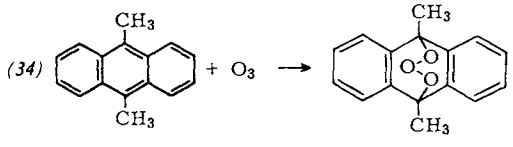


(33)

In the formation of the bisadduct *(33)* from phenyl isocyanate and isoquinoline, the isocyanate acts both as the electrophilic 1,4-dipole and as the dipolarophile [57].

4 + 3 → 7

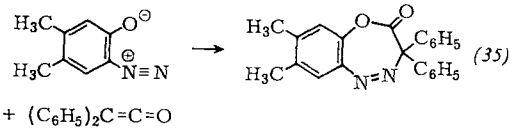
One of the few known examples of this type of reaction is the addition of ozone to the 9,10 positions of 9,10-dimethylanthracene *(34)* [58].



(34)

5 + 2 → 7

Ketenes react with aromatic *o*-diazo oxides to form 1:1 adducts, which are very probably 2,3-dihydro-1,4,5-oxadiazepin-2-ones *(35)* [59].



(35)

6 + 1 → 7

cis-1,3,5-Hexatriene adds sulfur dioxide across the ends of the conjugated system [60]. The formation of the seven-membered ring *(36)* is thus a vinylog of the 4 + 1 addition with formation of cyclic sulfones [52].

[50] *A. Michael*, J. prakt. Chem. (2) *48*, 94 (1893).

[51] *T. Wagner-Jauregg*, Ber. dtsch. chem. Ges. *63*, 3213 (1930).

[52] *S. D. Turk* and *R. L. Cobb* in *J. Hamer*: 1,4-Cycloaddition Reactions. Academic Press, New York 1967, p. 13.

[53] *R. Neidlein*, Chem. Ber. *97*, 3476 (1964).

[54] *R. Huisgen, W. Scheer*, and *G. Szeimies*, Tetrahedron Letters *1966*, 397.

[55] Most recent: *J. Sauer*, Angew. Chem. *78*, 233 (1966); Angew. Chem. internat. Edit. *5*, 211 (1966); earlier literature cited.

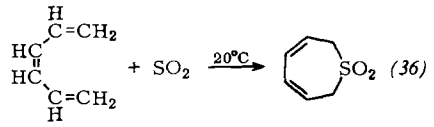
[56] *R. Huisgen, M. Morikawa, K. Herbig*, and *E. Brunn*, Chem. Ber. *100*, 1094 (1967).

[57] *R. Huisgen. K. Herbig*, and *M. Morikawa*, Chem. Ber. *100*, 1107 (1967).

[58] *R. E. Erickson, P. S. Bailey*, and *J. C. Davis*, Tetrahedron *18*, 389 (1962).

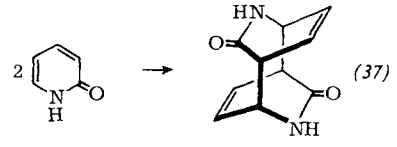
[59] *W. Ried* and *R. Dietrich*, Liebigs Ann. Chem. *666*, 113 (1963).

[60] *W. L. Mock*, J. Amer. chem. Soc. *89*, 1281 (1967).

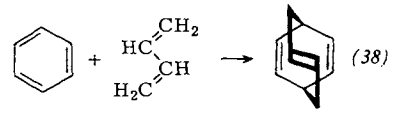


4 + 4 → 8

In the photodimerization of α-pyridone [61], two molecules combine in the 3,6-positions to give the *anti-trans* dimer *(37)*.

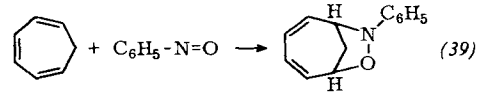


The *trans*-conformer of 1,3-butadiene adds to the 1,4-positions of benzene on UV irradiation to give the highly strained bicyclo[4.2.2]deca-3,7,9-triene *(38)*, which enters into a subsequent thermal reaction with butadiene [62].



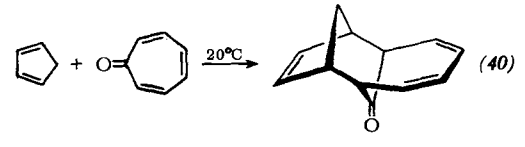
6 + 2 → 8

Whereas dienophiles normally add to the valence-tautomeric norcaradiene form of cycloheptatriene, nitrosobenzene apparently prefers a 1,6-addition to the monocyclic form to give the oxazolidine derivative *(39)* [63].



6 + 4 → 10

The 1,3,5-triene system in tropone also reacts as a unit with cyclopentadiene; the ease of formation of the ten-membered ring in *(40)* is remarkable [64].



6 + 6 → 12

The dimerization of *N*-ethoxycarbonylazepine *(41)* leads to a twelve-membered ring with two nitrogen bridges. However, there is some evidence that the 6π + 6π reaction, which is forbidden as a thermal multi-center addition, involves another dimer as an intermediate [65].

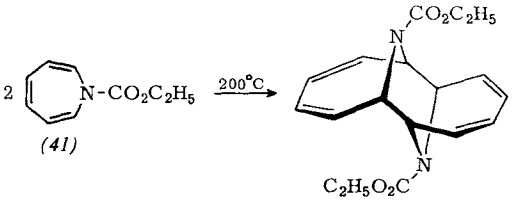
[61] *E.C.Taylor* and *R.O.Kan*, J.Amer.chem. Soc. *85*, 776 (1963).

[62] *K.Kraft* u. *G.Koltzenburg*, Tetrahedron Letters *1967*, 4357.

[63] *J. Hutton* and *W. A. Waters*, Chem. Commun. *1966*, 634.

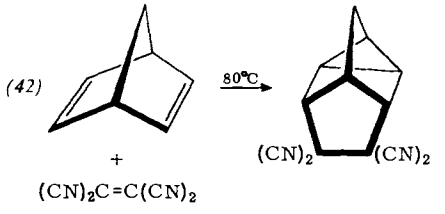
[64] *R. C. Cookson, B. V. Drake, J. Hudec*, and *A. Morrison*, Chem. Commun. *1966*, 15.

[65] *L. A. Paquette* and *J. H. Barrett*, J. Amer. chem. Soc. *88*, 2590 (1966); *A.L. Johnson* and *H. E. Simmons*, *ibid 89*, 3191 (1967).

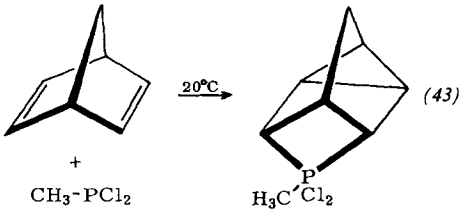


2.3. Three New σ Bonds

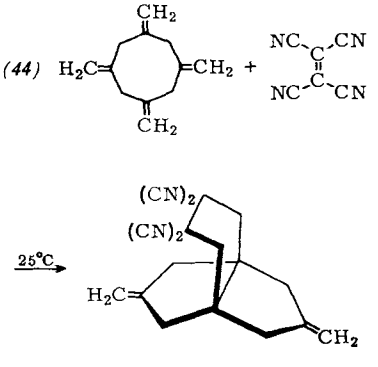
The reaction in this case leads in principle to more than one new ring. The homo-Diels-Alder reaction of norbornadiene *(42)* with tetracyanoethylene [66] may be regarded as a 5 + 2 cycloaddition; however, the reaction leads not to a seven-membered ring, but to a six-membered ring with a fused three-membered ring.



Similarly, the reaction of norbornadiene with dichloromethylphosphine leads in a 5 + 1 scheme to a polycyclic phospholane *(43)* with a new cyclopropane ring [67].



A 7 + 2 cycloaddition is found in the reaction of 1,3,5,7-tetramethylenecyclooctane *(44)* with tetracyanoethylene [68]. The new six-membered ring contains all three new σ bonds, but the eight-membered ring is simultaneously tied off into two five-membered rings.

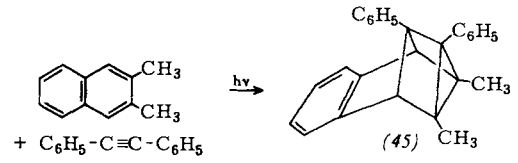


[66] *A.T. Blomquist* and *Y.C. Meinwald*, J. Amer. chem. Soc. *81*, 667 (1959).

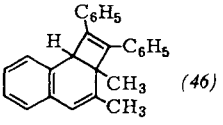
[67] *M. Green*, J. chem. Soc. (London) *1965*, 541.

[68] *J. K. Williams* and *R. E. Benson*, J. Amer. chem. Soc. *84*, 1257 (1962).

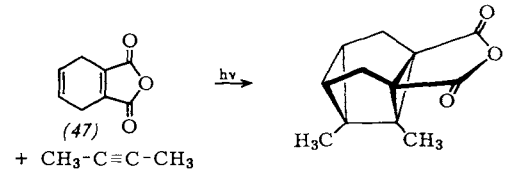
2.4. Four New σ Bonds



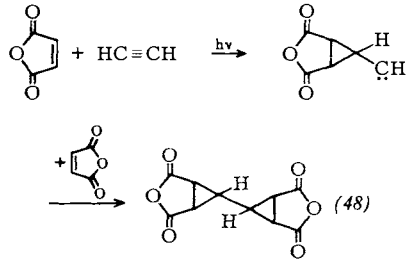
The triple bond of tolan undergoes a photoaddition to two quasi-double bonds of 2,3-dimethylnaphthalene[69]. However, it is questionable whether the polycyclic structure *(45)* is formed by a single photochemical act of addition. Two successive 2 + 2 cycloadditions could take place *via* the intermediate *(46)*.



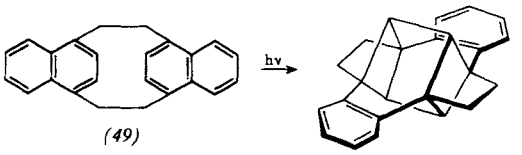
It is not so easy to break down the photoaddition of 2-butyne to 1,4-cyclohexadiene-1,2-dicarboxylic anhydride *(47)* into reaction steps[70], unless the intermediate resulting from the formation of the first cyclopropane ring is assumed to be a carbene.



This possibility cannot be ruled out, as is shown by the photosensitized cycloaddition of acetylene to two molecules of maleic anhydride to form the compound *(48)*[71]. The objections to a triple collision mechanism are so great that two successive 2 + 1 cycloadditions must again be considered. Thus it is not yet possible to prove the existence of cycloadditions



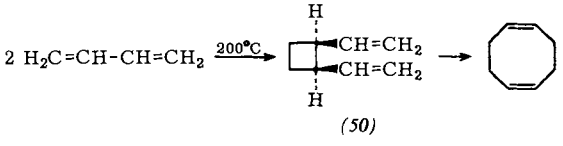
in which four new σ bonds are formed simultaneously. The situation is more favorable in intramolecular reactions, such as the photocyclization of [2,2]-paracyclonaphthane *(49)*[72].



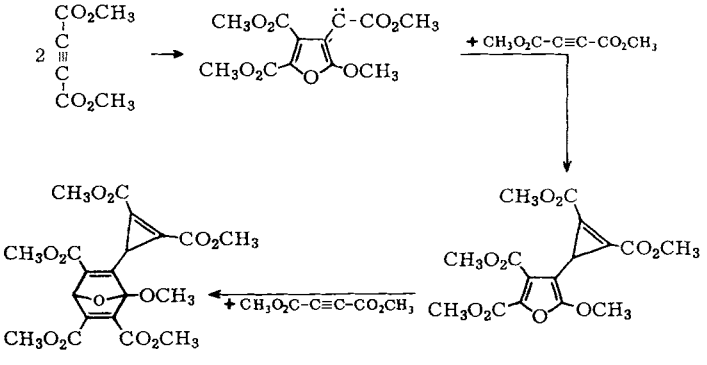
3. Concluding Remarks

The last few examples showed that even a heuristic classification principle is not always unambiguous. Mechanistic studies are sometimes necessary to determine whether several rings are formed simultaneously or consecutively.

Mention should also be made of the possibility that the ring compound isolated is not a primary cycloadduct, but the result of a cyclic rearrangement. In the thermal dimerization of butadiene to form 4-vinylcyclohexene, 10 % of *cis,cis*-1,5-cyclooctadiene was isolated as a by-product[73]. The formation of *trans*-1,2-divinylcyclobutane (5 %) as another by-product[74] suggests that the eight-membered ring was formed by a Cope rearrangement of the *cis*-1,2-divinylcyclobutane *(50)*; this has in fact been demonstrated[75]. Thus we are dealing not with a 4 + 4, but with a 2 + 2 cycloaddition.



There are also complex cases in which several cycloadditions take place consecutively. This is illustrated by the thermal tetramerization of dimethyl acetylenedicarboxylate (120 °C, 15 %)[76]. The sequence of



3 + 2, 2 + 1, and 4 + 2 cycloadditions is speculative; the first two steps may even take place in the reverse order.

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Carbonylation of Olefins under Mild Temperature Conditions in the Presence of Palladium Complexes

BY K. BITTLER, N. v. KUTEPOW, D. NEUBAUER, AND H. REIS[*]

Dedicated to Professor A. Steinhofer on the occasion of his 60th birthday

During a search for catalysts that allow carbonylation reactions on olefins to proceed below 100 °C, complex palladium(II) compounds having the formula L_mPdX_n were found to be catalytically active. L denotes a ligand such as a phosphine, nitrile, amine, or olefin, X is an acid residue, and m+n is 3 or 4. The catalysts permit the carbonylation of heat-sensitive compounds, as well as selective carbonylation of polyunsaturated olefins. The new process can also be carried out on the industrial scale, as is shown by the carbonylation of cyclododecatriene.

1. Introduction

In the carbonylation method developed by *Reppe*, carbon monoxide is allowed to react with organic compounds such as acetylenes, olefins, alcohols, ethers, and esters under the catalytic influence of metal carbonyls and carbonylmetal hydrides [1]. The carbonylation of unsaturated compounds usually involves the participation of compounds having an acidic hydrogen such as water, alcohols, thiols, ammonia, amines, or carboxylic acids. The end products are carboxylic acids and their functional derivatives, unsaturated products being obtained from acetylenes and saturated products from olefins [1].

The reaction of olefins with carbon monoxide and water or alcohols to form acids or esters was already known when *Reppe* and his co-workers turned their attention to this field. The earlier processes proceeded only at high pressures (700–900 atm) and high temperatures (about 300 °C), in the presence of catalysts such as phosphoric acids, heteropolyacids, boron trifluoride, and metal halides. The metal carbonyls were often regarded as reaction inhibitors, and even as poisons for the catalysts, so that a great deal of work was devoted to the suppression of their formation in catalytic reactions such as the methanol synthesis. However, *Reppe*'s experiments with acetylene and carbon monoxide under pressure showed that metal carbonyls and carbonylmetal hydrides are excellent carbonylation catalysts, which are effective at lower temperatures. These catalysts make possible many important and interesting syntheses.

Reppe's first catalytic carbonylation was the reaction of acetylene with CO and H_2O under pressure to form acrylic acid; nickel carbonyl was used as the catalyst. In contrast to the earlier processes for olefin carbonylation, this reaction proceeds under relatively mild conditions (about 30 atm and 170 °C). Esters of acrylic acid are obtained under the same conditions from acetylene, CO, and alcohols in the presence of halides of metals that form carbonyls, for example, $NiBr_2$ and NiI_2, as well as complex Ni halides.

The next obvious step was to apply the experience gained in the carbonylation of acetylene to that of olefins. The attempt to prepare propionic acid and its esters by the catalytic reaction of ethylene with CO and water or alcohols in the presence of Ni salts or $Ni(CO)_4$ was an immediate success. Corresponding to the lower reactivity of the double bond as compared with the triple bond, however, much more vigorous reaction conditions, *e.g.* 250–320 °C and 200–300 atm, must be used for the carbonylation of olefins.

Operation in this temperature range has certain disadvantages. Thus the carbonylation of olefins, particularly above about 150 °C, is always accompanied by side reactions, such as the water-gas reaction. The hydrogen that is formed hydrogenates unreacted olefin, and reacts with CO and the olefin to form aldehydes, alcohols, and ketones, as well as other products. Another disadvantage is that isomerizations, polymerizations, resinifications, and cleavages proceed more readily at higher temperatures. There is also a danger of increased corrosion.

$$CO + H_2O = CO_2 + H_2$$

Some (mainly straight-chain) olefins can be carbonylated to form carboxylic acids at 120–190 °C if water is present in excess and if the reaction is carried out in solvents such as ketones, dioxane, amides, or alcohols with octacarbonyldicobalt as the catalyst [2]. In these cases the solvents must dissolve both the olefins and the carboxylic acids formed.

Olefins can be carbonylated at even lower temperatures to give esters in a process developed by du Pont [3].

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[1] *W. Reppe*, Liebigs Ann. Chem. *582*, 1 (1953).

[2] *R. Ercoli*, DAS 1092015 (1956), Montecatini.

[3] *E. L. Jenner* and *R. V. Lindsey, jr.*, US-Pat. 2876254 (1959), Du Pont.

The process is based on the reaction of the olefin with CO and a primary monofunctional alcohol in the presence of a catalyst system (an alcohol-soluble Sn or Ge salt and an alcohol-soluble salt of a rare metal of group VIII in a molar ratio of 1:1 to 20:1) at 100 to 3000 atm and 50–325 °C. Below 250 °C the reaction is successful only with platinum salts. The reaction temperature required for the cheaper palladium salts is above 250 °C and these compounds therefore offer no advantage over conventional catalysts.

This situation led to a search for new catalysts that would act at lower temperatures than the conventional catalysts, and would at the same time be relatively cheap and accessible. We chose the Pd compounds, which readily form complexes with olefins, since we believed that the olefin could be carbonylated at a lower temperature when activated *via* a Pd-olefin complex than when the carbon monoxide is activated *via* a metal carbonyl catalyst, as in the usual process. The investigations soon led to Pd complexes such as bis(triphenylphosphine)palladium dichloride that satisfied our requirements and permitted *e.g.* the synthesis of esters of carboxylic acids below 100 °C [4].

Tsuji et al. [5–8] discovered independently that the reaction of olefins with CO in an alcoholic solution of hydrogen chloride in the presence of $PdCl_2$ under conditions such as 80 °C and 100 atm leads to esters of saturated or unsaturated acids. However, this process is accompanied by side reactions, such as the addition of hydrogen chloride to the olefin. Moreover, $PdCl_2$ in aqueous or alcoholic solution is readily reduced to the metal by carbon monoxide.

2. Palladium Complexes and their Catalytic Activity

Palladium metal, palladium carbonyl halides [9,10], olefinpalladium halides [11], and complex palladium(0) compounds have been considered for use as catalysts for the carbonylation of olefins below 100 °C.

By analogy with the pure metal carbonyls used in Reppe syntheses, palladium(0) compounds were examined first. Since palladium does not form metal carbonyls, the complexes *(1)* and *(2)* were chosen.

$[(C_6H_5)_3P]_4Pd$ *(1)* $[(o\text{-}CH_3\text{-}C_6H_4O)_3P]_4Pd$ *(2)*

Complex *(1)* is the more readily obtainable of these. It can be prepared, for example, by reactions (a) [12] and (b) [14]

$$Pd(NO_3)_2 + 9\,(C_6H_5)_3P \rightarrow \underset{(1)}{Pd[P(C_6H_5)_3]_4} + N_2O + 5\,(C_6H_5)_3PO \quad (a)$$

$$[(C_6H_5)_3P]_2PdCl_2 + CO + 2\,P(C_6H_5)_3 \rightarrow \underset{(1)}{Pd[P(C_6H_5)_3]_4} + COCl_2 \quad (b)$$

A method (c) using cyclohexadiene [13, 13a] has also proved useful:

$$PdCl_2 + 2\,C_6H_8 \rightarrow C_6H_6 + HCl + 1/2\,[C_6H_9PdCl]_2 \xrightarrow{+NaC_5H_5} C_6H_9PdC_5H_5 \xrightarrow{P(C_6H_5)_3} \underset{(1)}{Pd[P(C_6H_5)_3]_4} \quad (c)$$

Synthesis (c) can be simplified by the use of allyl alcohol instead of cyclohexadiene, *via* the intermediates π-allylpalladium chloride [15] and π-allyl-π-cyclopentadienylpalladium [16]. This modified route is also the most suitable for the preparation of *(2)*.

The carbonylation of ethylene and propylene with alcohol as a reactant and 0.05–0.5% of tetrakis(triphenylphosphine)palladium as the catalyst does not proceed below 100 °C. On addition of catalytic quantities of hydrogen chloride to the reaction mixture, however, the desired esters are formed, even at temperatures between 40 and 80 °C.

After the reaction, a yellow crystalline precipitate containing Pd was always observed; this was identified as the known compound $[(C_6H_5)_3P]_2PdCl_2$ [17], which is readily obtainable and very stable. This complex is so active in the pure state that it can catalyze the carbonylation of olefins below 100 °C with or without the addition of HCl.

Since Pd(0) compounds are evidently inactive in the absence of HCl, whereas complex Pd(II) halides exhibit high activity, a number of Pd(II) complexes were prepared (some for the first time), and their activities as carbonylation catalysts at low temperatures were tested with many olefins. A selection of these Pd complexes is given in Table 1.

Bis(triphenylphosphine)palladium dichloride and palladium complexes [4] containing triphenylphosphine together with a more weakly bound ligand, such as triphenylphosphinepiperidinepalladium dichloride or triphenylphosphinebenzylaminepalladium dichloride, have the highest catalytic activities, whereas olefin-

[4] *N. v. Kutepow, K. Bittler,* and *D. Neubauer,* German Pat. 1221224 (1963), BASF; German Pat. 1227023, German Pat. 1229089, both patents are supplements to German Pat. 1221224, BASF.

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Table 1. Relative activities of palladium catalysts in carbonylations.

Very good:

$[(C_6H_5)_3P]_2PdCl_2$; $(C_5H_{11}N)\cdot PdCl_2\cdot P(C_6H_5)_3$ [a];
$(C_6H_5CH_2NH_2)\cdot PdCl_2\cdot P(C_6H_5)_3$;
$C_3H_5\cdot PdCl\cdot P(C_6H_5)_3$ [b]

Good:

$[(C_6H_5)_3P]_2PdBr_2$; $(C_6H_5CN)_2PdCl_2$;
$(C_5H_{11}N)_2\cdot PdCl_2$ [a]; $[(C_6H_5)_3P\cdot PdCl\cdot SC_6H_5]_2$

Moderate:

$[(C_6H_5)_3P]_2PdI_2$; $[(C_6H_5)_3P]_2PdSO_4$;
$[(C_6H_5)_3P]_2Pd(CH_3COO)_2$; $[(C_6H_5)_3P]_2Pd(NO_3)_2$;
$[(n\text{-}C_4H_9)_3P]_2PdCl_2$; $[(n\text{-}C_4H_9)_3N]_2PdCl_2$

Poor:

$[(o\text{-}CH_3\text{—}C_6H_4O)_3P]_2PdCl_2$; $(NH_3)_2PdCl_2$;
$(CH_2=CH\text{—}CH_3)_2\cdot PdCl_2$; $C_{12}H_{18}\cdot PdCl_2$ [c]

Ineffective:

$[HCON(CH_3)_2]_2PdCl_2$

[a] $C_5H_{11}N$ = piperidine. [b] C_3H_5 = π-allyl. [c] $C_{12}H_{18}$ = 1,5,9-cyclododecatriene.

palladium chloride complexes and even $PdCl_2$ [5] itself are less active as catalysts. This can be explained by insufficient stabilization of bivalent palladium by olefins as ligands in the presence of carbon monoxide, so that it is reduced by CO to the metal, which is inactive in this reaction unless hydrogen halide is added. The activity of the olefinpalladium chlorides increases at higher hydrogen chloride concentrations. The activity is reduced by high temperatures and by high carbon monoxide pressures.

Apart from the complex ligands, the anion also plays an important part. Only chlorides and bromides exhibit pronounced activity; palladium complexes that contain a nitrate, iodide, acetate, or sulfate anion are only moderately active catalysts.

3. Carbonylation of Olefins in the Presence of Palladium Complexes

A wide range of esters can be prepared from olefins and alcohols by carbonylation at low temperatures in the presence of the palladium complexes listed in Table 2 [4].

These palladium catalysts can be used for the preparation not only of esters, but also of acids, by the use of water instead of alcohols [4]. However, temperatures about 50 °C higher are generally required for the preparation of acids, so that greater demands are made on the stability of the palladium catalyst toward reduction.

Table 2. Synthesis of esters by carbonylation of olefins in the presence of alcohols. Catalyst: *e.g.* $[(C_6H_5)_3P]_2PdCl_2$, reaction conditions 300—700 atm CO.

Olefin	Temp. (°C)	Reaction product	Yield based on reacted olefin (%)
$CH_2=CH_2$	60—100	$CH_3\text{—}CH_2\text{—}COOC_2H_5$	90
$CH_3\text{—}CH=CH\text{—}CH_3$	70	$CH_3\text{—}CH_2\text{—}CH(CH_3)\text{—}COOCH_3$	95
$CH_3\text{—}CH=CH_2$	50—70	$CH_3\text{—}CH_2\text{—}CH_2\text{—}COOC_2H_5$ + $(CH_3)_2CH\text{—}COOC_2H_5$	90
Diisobutylene	120	$(CH_3)_3C\text{—}CH_2\text{—}C(CH_3)_2\text{—}COOC_2H_5$ and isomers	92
$CH\text{—}COOC_2H_5$ ‖ $CH\text{—}COOC_2H_5$	140	$H_5C_2OOC\text{—}CH\text{—}COOC_2H_5$ | $CH_2\text{—}COOC_2H_5$	70
$CH_2=CH\text{—}CH_2OH$	100	$CH_2=CH\text{—}CH_2\text{—}COOCH_3$	65
$CH_2=CH\text{—}CH=CH_2$	70	$CH_3\text{—}CH=CH\text{—}CH_2\text{—}COOC_2H_5$	71.5
Styrene	90	$C_6H_5\text{—}CH(CH_3)\text{—}COOC_2H_5$	95
Diethyl-4-cyclohexene-1,2-dicarboxylate *(3)*	90	Triethyl 1,2,4-cyclohexanetricarboxylate *(4)*	88
4-Vinylcyclohexene *(5)*	60	Methyl 2-(3-cyclohexenyl)-propionate *(6)*	85
4-Vinylcyclohexene *(5)*	120	Methyl 2-(methoxycarbonylcyclohexyl)propionate *(7)*	80
1,5-Cyclooctadiene	60	Ethyl 4-cyclooctene-1-carboxylate	95
1,5-Cyclooctadiene	100	Diethyl cyclooctanedicarboxylate	80
1,5,9-Cyclododecatriene *(8)*	35—50 [a]	Ethyl 4,8-cyclododecadiene-1-carboxylate *(9)*	> 90
1,5,9-Cyclododecatriene *(8)*	50—70 [a]	Diethyl 5-cyclododecene-dicarboxylate *(10)* [+*(9)* + *(11)*]	70—80 *(10)*
1,5,9-Cyclododecatriene *(8)*	> 70 [a]	Triethyl cyclododecanetricarboxylate *(11)* [+*(9)* + *(10)*]	70—80 *(11)*
Cyclooctatetraene	90	Ethyl bicyclo[4.2.0]octa-2,4-diene-7-carboxylate	33

[a] The temperature limits depend on the HCl concentration, the catalyst concentration, and in some cases the catalyst used; the temperature limits indicated are valid for 0.35% of $[(C_6H_5)_3P]_2PdCl_2$ and 10% of HCl in C_2H_5OH.

The palladium(II) complexes which are always added only in catalytic quantities, also catalyze the formation of acyl chlorides from olefins, CO, and hydrogen chloride [18], and of anhydrides from olefins, CO, and acid

[18] *N. v. Kutepow, K. Bittler, D. Neubauer*, and *H. Reis*, German Pat. 1237116 (1964), BASF.

Whereas carbonylation of olefins with isolated double bonds always results in the loss of the double bond, allyl alcohol and allyl chloride are carbonylated with retention of the double bond [4, 19].

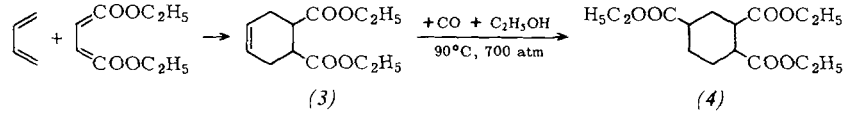
$$CH_2=CH-CH_2X + CO + ROH \rightarrow CH_2=CH-CH_2COOR + HX$$

X = halogen or OH
R = alkyl or aryl

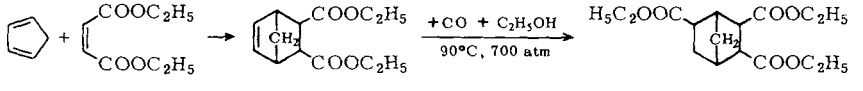
4. Advantages of the Complex Palladium Catalysts

The greatest advantage of the complex palladium catalysts, which catalyze the carbonylation even at concentrations of 0.05% and less, is their activity at low temperatures. Carbonylation with conventional catalysts, such as metal carbonyls of the iron group, takes place only at temperatures above 160 °C, *i.e.* temperatures at which the heat-sensitive olefins decompose, polymerize, isomerize, or in the presence of water and carbon monoxide, are hydrogenated by the hydrogen formed.

Thus Diels-Alder adducts such as the cyclohexene derivative *(3)* and the corresponding norbornene derivative, which readily dissociate into their components at high temperatures, were carbonylated for the first time with palladium complexes.



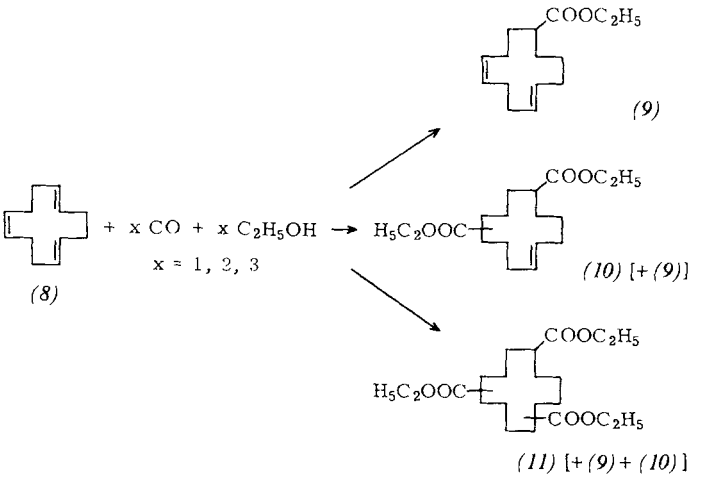
(3) *(4)*



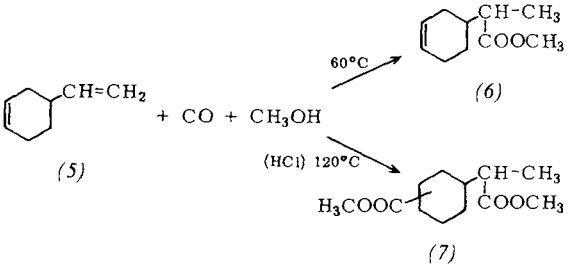
Another surprising advantage of the palladium complexes is that polyunsaturated olefins can be selectively carbonylated in their presence. For example, it was not previously possible to convert 1,5,9-cyclododecatriene *(8)* into 4,8-cyclododecadiene-1-carboxylic acid or its esters or to corresponding polycarbonylated compounds, since acenaphthene derivatives and polymerization products were formed instead. Although *Rüll* [19] recently obtained esters of cyclododecanecarboxylic acid by the reaction of *(8)* with CO and alcohol in the presence of $[Co(CO)_4]_2$ as catalyst, this process leads to many by-products. The complex palladium(II) catalysts, on the other hand, made it possible to cause one, two, or all three double bonds in cyclododecatriene to react, depending on the reaction conditions, to give mainly the mono- *(9)*, di- *(10)*, and triester *(11)*; the monoester can in fact be obtained without by-products.

When *trans,trans,cis*-1,5,9-cyclododecatriene is used, one of the two *trans* double bonds reacts first, and then the *cis* double bond.

[19] *Th. Rüll*, Bull. Soc. chim. France *10*, 2680 (1964).



Vinylcyclohexene *(5)* can also be converted either into the cyclohexenylpropionate *(6)* or into the diester *(7)* by variation of the conditions.



5. Mechanism of the Reaction

The catalyst could promote carbonylation by activation either of the carbon monoxide or of the olefin by addition to the central atom of the complex.

Activation of CO below 150 °C may be ruled out, since non-olefinic compounds, such as alcohols and alkyl halides, that can be satisfactorily carbonylated with conventional catalysts cannot be carbonylated with palladium(II) complexes.

Thus the catalyst must activate the double bond of the olefin. A feasible explanation for this process is that the olefin displaces a ligand from the palladium complex, and is itself bonded to the palladium by a π bond. This intermediate has not yet been isolated, but the above assumption is supported by the fact that complexes in which two ligands are bound unequally strongly to the central atom are particularly active. The carbonium ion of the polarization-activated

Table 3. Isomer distribution in the reaction products from olefins $R^1R^2C{=}CH_2$, alcohols ROH, and CO. Catalyst: $[(C_6H_5)_3P]_2PdCl_2$, reaction conditions: 90–120 °C; 700 atm CO; 3–4% HCl in ROH.

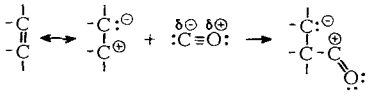
R^1	R^2	Olefin	Principal product	By-product	R
H	CH_3	$CH_3{-}CH{=}CH_2$	60% $(CH_3)_2CHCOOR$	30% $CH_3{-}(CH_2)_2{-}COOR$	C_2H_5
H	Cl	$CH_2{=}CHCl$	80% $CH_3{-}CHCl{-}COOR$	5% $Cl{-}(CH_2)_2{-}COOR$	C_2H_5
H	CH_2COOR	$CH_2{=}CH{-}CH_2COOR$	80% $CH_2{-}COOR$ / $H_3C{-}CH{-}COOR$	10% $ROOC{-}(CH_2)_3{-}COOR$	CH_3
CH_3	CH_3	$(CH_3)_2C{=}CH_2$	60% $(CH_3)_3C{-}COOR$	30% $(CH_3)_2CH{-}CH_2{-}COOR$	C_2H_5

Table 4. Influence of the reaction conditions on the distribution of products in the carbonylation of 1,5,9-cyclododecatriene (CDT) in the presence of ethanol. Pressure: 300 atm CO (parts a, c, and d) or 700 atm CO (part b).

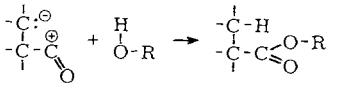
Catalyst	Concn. based on feed (wt.-%)	C_2H_5OH :CDT (molar ratio)	HCl in C_2H_5OH ≈ (wt.-%)	Temp. (°C)	Crude discharge (parts)	After vacuum distillation (parts) CDT	mono-ester *(9)*	diester *(10)*	triester *(11)* + residue
Part a									
$[(C_6H_5)_3P]_2PdCl_2$	0.35	≈ 2:1	10	50	278 [a]	88	99	—	6.5
$(C_6H_5CN)_2PdCl_2$	0.35	≈ 2:1	10	50	270 [a]	95	55	—	4
$(C_5H_{11}N)_2PdCl_2$ [b]	0.35	≈ 2:1	10	50	276 [a]	64.5	76.5	—	11
$(C_6H_5CH_2NH_2)PdCl_2{\cdot}P(C_6H_5)_3$	0.35	≈ 2:1	10	50	268 [a]	26	133	38	12
$C_5H_{11}N{\cdot}PdCl_2{\cdot}P(C_6H_5)_3$ [b]	0.35	≈ 2:1	10	50	299 [a]	13	120	86.5	15
Part b									
$[(C_6H_5)_3P]_2PdCl_2$	0.35	≈ 2:1	10	50	281 [a]	78	84	—	8
$[(C_6H_5)_3P]_2PdCl_2$	0.35	≈ 2:1	10	60	288 [a]	35	118	50.5	16
$[(C_6H_5)_3P]_2PdCl_2$	0.35	≈ 2:1	10	70	302 [a]	5	94	121	25
$[(C_6H_5)_3P]_2PdCl_2$	0.35	≈ 2:1	10	80	306 [a]	<5	63	117	27
$[(C_6H_5)_3P]_2PdCl_2$	0.35	≈ 2:1	10	90	308 [a]	4	53.5	135	51
$[(C_6H_5)_3P]_2PdCl_2$	0.35	≈ 2:1	10	100	298.5 [a]	2.4	44	127	49
Part c									
$[(C_6H_5)_3P]_2PdCl_2$	0.45	≈ 1:1	3.26	50	225 [c]	55	130	—	5
$[(C_6H_5)_3P]_2PdCl_2$	0.06	≈ 1:1	3.26	75	167 [c]	45	95	—	8
Part d									
$[(C_6H_5)_3P]_2PdCl_2$	0.35	≈ 1:1	10	50	226 [c]	83	84.5	—	7
$[(C_6H_5)_3P]_2PdCl_2$	0.35	≈ 1:1	0	80	222 [c]	91.5	84	—	10

[a] The crude discharge is washed twice with a solution of $CaCl_2$, washed once with a solution of Na_2CO_3, and dried over solid $CaCl_2$ before vacuum distillation. [b] $C_5H_{11}N$ = piperidine. [c] Alcohol distilled off at atmospheric pressure.

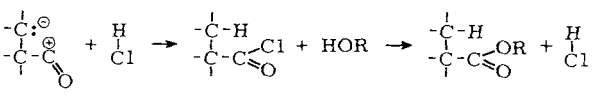
double bond then undergoes nucleophilic attack by carbon monoxide in its resonance form $:C^{\delta\ominus} \equiv O^{\delta\oplus}:$



In the absence of hydrogen chloride, the intermediate then reacts with alcohol, and the reaction product is simultaneously released from the catalyst.



Small quantities of hydrochloric acid very greatly increase the reaction rate. This effect is probably due to the higher acidity of the hydrogen in HCl as compared with alcohols; the synthesis of the esters probably proceeds *via* an intermediate acyl chloride.



Acyl chlorides are in fact obtained in the absence of alcohol or water[6, 18]. Moreover, hydrogen chloride may catalyze the addition of the olefin to the catalyst, since it forms quaternary salts with basic complex ligands, and these ligands can therefore be removed more readily.

In the carbonylation of olefins of the type $R^1R^2C{=}CH_2$, where R^1 and R^2 are first order substituents, carbon monoxide preferentially attacks the carbon atom carrying the smaller number of hydrogen atoms (Table 3). This behavior is reminiscent of the rules for the addition of hydrogen halides (Markovnikov rule).

6. Selective Carbonylation of 1,5,9-Cyclododecatriene

The carbonylation of the heat-sensitive 1,5,9-cyclododecatriene[4] was studied closely, since this is an ideal example of a selective carbonylation; moreover, there has been considerable interest for a long time in the preparation of 13-tridecanolactam[20] by conversion of 1,5,9-cyclododecatriene *via* 4,8-cyclododecadiene-1-carboxylate into cyclododecanecarboxylate, followed by reaction of the latter ester with nitrosylsulfuric acid.

Bis(triphenylphosphine)palladium dichloride was found to be the best catalyst because of its selective action, resistance to reduction, relative activity, and ready availability (see Table 4, Part a).

Table 4, Part b, illustrates the temperature-dependence of the reaction. Higher temperatures favor the formation of the

[20] *H. Metzger* and *H. Urbach*, German Pat. 1192649 (1961), BASF.

diester, and ultimately of the triester. At sufficiently low temperatures (about 50 °C), only the monoester *(9)* is formed. A very close relationship exists between the catalyst concentration and the temperature. It can be seen from Table 4, Part c, that if the catalyst concentration is decreased, the temperature must be raised in order to obtain roughly the same conversions and yields under otherwise identical conditions.

Cyclododecatriene can in principle be carbonylated even in the absence of hydrogen halide. However, higher reaction temperatures are required in neutral than in acidic media under otherwise identical conditions. The strong influence of hydrogen chloride on the reaction rate can be seen from the fact that no diester is formed in the absence of hydrogen chloride, despite the higher temperature (see Table 4, Part d). Cyclododecatriene and alcohol can be made to react in stoichiometric quantities. If necessary, alcohol can be used in excess. Carbon monoxide is sufficiently soluble in the reaction mixture at 300 atm to permit the reaction to be carried out in an industrially favorable pressure range.

The influence of the contact time and in particular its effect on the influence of the other parameters was studied in the apparatus shown in Figure 1 (see also Table 5).

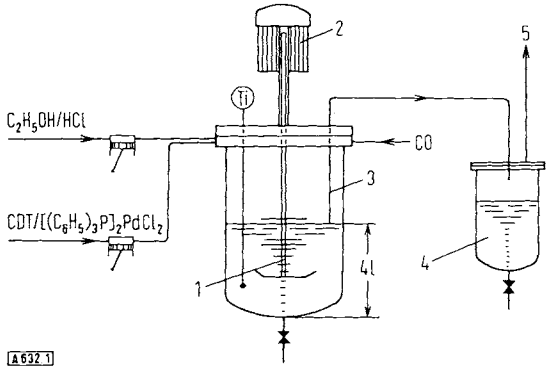


Fig. 1. Apparatus for the carbonylation of *trans,trans,cis*-1,5,9-cyclododecatriene (CDT). 10 l Hofer autoclave fitted with a magnetic lifter agitator and lined with Hastelloy B; continuous operation.
1 = stirrer, 2 = magnet, 3 = immersion tube, 4 = discharge vessel, 5 = waste gas outlet.

Alcoholic hydrochloric acid and bis(triphenylphosphine)-palladium dichloride in cyclododecatriene are pumped into the 10-l autoclave. Liquid and gas are continuously withdrawn into a pressureless glass vessel through an immersion tube fitted in such a way that 4 l of liquid are always present in the autoclave. The distance between the sieve plates on the magnetic lifter agitator and the frequency and stroke are determined beforehand in model experiments for optimum mixing of the gas and liquid phases.

Table 5 shows, *inter alia*, that diester formation can be suppressed by the use of a shorter contact time, since diethyl cyclododecenedicarboxylate is not formed directly from cyclododecatriene, but from the monoester.

7. Re-use of the Catalyst

The recovery and re-use of the catalyst is of the utmost importance in the industrial use of the synthesis. It was found preferable not to isolate the complex as such, but to return it to the synthesis in the form of the "catalyst residue" obtained when the alcohol, the cyclododecatriene, and the monoester are distilled off.

The first experiments were carried out in autoclaves with glass inserts to exclude any effects due to foreign ions from the wall of the autoclave. It is shown in Table 4, Part d, that higher temperatures are necessary in order to obtain the same conversion and yield in the absence of hydrogen chloride. However, to allow the catalyst tests with and without hydrogen chloride to be carried out at approximately the same temperatures, the catalyst concentration was increased by a factor of about ten for the experiments without HCl to ensure that the same conversions and yields would be obtained. When the catalyst is re-used, hydrogen halide must be added, since the catalyst is otherwise inactive, even at higher concentrations, after having been used once.

Figure 2 shows the behavior of the catalyst in the presence of and in the absence of HCl.

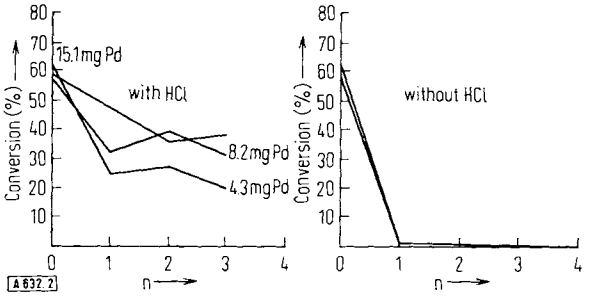


Fig. 2. Attempts to re-use the catalyst. Experiments with HCl (left): 75 °C, 300 atm CO, ≈ 0.055 wt.-% of $[(C_6H_5)_3P]_2PdCl_2$, molar ratio ethanol:cyclododecatriene = 1.2:1, 3.3 wt.-% of HCl in C_2H_5OH. Experiments without HCl (right): 80 °C, 300 atm CO, 0.45 wt.-% of $[(C_6H_5)_3P]_2PdCl_2$, molar ratio ethanol:cyclododecatriene 1.2:1.
Abscissa: n = frequency of re-use.

In the presence of HCl, the catalyst is sufficiently active even after being re-used three times. The decrease in activity after repeated use is due mainly to mechanical losses during the

Table 5. Relationships between contact time, temperature, catalyst concentration, alcohol concentration, monoester and diester formation, and space-time yield in the carbonylation of *trans, trans,cis*-1,5,9-cyclododecatriene (CDT). Catalyst: $[(C_6H_5)_3P]_2PdCl_2$; CO pressure: 300 atm.

Temp. (°C)	Catalyst concn. based on feed (wt.-%)	Feed CDT (l/h)	Feed C_2H_5OH/HCl (l/h) [a]	Contact time (h)	Space-time yield kg.l^{-1}d^{-1}	Monoester (%) in discharge	Diester (%) in discharge
75	0.06	0.8	0.8	2.4	1.8	26	0
105	0.06	1.33	1.33	1.5	3.9	33	13.5
105	0.04	1.33	1.33	1.5	3.7	30.5	10.5
105	0.04	1.66	1.66	1.2	4.8	30.4	5.5
105	0.05	1.7	0.85	1.6	3.8	31	2
115	0.05	1.85	1.0	1.4	4.7 (max. 5.4)	43.5	6.5
115	0.04	1.85	1.0	1.4	4.2	29.5	2.5
120	0.04	1.85	1.0	1.4	5.3 (max. 5.9)	38.5	6
120	0.03	1.85	1.0	1.4	4.0	30	2
120	0.02	1.85	1.0	1.4	2.4	17	0

[a] Acid value of the alcohol = 25.

preparation of the catalyst residue. Slight losses also occur, particularly at higher temperatures, as a result of the reduction of palladium(II) to metallic palladium; this reduction becomes even more pronounced when the "more water-like" methanol is used instead of ethanol.

It is advantageous to add one mole of triphenylphosphine per g-atom of palladium [21] to the catalyst residue.

8. Industrial Synthesis of Cyclododecadienecarboxylate

On the basis of the above results, a pilot plant (synthesis and isolation sections) was constructed for the continuous production of the monoester. Hastelloy alloys, particularly Hastelloy B, must be used for parts subjected to high pressures. Low-pressure parts were made of glass. A scheme of the pilot plant is shown in Figure 3.

Alcohol containing HCl was fed, together with dissolved catalyst residue, cyclododecatriene with fresh catalyst, and technical carbon monoxide (300 atm), into a 3-l reactor lined with Hastelloy B. Unreacted carbon monoxide is re-introduced into the reactor; inert gases are displaced from the reactor as waste gas. The product discharged from the reactor is freed from alcohol in the first thin-film evaporator. The alcohol is condensed and returned to the reaction after the addition of hydrogen chloride. The residue containing the catalyst is separated from unreacted cyclododecatriene and monoester in the second thin-film evaporator. Most of the catalyst

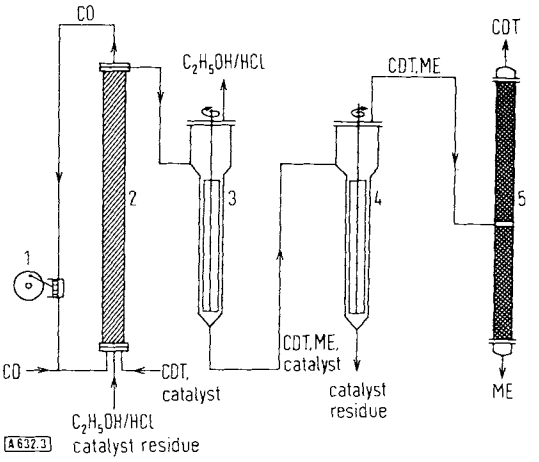


Fig. 3. Experimental plant for the industrial synthesis of cyclododecadienecarboxylate. 1 = circulating gas pump, 2 = reactor, 3 = first thin-film evaporator, 4 = second thin-film evaporator, 5 = column. CDT = cyclododecatriene, ME = monoester.

residue is also returned to the synthesis. The mixture of monoester and cyclododecatriene vapors from the second thin-film evaporator is passed into a separating column, unreacted cyclododecatriene being obtained as the head product. The pure ethyl cyclododecadienecarboxylate is obtained as a residue at the bottom of the column in a yield of 90%, based on reacted cyclododecatriene.

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German version: Angew. Chem. *80*, 352 (1968)
Translated by Express Translation Service, London

[21] *N. v. Kutepow, K. Bittler, D. Neubauer*, and *H. Reis*, German Pat. Appl. B 79819 IVb/12o (BASF).

Sulfonyl Hydrazones of Cyclic Amides and Quaternary Azo Sulfones of Heterocycles as Reagents in Azo Chemistry [1]

BY S. HÜNIG [*]

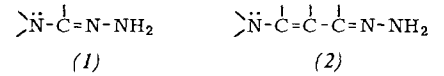
IN COLLABORATION WITH W. BRENNINGER, H. GEIGER, G. KAUPP, W. KNIESE, W. LAMPE, H. QUAST, R. D. RAUSCHENBACH, AND A. SCHÜTZ

Dedicated to Professor A. Steinhofer on the occasion of his 60th birthday

Sulfonyl hydrazones of cyclic amides undergo oxidative coupling with phenols and reactive methylene components. The reaction proceeds via the azo sulfones, which may be used as such, and which, as ambident cations, enter into many reactions with nucleophiles and extend the scope of oxidative coupling. The reaction with phenols is a two-step process, in which the limiting cases $k_1 \ll k_2$, $k_1 \approx k_2$, and $k_1 \gg k_2$ can be realized by slight variation of the reactants.

1. Introduction

Some years ago, two articles [2] were published concerning a new principle for the introduction of the azo group into aromatic amines, phenols, and reactive methylene compounds. These nucleophilic reactants exhibit general coupling with amidrazone systems *(1)* or their vinylogs *(2)* under the action of oxidizing agents. Typical examples of these com-



(1) *(2)*

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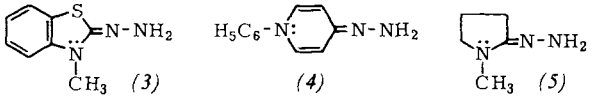
[1] Part XXIX of the series "Azo dyes by oxidative coupling". For Part XXVIII, see [26].

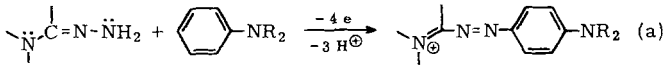
[2] a) *S. Hünig, H. Balli, K. H. Fritsch, H. Herrmann, G. Köbrich, H. Werner, E. Grigat, F. Müller, H. Nöther*, and *K.-H. Oette*, Angew. Chem. *70*, 215 (1958); b) *S. Hünig, H. Balli, E. Breither, F. Brühne, H. Geiger, E. Grigat, F. Müller*, and *H. Quast*, Angew. Chem. *74*, 818 (1962); Angew. Chem. internat. Edit. *2*, 640 (1962).

pounds, which will be referred to in the following discussion as "hydrazones" are shown in formulas *(3)* to *(5)*.



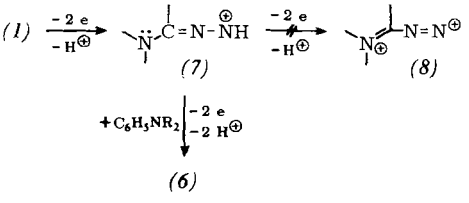
(3) *(4)* *(5)*

Equation (a) shows the stoichiometry for the oxidative coupling with an aromatic amine. It might have been concluded from the structure of the coupling product



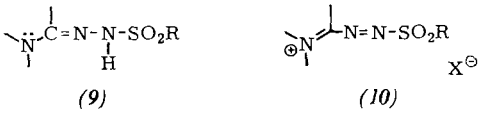
(1) *(6)* (a)

(6) that *(1)* is oxidized to *(8)*, an unusually electrophilic diazonium ion which would react immediately with the nucleophilic component. It is certain, however, that the quaternary diazonium ions *(8)*, which are unknown, do not occur even as unstable intermediates. The coupling actually proceeds *via* the resonance-stabilized form *(7)*, and is exactly analogous to



(7) *(8)* *(6)*

the oxidative coupling of *p*-phenylenediamines [2]. However, since aromatic azo sulfones Ar–N=N–SO_2R couple smoothly [3] it should be possible to use the hydrazones *(1)* and *(2)* at the oxidation level *(7)* or *(8)* if the β–N atom is attached to a sulfonyl group. This structural condition is met by the sulfonyl hydrazones *(9)* and the quaternary azo sulfones *(10)*. Both types of compounds do in fact couple smoothly



(9) *(10)*

[*(9)* oxidatively], and have even wider ranges of application than the hydrazones *(1)* and *(2)*. The following sections treat the synthesis and reactions of compounds of the types *(9)* and *(10)* and the coupling mechanism.

[3] Cf. *R. Pütter* in Houben-Weyl: Methoden der organischen Chemie. 4th Edit. Vol. 10/3, p. 579, Thieme-Verlag, Stuttgart 1965.

[4] *S. Hünig, R. D. Rauschenbach,* and *A. Schütz,* Liebigs Ann. Chem. *623*, 191 (1959).

[5] *S. Hünig* and *W. Lampe,* Liebigs Ann. Chem. *647*, 66 (1961).

[6] *S. Hünig* and *F. Müller,* Liebigs Ann. Chem. *651*, 89 (1962).

[7] *S. Hünig, H. Geiger, G. Kaupp,* and *W. Kniese,* Liebigs Ann. Chem. *697*, 116 (1966).

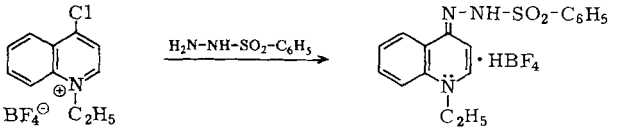
[8] *A. Schütz,* Dissertation, Universität Marburg 1959.

2. Sulfonyl Hydrazones *(9)*

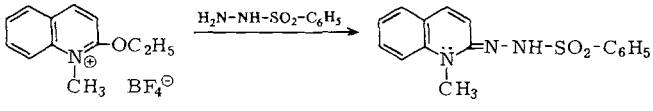
2.1. Synthesis [4-8]

Sulfonyl hydrazones *(9)* may be synthesized by one of the following routes, depending on the availability of the starting material:

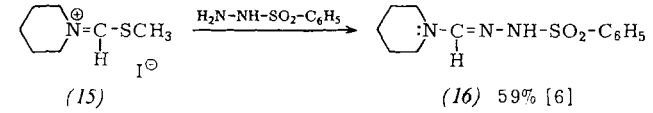
a) By analogy with the preparation of the hydrazones *(1)* and *(2)*, reactive quaternary salts such as *(11)*, *(13)*, or *(15)* are allowed to react with sulfonyl hydrazines.



(11) *(12)* 84% [7]



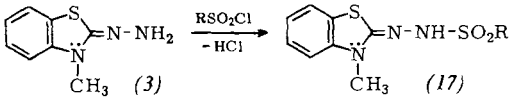
(13) *(14)* 72% [8]



(15) *(16)* 59% [6]

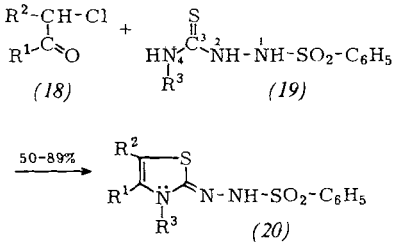
Halogen, SR, and OR have been found to be good leaving groups. Most of the sulfonyl hydrazones were obtained in this way.

b) If the hydrazone itself is readily obtainable [9], as in the case of *(3)*, it may be sulfonated with sulfonyl chlorides, *e.g.* to form *(17)* [4]. This is the most convenient way of varying the substituent R in the sulfonyl group.



(3) *(17)*

c) 2-Thiazolonesulfonyl hydrazones *(20)* are most easily synthesized from α-halogeno ketones *(18)* and benzenesulfonyl thiosemicarbazides *(19)* [5]. Independent of the nature of R^3, the ring closure always takes place at the N^4 atom [10].



(18) *(19)* *(20)*

R^1 = H, alkyl, aryl; R^2 = H, alkyl; R^3 = alkyl, aryl.

[9] *R. Riemschneider* and *S. Georgi,* Mh. Chem. *91*, 623 (1960).

[10] This is not self-evident. The corresponding benzoyl thiosemicarbazones undergo ring closure on the N^4 atom for R^3 = alkyl and on the N^3 atom for R^3 = aryl (cf. [5]).

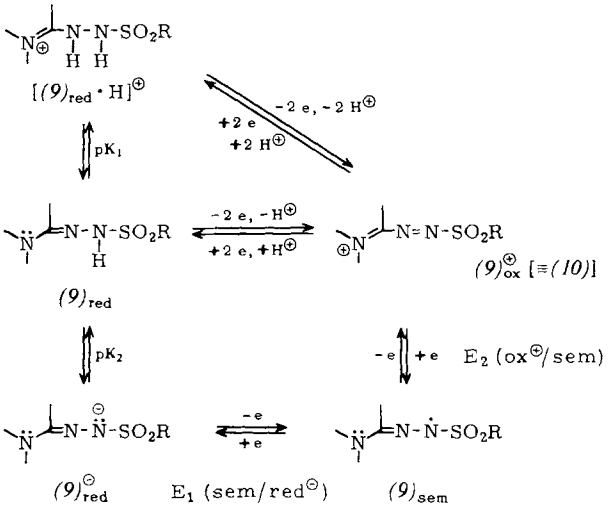
2.2. General Properties

In comparison with the hydrazones *(1)* and *(2)*, the sulfonyl derivatives are less soluble and are much more stable on standing. The acidity of the NH group is frequently sufficiently high to enable them to dissolve in sodium hydroxide (method of purification[4]) and their equivalent weights to be determined with tetrabutylammonium hydroxide in benzene/methanol[11]. Moreover, the basicity of the amidrazone grouping allows protonation, and hence titration with perchloric acid/glacial acetic acid[12].

2.3. Polarographic Behavior[8]

In reversible redox reactions, the underlying process can be positively deduced from the position and number of polarographically measured half-wave potentials and from the slope and pH-dependence of the curves[13]. It has been shown that both the free hydrazones *(1)* and the cations $[(1)\,H]^{\oplus}$ lose *two* electrons in *one* step during the oxidation, with formation of the oxidized stage *(7)*, which cannot be isolated[2,14].

The sulfonyl hydrazones *(9)* and the cations $[(9)\,H]^{\oplus}$ behave similarly. They may be regarded as the reduced stages (red) $(9)_{red}$ and $[(9)_{red}\cdot H]^{\oplus}$ of a reversible redox system, which lose $2e + H^{\oplus}$ and $2e + 2\,H^{\oplus}$ respectively to give the completely oxidized stage (ox), for which the only possible structure is the azo sulfone *(10)*. In contrast to the hydrazones *(1)*, the sulfonyl hydrazones *(9)* have a second pK value in the alkaline range, which links *(9)* with the corresponding anion $(9)^{\ominus}$. This anion has two pH-independent oxidation stages, which must be ascribed to the radical $(9)_{sem}$



and the oxidized stage $(9)_{ox}^{\oplus}$ [≡ *(10)*]. We thus have a reversible two-step redox system of the type

$$red^{\ominus} + ox^{\oplus} \underset{}{\overset{K}{\rightleftarrows}} 2\ sem$$

The formation constant K of the semiquinone, which is a measure of the thermodynamic stability of the radical, can assume surprisingly high values, as can be seen from Table 1.

It can also be deduced from Table 1 that the half-wave potentials decrease with increasing basicity of the sulfonyl hydrazones, as is the case with the free hydrazones[2,14]. The potentials also show that the quaternary azo sulfone stage *(10)* can be reached under the conditions of oxidative coupling, and that it must be possible to obtain *(10)* from *(9)*.

Table 1. Half-wave potential (against the saturated calomel electrode) of benzenesulfonyl hydrazones (as anions) at pH = 10.9 in *N*-methylpyrrolidone/water and semiquinone formation constants K.

Benzenesulfonyl hydrazone of	1st (mV)	2nd (mV)	K (± 10%)
1,3,3-Trimethyl-2-indolone	75	463	2.9×10^6
3-Methyl-2-benzothiazolone	106	446	4.7×10^5
1,3-Dimethyl-2-benzimidazolone	−153	175	2.9×10^5
1-Methyl-2-quinolone	−44	218	2.3×10^4
1-Methyl-4-quinolone	−67	141	2.9×10^3
10-Methyl-9-acridone	69	247	9.3×10^2

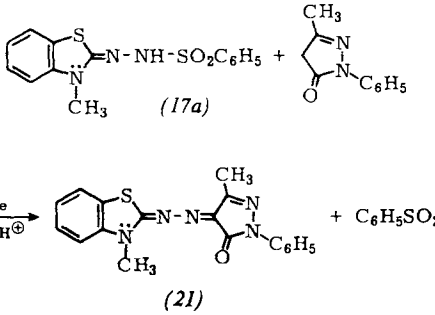
2.4. Oxidative Coupling

2.4.1. The Partners

Phenols and reactive methylene compounds in the widest sense are excellent partners for oxidative coupling (see below). On the other hand, pure coupling products can be obtained only with difficulty from aromatic amines, even under carefully controlled conditions[8].

2.4.2. Stoichiometry of Oxidative Coupling

The reaction proceeds by the path shown in the following example.



(17a) (b)

(21)

In contrast to the coupling of the hydrazones *(1)* and *(2)* (eq. (a)), evidently only two oxidation equivalents are consumed in the formation of *(21)*. The sulfonyl residue appears as sulfinate, which can be trapped with 1,4-naphthoquinone.

[11] *R. H. Cundiff* and *P. C. Markunas*, Analytic. Chem. *28*, 792 (1956).

[12] *P. C. Markunas* and *J. A. Riddick*, Analytic. Chem. *23*, 337 (1951).

[13] Cf. *M. v. Stackelberg* in [3], 4th Edit. Vol. 3/2 p. 255, 295, Thieme-Verlag, Stuttgart 1955; *F. Ender* in Hoppe-Seyler/Thierfelder: Handbuch der physiologisch- und pathologisch-chemischen Analyse. Vol. 1, p. 628, Springer-Verlag, Heidelberg 1953; *O. H. Müller* in *A. Weissberger*: Technique of Organic Chemistry. Interscience, New York 1960, Vol. I/4, p. 3155.

[14] *S. Hünig* and *H. Balli*, Liebigs Ann. Chem. *628*, 56 (1960).

2.4.3. pH-Dependence of the Coupling Yield

In the oxidative coupling of the sulfonyl hydrazone *(22)* with phenol (which is a medium-activity partner) between pH 6 and 12, the basicity of the medium is found to have a considerable influence on the yield of dye *(23)* (Fig. 1).

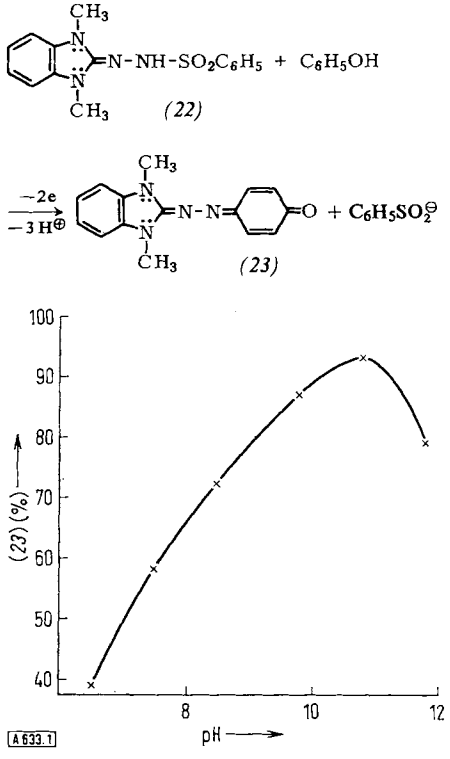


Fig. 1. Yield of *(23)* as a function of the pH value in the oxidative coupling of *(22)* with phenol in the ratio of 1:10.

The result can be generalized. The highest coupling yields are obtained between pH 10 and 12; the oxidative decomposition of sulfonyl hydrazones becomes predominant only in more strongly alkaline media. On the other hand, the coupling optimum for the free hydrazones *(1)* and *(2)* occurs at pH 8–10 and oxidative decomposition is practically the only reaction observed at pH 11.5 [14, 15]. For this reason weak C–H acids such as benzyl cyanide and phenylacetone, which cannot be oxidatively coupled with the hydrazone *(3)*, can be coupled with the sulfonyl hydrazone *(17a)* to form the azines *(24)* and *(25)* [4].

(24), R = CN (29%)
(25), R = CO-CH_3 (38%)

2.4.4. Influence of the Structure of the Sulfonylhydrazone on the Coupling Activity

Sulfonyl hydrazones with an amidrazone structure, *e.g. (16)*, generally give the lowest coupling yields (5–40% in the reaction with 1-hydroxy-2-naphthanilide [6]). Incorporation of the substituted amide N atom (N-4 of the amidrazone) into a ring [6] increases the coupling activity only if the sulfonyl hydrazone is derived from an aromatic heterocycle [*e.g. (12)*, *(14)*, *(17)*, *(20)*, and *(22)*]. It is observed [4] that the coupling yield increases with the basicity of the parent heterocycle; the opposite is true of the hydrazones *(1)* and *(2)* [2, 14]. Table 2 shows a quantitative comparison with phenol as the coupling component.

(26) *(27)* *(23)*

R = =O

Table 2. Maximum yields of dye in oxidative coupling under standard conditions. Path A — from free hydrazone/phenol 1:100, pH = 8–10, in methanol/water, oxidizing agent: $K_3Fe(CN)_6$. Path B — from benzenesulfonyl hydrazone/phenol 1:10, pH = 11 in *N*-methylpyrrolidone/water, oxidizing agent: $K_3Fe(CN)_6$.

Dye	Path A yield (%)	Path B yield (%)
(26)	90	55
(27)	21	66
(23)	7	94

The influence of the heterocycle is far less noticeable with the much more reactive α-naphthol.

2.4.5. Influence of the Sulfonyl Residue on the Coupling Yield

The nature of the sulfonyl residue also affects the coupling yield, as is shown by a quantitative study of the oxidative formation of *(26)* from *(17)* (Table 3).

Table 3. Yields of dye *(26)* from the hydrazones *(17)* and phenol (1:1) in sodium hydroxide/methanol; oxidation with $K_3Fe(CN)_6$. The free hydrazone *(3)* reacts to give a yield of 3%.

(17)

R (aliphatic)	Yield (%)	R (aromatic)	Yield (%)
		4-CH_3–C_6H_4	31
HO	4 [a]	C_6H_5	38
$(CH_3)_2N$	25	2-NO_2–C_6H_4	59
		3-NO_2–C_6H_2	61
Morpholino	28	2,5-Cl_2–C_6H_3	61
CH_3	31		
	23 [a]		
$ClCH_2$	58		
	30 [a]		

[a] With ethanolamine instead of sodium hydroxide solution.

Comparison with the hydrazone *(3)* again makes it clear that oxidative coupling of the free hydrazones does not take place in strongly alkaline media. The groups are arranged in Table 3 in order of their effect. Thus the coupling yield increases with the acidity of

[15] *S. Hünig* and *G. Köbrich*, Liebigs Ann. Chem. *617*, 203 (1958).

the sulfinic acid cleaved [16]. Benzene- or methylsulfonyl hydrazones are satisfactory for practical purposes.

3. Quaternary Azo Sulfones *(10)*[7]

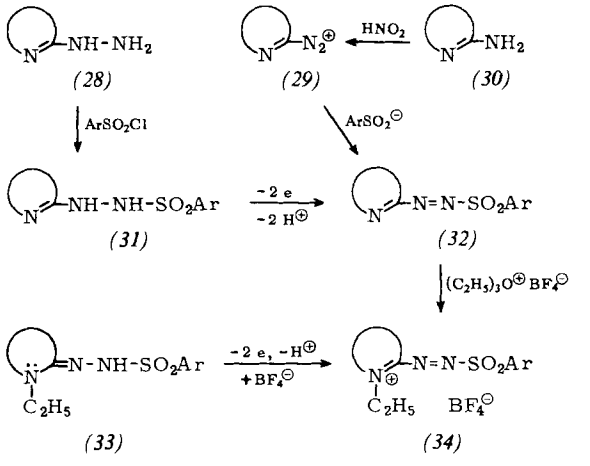
The only examples of this type of compound studied so far are derived from aromatic heterocycles. However, it should be possible in principle to prepare quaternary azo sulfones of the general type *(10)*.

3.1. Syntheses[7]

Heterocyclic quaternary azo sulfones can be prepared by three routes, which allow the use of different starting materials.

a) If the 2-amino heterocycle *(30)* can be diazotized (*e.g.* 2-aminobenzothiazole), the azo sulfone *(32)* is obtained smoothly from the diazonium salt *(29)* with sulfinate. Alkylation of *(32)* yields the desired quaternary azo sulfone *(34)*. The last step limits the application of this route, since diazonium salts can generally be obtained only from amines *(30)* of weakly basic heterocycles, the basicity of which is further weakened in the azo sulfone *(32)* to such a degree that *e.g.* the benzothiazole derivative can no longer be alkylated even with triethyloxonium fluoroborate [17].

b) This difficulty can be overcome if the hydrazine derivative *(28)* or *(31)* of a more strongly basic heterocycle (*e.g.* quinoline) is available. The azo sulfone *(32)*, which is readily obtainable by dehydrogenation of *(31)*, can then be smoothly alkylated to give *(34)*.



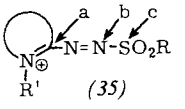
c) The starting materials having the widest applicability are the sulfonyl hydrazones *(33)*. These are converted by various oxidizing agents, particularly lead(IV) acetate in glacial acetic acid or strong nitric acid, into the quaternary azo sulfones *(34)* in 80 to 100% yield.

3.2. Properties

In contrast to the highly brisant perchlorates of the quaternary azo sulfones, the orange fluoroborates *(34)* are insensitive to shock and can be stored indefinitely. Their purity can be checked by reduction to the sulfonyl hydrazones *(33)* by titration with $Ti^{3\oplus}$ or $I^{\ominus}$ [7]. The susceptibility of quaternary azo sulfones *(34)* toward nucleophiles increases rapidly with decreasing basicity of the parent heterocycle, so that reactions are best carried out in non-basic, aprotic solvents such as acetonitrile or acetone. It is also possible in this way to extend the limits of application of oxidative coupling with sulfonyl hydrazones. Owing to their high coupling activity and the intense color of the products formed, the quaternary azo sulfones [particularly 6-methoxy-3-methyl-2-(tosylazo)benzothiazolium tetrafluoroborate *(44)*] are highly suitable for use as spray reagents in the chromatographic detection of the components discussed in Sections 3.3.3 to 3.3.6.

3.3. Reaction with Nucleophiles

The quaternary azo sulfones *(35)* are ambident cations [18] and the attack by nucleophiles is expected

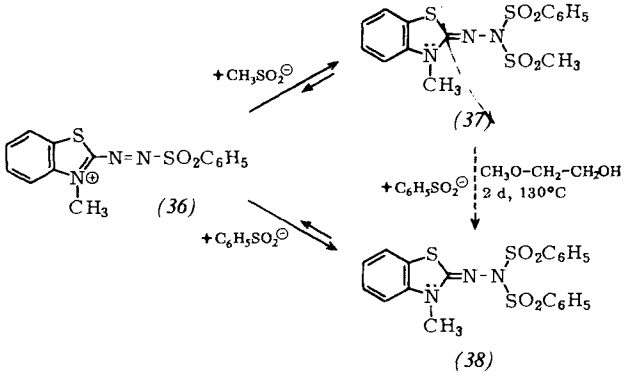


(35)

to take place mainly *via* path a or b. However, the strongly electron-attracting azo system could behave as a "pseudohalogen", so that the nucleophile should also be able to attack the sulfonyl group by path c.

3.3.1. Reaction with Sulfinate

The addition of sulfinate ions by path b is extremely rapid, yielding the sparingly soluble, very stable bis-sulfonyl compounds, *e.g.* *(36)* → *(37)*. The reaction is reversible, since prolonged heating of *(37)* with an excess of benzenesulfinate leads to *(38)* [7], a product that can only be formed *via* *(36)*. An important consequence of this reversibility is discussed in Section 3.4.



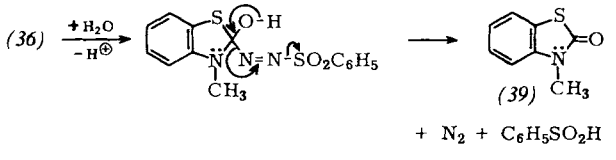
[16] *C. D. Ritchie, J. D. Saltiel,* and *E. S. Lewis,* J. Amer. chem. Soc. *83*, 4601 (1961).

[17] Stronger alkylating agents such as alkyl iodide and silver fluoroborate in nitromethane (*H. Meerwein* and *K. Wunderlich,* Angew. Chem. *69*, 481 (1957)) or dialkoxycarbonium salts (*K. Dimroth* and *P. Heinrich,* Angew. Chem. *78*, 714 (1966); Angew. Chem. internat. Edit. *5*, 676 (1966); *S. Kabuss,* Angew. Chem. *78*, 714 (1966); Angew. Chem. internat. Edit. *5*, 675 (1966)) might work.

[18] For the chemistry of ambident cations, cf. *S. Hünig,* Angew. Chem. *76*, 400 (1964); Angew. Chem. internat. Edit. *3*, 548 (1964); ambident behavior of other azo quaternary salts; *S. Hünig* and *W. Kniese,* Liebigs Ann. Chem. *708*, 170 (1967).

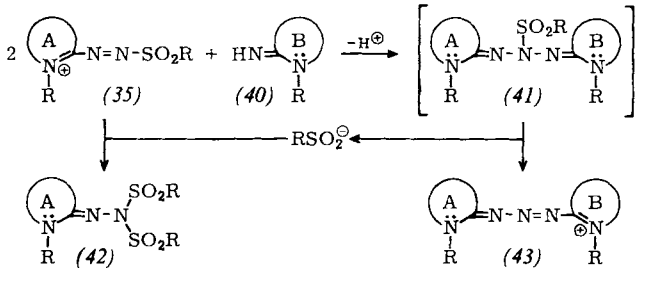
3.3.2. Reaction with Simple O- and N-Nucleophiles

Nucleophiles such as acetate, sulfite, secondary amines, and even cyanide decompose the quaternary azo sulfones, also in aprotic solvents, to give numerous products. Prominent among these are the bissulfonyl compounds *(42)*, an indication that sulfinate is liberated in the reaction. Furthermore, symmetrical azines (*e.g. (62)*, cf. Section 3.3.7) are always present. Reagents containing hydroxyl groups behave similarly. The reaction of *(36)* with steam gives 35% of *(39)*; this can be interpreted by the attack of the nucleophile by path a followed by fragmentation.

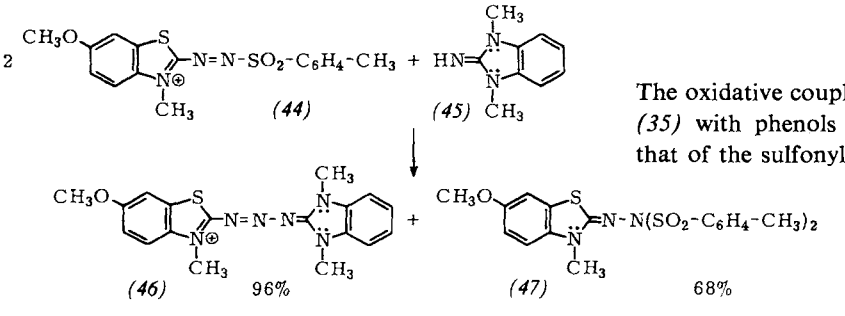


3.3.3. Reaction with Heterocyclic Imines

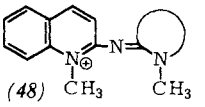
Imines of aromatic heterocycles of the type *(40)* attack the azo quaternary salts *(35)* in the β position by path b.



The adduct *(41)* immediately achieves stability by formation of the triazacyanine *(43)*, the sulfinate released being trapped by the excess of azo sulfone *(35)* to form the bissulfonyl compound *(42)* [7]. Asymmetric triazacyanines can also be obtained in this way, *e.g. (46)* from *(44)* and *(45)* [19]. This provides a

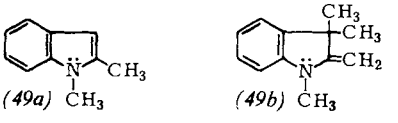


welcome addition to the known methods for the synthesis of triazacyanines [20, 21]. The imine *(40)* may be varied widely without affecting the reaction. On the other hand, attack by path a becomes more important when *(35)* is a 2-quinolinium derivative, so that the main products are asymmetric monoazacyanines of the type *(48)*.

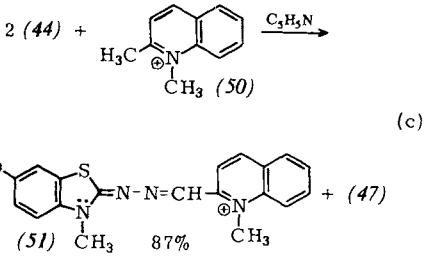


3.3.4. Reaction with C-Nucleophiles of the Enamine Type [22]

It was shown in 1957 that compounds containing the enamine grouping undergo oxidative coupling with the hydrazone *(3)* if their basicity is so low that they are at least partly unprotonated in the acidic medium required. This is true of the indole derivatives *(49a)* and *(49b)* (Fischer bases), which couple smoothly [2, 23]. However, oxidative coupling does not take place with most heterocyclic 2-methyl quaternary salts [*e.g. (50)*],



since they can be deprotonated to give the reactive enamine form only in basic media. By the use of azo sulfones *(35)*, the coupling reaction with 2-methyl quaternary salts can be carried out in an aprotic solvent in the presence of weak bases, as shown by the example in eq. (c). This provides a new approach to the diazatrimethinecyanines [21].



(c)

3.3.5. Reaction with Phenols

The oxidative coupling of the quaternary azo sulfones *(35)* with phenols proceeds even more readily than that of the sulfonyl hydrazones *(9)*. The resulting diazamerocyanines (*e.g. (54)*, $\lambda_{max}^{CH_3OH}$ = 484 nm (ε = 46000)) are obtained in a very pure state and in high yields, even when the reactants are used in a molar ratio of 1:1. Since the sulfinic acid formed does not

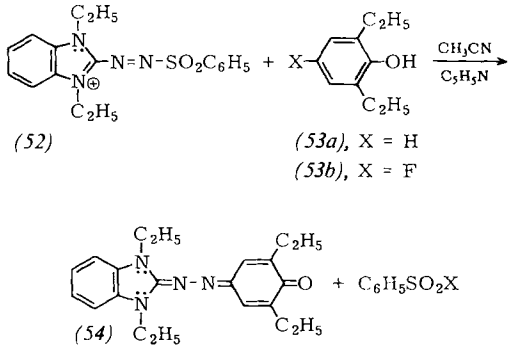
[19] *H. Quast* and *S. Hünig*, Chem. Ber. *101*, 435 (1968).

[20] *H. Balli* and *F. Kerstling*, Liebigs Ann. Chem. *663*, 96, 103 (1963).

[21] *J. Voltz*, Angew. Chem. *74*, 680 (1962); Angew. Chem. internat. Edit. *1*, 532 (1962); Chimia *15*, 168 (1961).

[22] *H. Quast*, *S. Hünig*, and *E. Schmitt*, Chem. Ber. *101*, 1522 (1968).

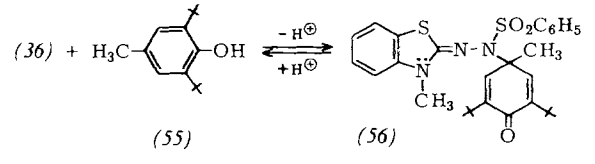
[23] *S. Hünig* and *K. H. Fritsch*, Liebigs Ann. Chem. *609*, 143 (1957).



(52) (53a), X = H (53b), X = F

(54)

compete with the phenol for the azo quaternary salt, the reaction must proceed in two stages, the formation of an adduct [*e.g.* from *(52)* and *(53a)* or *(53b)*] being faster than the further reaction to form the end products. A colorless adduct having the structure *(56)* can in fact be isolated from the azo sulfone *(36)* and 2,6-di-*tert*-butyl-4-methylphenol[7]. Since the adduct *(56)* cannot proceed to the merocyanine, it couples with phenols [*e.g.* *(53a)*], probably after conversion back into *(36)* and *(55)* by protonation.

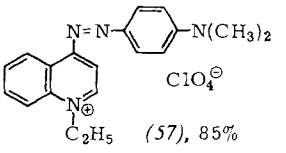


(55) (56)

As in the oxidative coupling of the hydrazones *(1)*, *p*-halogenophenols such as *(53b)*, are particularly suitable for coupling with quaternary azo sulfones. In the reaction *(52)* + *(53b)* → *(54)*, the sulfonyl residue is cleaved off at the sulfonic acid oxidation level, and so cannot compete with the phenol.

3.3.6. Reaction with Aromatic Amines[7]

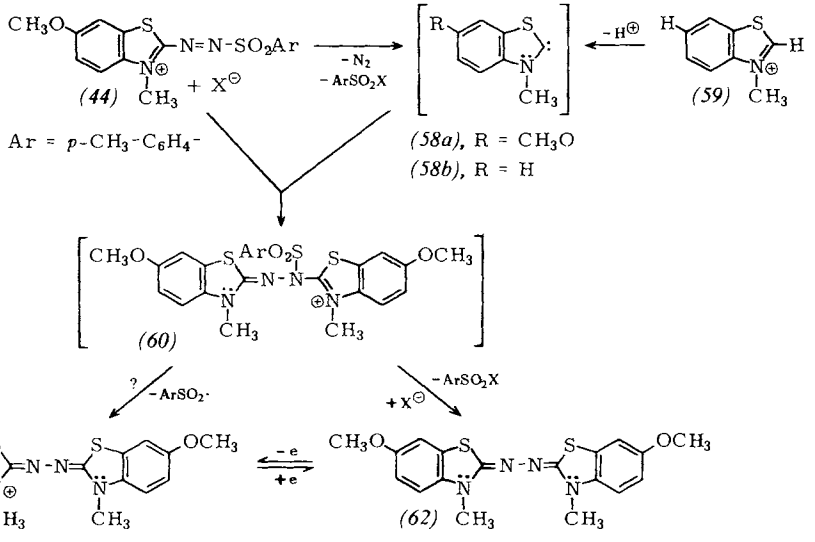
Quaternary azo sulfones couple smoothly with aromatic amines, even in cases in which oxidative coupling with the hydrazones *(3)* or sulfonyl hydrazones *(9)* does not take place. A typical example is the formation of the blue dye salt *(57)* ($\lambda_{max}^{CH_3OH}$ = 610 nm (ε = 62000)), which can be obtained only from the azo sulfone.



(57), 85%

3.3.7. Reaction with Nucleophilic Carbenes[7]

It was mentioned in Section 3.3.2. that azines [*e.g.* *(62)*] always occur among the products of the decomposition of azo sulfones [*e.g.* *(44)*] with nucleophiles. In this case the nucleophile evidently attacks the sulfonyl group by path c to give the nucleophilic carbene *(58a)*[24] as a reactive cleavage product, which decomposes *via* the adduct *(60)* by heterolysis to give the azine *(62)* or by homolysis to give the stable radical cation *(61)*, which is easily recognizable by its characteristic electronic spectrum[25]. This proposed reaction course is supported by the fact that the carbene *(58b)* formed from the quaternary salt *(59)* under the reaction conditions takes part in the reaction. Thus in the presence of compound *(59)*, both the symmetrical azine *(62)* and the azine having only one methoxyl group are formed.



(44) Ar = *p*-CH_3-C_6H_4- (58a), R = CH_3O (58b), R = H (59) (60) (61) (62)

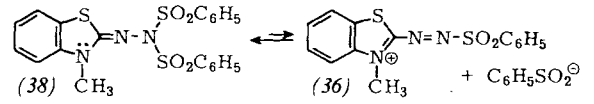
3.4. Coupling of Bissulfonyl Hydrazones

If the quaternary azo sulfones *(10)* [or *(35)*] are regarded as stabilized quaternary heterocyclic diazonium salts, the bissulfonyl compounds *(42)* must be described as extremely highly stabilized diazonium

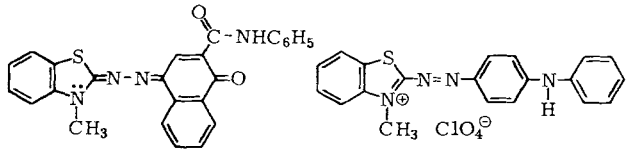
[24] For the chemistry of nucleophilic carbenes, cf. *H. Quast* and *S. Hünig*, Chem. Ber. *99*, 2017 (1966).

[25] *S. Hünig, H. Balli, H. Conrad*, and *A. Schott*, Liebigs Ann. Chem. *676*, 36, 52 (1964).

salts. Their solutions remain unchanged for several weeks, even in the presence of phenol or amine. However, when the components are heated in nitrobenzene, they rapidly couple to form the dye. As described



(38) *(36)* + $C_6H_5SO_2^{\ominus}$



(63), 62% *(64)*, 68%

earlier (Section 3.3.1.), the dissociation of *(38)* can be brought about by heating. In the presence of 1-hydroxy-2-naphthanilide or of diphenylamine, the azo quaternary salt *(36)* is rapidly removed from the equilibrium, and the dye *(63)* ($\lambda_{max}^{CH_3CN}$ = 540 nm (ε = 46000)) or *(64)* ($\lambda_{max}^{CH_3CN}$ = 604 nm (ε = 82000)) is formed within a few minutes. This unusual azo coupling could be important in some cases.

4. Mechanism of the Oxidative Coupling of Sulfonyl Hydrazones with Phenols[26]

4.1. Conclusions from Preparative Studies

The following conclusions regarding the mechanism may be drawn from the preparative experiments:

a) Oxidation of the sulfonyl hydrazones *(9)* yields azo sulfones *(10)* which couple smoothly with phenols. It is thus possible to eliminate the oxidation step and to study only the coupling of the quaternary sulfone with phenol.

b) The coupling proceeds *via* an adduct.

4.2. Kinetics of the Coupling of Quaternary Azo Sulfones with Phenols

4.2.1. Substances and Conditions

The reactants are the azo sulfone *(36)* and the phenols *(53a)* and *(53b)*, whose blocked *o*-positions guarantee exclusive *p*-coupling. The solvent is very pure acetonitrile with pyridine as the base. A 20-fold excess of pyridine and phenol, which reacts as a hydrogen-bonded complex *(65)* in acetonitrile, ensures a pseudo-first order reaction. The disappearance of azo sulfone and the formation of dye are followed optically as functions of time.

[26] *S. Hünig* and *G. Kaupp*, Tetrahedron *23*, 1411 (1967).

4.2.2. Coupling with 2,6-Diethylphenol *(53a)*

The kinetic experiment, in which 80–90% of dye *(70)* is ultimately formed, proceeds in a remarkable manner (Fig. 2). After a reaction time of about 10 min, the azo sulfone *(36)* is completely consumed (curve A) whereas only about 5% of dye has been formed (curve F). The main constituent of the reaction mixture at this point is a relatively stable intermediate, which slowly decomposes to form the dye *(70)* (curve 100-F-A).

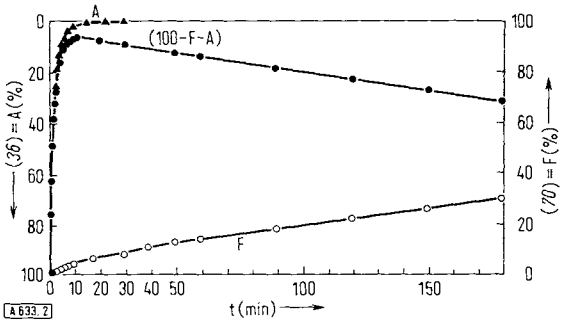
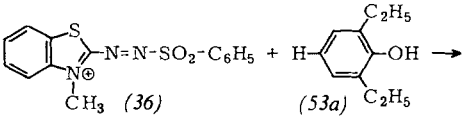
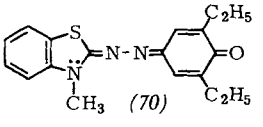


Fig. 2. Coupling of the azo sulfone *(36)* (2.36×10^{-5} mole/l) with 2,6-diethylphenol *(53a)* (5.6×10^{-4} mole/l) in the presence of pyridine (5.6×10^{-4} mole/l) in acetonitrile at 20 °C to form the dye *(70)*.



(36) *(53a)*



(70)

An adduct that is kinetically identical with the intermediate can in fact be obtained from *(36)* and *(53a)*. By analogy with *(56)*, this would be expected to have the structure *(66)*. However, IR data and results of H–D exchange experiments point conclusively to the constitution *(67)*. Thus the compound *(66)*, which is undoubtedly the initial product, very rapidly rearranges to *(67)*, from which the dye *(70)* is then formed.

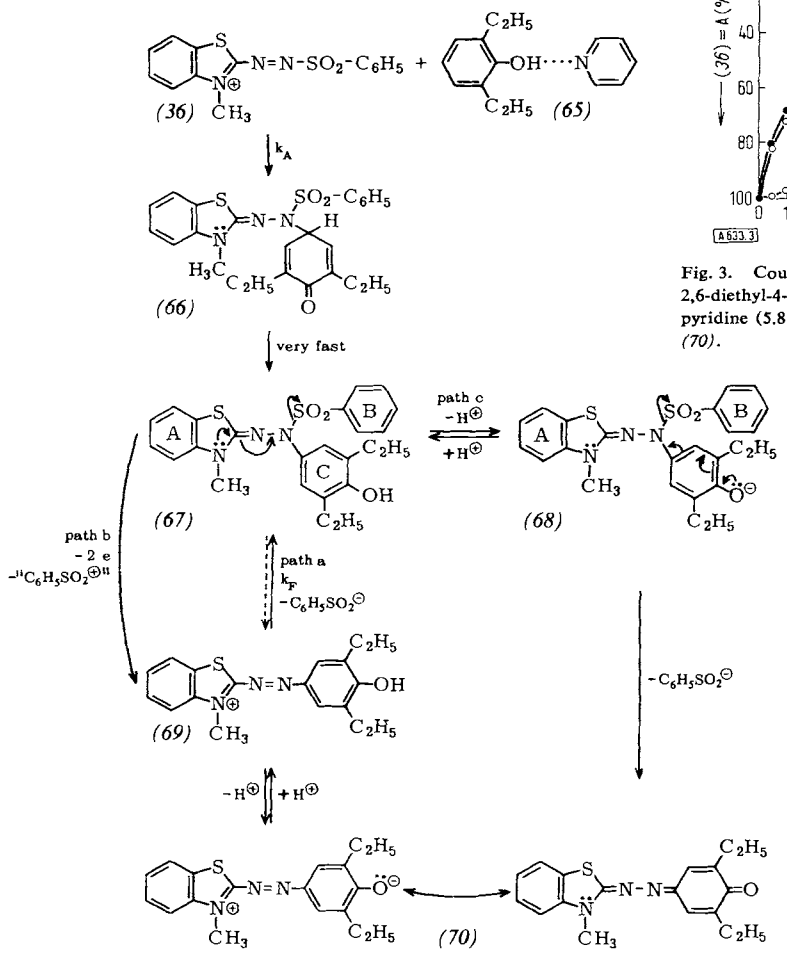
The behavior of *(67)* is very unusual, since this intermediate can liberate the dye *(70)* in three ways:

Path a: Under the conditions of the reaction, *(67)* dissociates almost exclusively into the benzenesulfinate anion and the dye cation *(69)*. Though the phenolic structure of *(67)* suggests the possibility of participation of pyridine as in *(65)*, this does not occur since only two of the three rings A, B, and C in *(67)* can lie in one plane, and decomposition with the assistance of ring A is favored. The cation *(69)* is immediately deprotonated in the presence of pyridine to form the weakly basic dye *(70)*. Compound *(70)* can be converted back into the adduct *(67)* by an excess of benzenesulfinic acid in the absence of pyridine.

Path b: More ($\approx$ 5%) dye *(70)* is formed during the first few minutes than is calculated from k_A and k_F. Comparative experiments show that this is due to the azo sulfone *(36)* that is still present during this period and which oxidizes the adduct *(67)* to the dye *(69)* or *(70)*.

Path c: This path is of no importance under the conditions of the reaction. The dye formation is accelerated by about two

orders of magnitude only in the presence of strong bases such as sodium methoxide or sodium phthalimide. The anion *(68)* is evidently involved in this reaction.



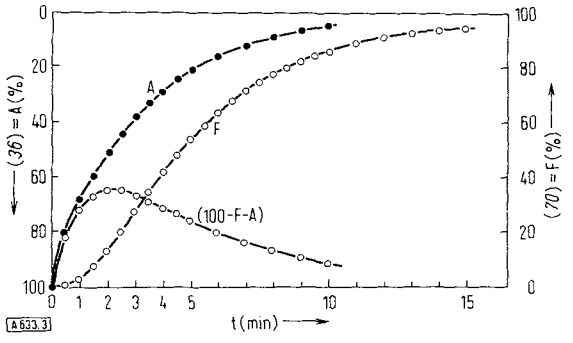


Fig. 3. Coupling of the azo sulfone *(36)* (2.75×10^{-5} mole/l) with 2,6-diethyl-4-fluorophenol *(53b)* (5.8×10^{-4} mole/l) in the presence of pyridine (5.8×10^{-4} mole/l) in acetonitrile at 20.0 °C to form the dye *(70)*.

Coupling may be summarized as follows:

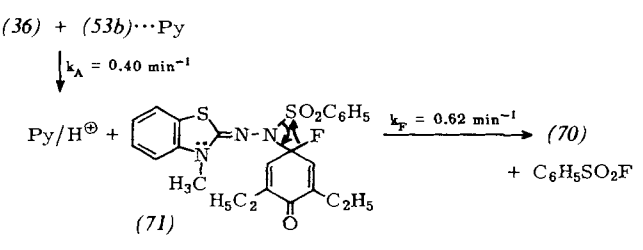
$$(36) + (65) \xrightarrow{k_A = 0.43\ \text{min}^{-1}} (66) \xrightarrow[\text{fast}]{\text{very}}$$

$$(67) \xrightarrow[\text{path a}]{k_F = 1.86 \times 10^{-3}\ \text{min}^{-1}} (69) \xrightarrow[\text{fast}]{\text{very}} (70)$$

Thus the reaction takes place in several stages, the ratio of the rates of the two slowest steps being $k_A : k_F \approx 200:1$.

4.2.3. Coupling with 2,6-Diethyl-4-fluorophenol *(53b)*

Under the same conditions as those described for *(53a)*, the coupling of *(36)* with *(53b)* proceeds differently. Whereas only 50% of dye is formed after 30 min with *(53a)*, coupling with *(53b)* is complete after only 12 min. The intermediate must therefore be shorter-lived in this case. Nevertheless, 34% of the intermediate (curve 100-F-A, Fig. 3) is present after an induction period of 1.85 min.

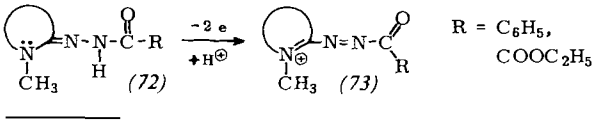


In this reaction the intermediate must have the structure *(71)*. Since its decomposition is practically unaffected by pyridine and *(53b)*, it must be assumed that an intramolecular reaction takes place with formation of the dye *(70)* and benzenesulfonyl fluoride. The ratio $k_A : k_F$ in this case is approximately 1:1.

4.3. Coupling of Carbonylazo Quaternary Salts with Phenols

4.3.1. General

Carbonylazo quaternary salts of the type *(73)* can be prepared by oxidation of the "carbonylhydrazones" *(72)* [27], the reaction being completely analogous to *(9)* → *(10)*.



[27] *S. Hünig* and *G. Kaupp*, Liebigs Ann. Chem. *700*, 65 (1966).

The carbonylazo quaternary salts, like the sulfonylazo quaternary salts, are reduced smoothly; they add sulfinate and 2,6-di-*tert*-butyl-4-methylphenol *(55)* to form adducts corresponding to the compounds *(42)* and *(56)*. In particular, they couple in high yields with *p*-halogenophenols to give the same dyes [*e.g. (54)*] as are formed from the corresponding quaternary azo sulfones [27]. This reaction can therefore be included in the kinetic investigation.

4.3.2. Mechanism of the Coupling of the Carbonylazo Quaternary Salt *(74)* with 2,6-Diethyl-4-fluorophenol *(53b)* [26]

Under the conditions described earlier (see Sections 4.2.2. and 4.2.3.), the coupling of *(74)* with *(53b)* takes roughly twice as long as the coupling of the azo

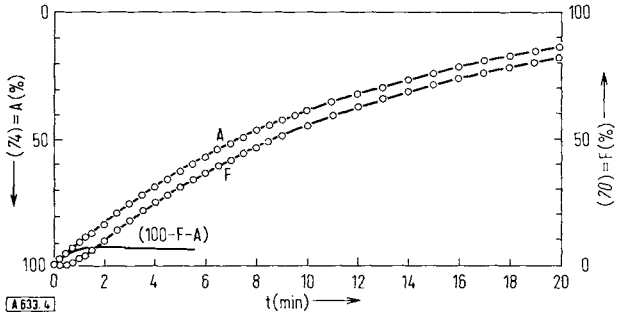
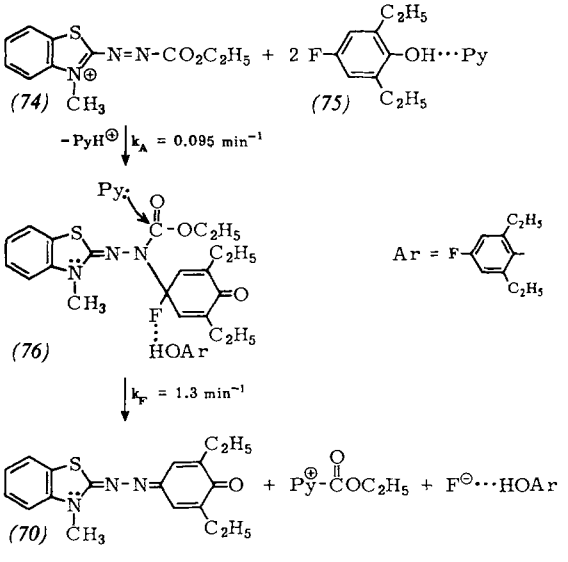


Fig. 4. Coupling of the carbonylazo quaternary salt *(74)* (2.49×10^{-5} mole/l) with 2,6-diethyl-4-fluorophenol *(53b)* (5.10×10^{-4} mole/l) in the presence of pyridine (5.0×10^{-4} mole/l) in acetonitrile at 20.0 °C to form the dye *(70)*.

sulfone *(36)*, probably because of the weaker electrophilic character of *(74)* as compared with that of *(36)* (Fig. 4).



The consumption of *(74)* (curve A) is directly related to the formation of the dye (curve F), so that it may again be concluded that an intermediate accumulates in the reaction mixture (maximum 7%, curve 100-F-A). It can be deduced from the kinetic data that *(74)* and *(75)* first combine to form the adduct *(76)*, the decomposition of which is distinctly dependent upon the concentrations of pyridine and of *(53b)*. These reactants probably participate in the manner shown. The ratio of the rates for the two-step reactions is $k_A : k_F \approx 1:130$.

4.3.3. Coupling of the Carbonylazo Quaternary Salts *(73)* with Phenols Possessing No *p*-Substituent

The coupling mechanism deduced above for *p*-halogenophenols suggests that the carbonylazo quaternary salts *(73)* should not react with phenols possessing no *p*-substituent. The carbonyl residue would have to be cleaved from the intermediate (cf. *(76)*, with H instead of F) as C_6H_5CHO or C_2H_5OCHO and this reaction would have very unfavorable energy requirements in comparison with the formation of $Py^{\oplus}-COOC_2H_5 + F^{\ominus}\ldots HOAr$ and $C_6H_5SO_2^{\ominus}$ (cf. Section 4.2.2.). Nevertheless, approximately 30% dye formation is observed. This is due to the oxidation of the intermediate (cf. *(67)*, with COR instead of $SO_2C_6H_5$) by unreacted azo quaternary salt *(73)*, corresponding to the conversion *(67)* → *(70)* by path b (Section 4.2.2.).

4.3.4. Comparison of the Coupling Mechanisms

The three couplings studied [*(36)* + *(53a)*, Fig. 2; *(36)* + *(53b)*, Fig. 3; *(74)* + *(53b)*, Fig. 4] proceed as two-step reactions with an adduct intermediate. The situation is rare in that the three limiting cases

$$k_1 \ll k_2 \qquad k_1 \approx k_2 \qquad k_1 \gg k_2$$

are observed with closely related reactants whose overall reactions lead to very similar products.

These investigations have been supported for some time by various grants. We are grateful to the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft, and the Badische Anilin- und Sodafabrik AG, Ludwigshafen/Rhein, for their generous assistance. We also thank the Adox Fotowerke Dr. C. Schleussner, Frankfurt/M., for their support at the beginning of this work.

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"Bicarburet of Hydrogen". Reappraisal of the Discovery of Benzene in 1825 with the Analytical Methods of 1968

BY R. KAISER [*]

Dedicated to Professor A. Steinhofer on the occasion of his 60th birthday

The historical background and the admirable analytical procedure that led Michael Faraday to the discovery of benzene in 1825 are discussed. Using modern techniques of instrumental analysis, the author retraces the isolation and analysis of benzene, and shows that the starting material used by Faraday must have been a very complex mixture of hydrocarbons, which would make severe demands even on present-day preparative analytical techniques, since it contains more than 300 components at concentrations greater than 100 ppm. The magnitude of the changes in analytical techniques can be seen from the fact that it is no longer necessary to isolate individual compounds, and that a great deal of information can be obtained with a much smaller quantity of material and in a much shorter time. Nevertheless, Faraday's persistence, experimental skill, and accuracy of measurement remain an example to the analyst of today.

1. The Beginnings of Gas Lighting

On July 16, 1825, at the Royal Institution, London, *Michael Faraday* (1791–1867) reported on new compounds of carbon and hydrogen and on other products from the pyrolysis of (sperm) oil. Soon afterward, *Berzelius* described *Faraday*'s discovery of benzene as the most important chemical result of 1825, and at the "Benzene Festival" in Berlin in 1890, *A. W. Hofmann* was able to show his enthusiastic audience a small glass ampoule containing about 3 ml of benzene that had been enriched, isolated, purified, and accurately described by *Faraday* in 1825 in a beautifully consistent analytical investigation.

The significance of *Faraday*'s discovery has only recently been appreciated by chemists, and today 10000 tonnes of benzene is being produced anually by the industry [1]. Even more impressive than the discovery of benzene, however, is *Faraday*'s analytical achievement, in view of the enormous complexity of the starting material used, as we realized when we retraced this historic work with the aid of modern methods.

The first steps in artificial lighting by gas had been taken around the end of the 18th and the beginning of the 19th century. Flames that gushed out of the earth and lit up wide areas were reported by the earliest historians, but it was not until 1664 that *Clayton* observed that heating (dry distillation) of coals results in the liberation of a gas that burns with a luminous flame, and which can be collected. (From a letter written by *Clayton* to *Robert Boyle* [2].)

In 1667, *Shirley* wrote in the "Philosophical Transactions" about the presence of a burning spring at the Wigan collieries in Lancashire, and showed that the combustibility was a property, not of the water from the spring, but of the gas that was mixed with the water. In 1726, *Hales* ("Plant Statics") described an experiment in which the combustible gas formed on distillation of coal was quantitatively determined. In the second volume of his "Chemical Investigations" (1767), *Watson* reported that coal gas does not lose any of its illuminating power when passed through water; this observation proved to be particularly important in the subsequent development of the purification of gases. The problem of the lighting power was, at a later date, also of special interest to *Faraday* in his work.

It was in 1790 that gas lighting was first developed to a practical stage by *William Murdoch*. Two years later, *Murdoch* installed gas lighting in his house in Redruth. He distilled coal in iron retorts and led the resulting gas over distances of more than 20 m through tinned iron and copper pipes to the lighting points. In 1798 he lit part of *Boulton* and *Watt*'s large spinning mill in Soho (Birmingham), and in 1805 he presented accurate calculations to show that lighting is cheaper with gas than with candles. The first large gasworks, the "*Privileged Gas Lighting Company*", was founded in 1809 to light London and Westminster, and Westminster Bridge was lit for the first time in 1813. In 1815, *John Taylor* was granted a patent for the production of lighting gas by pyrolysis of fatty oils (at about 600 °C). This type of lighting was introduced in Liverpool, Bristol, and Hull, and in 1819, *David Gordon* patented the production of "portable gas" [3]; this portable gas was the source of *Faraday*'s starting material in which he discovered "three new hydrocarbons".

The ideas that led *Gordon* to use oil gas and "to make gaslight portable" may well have been as follows. Oil gas at that time gave a flame three times as bright as that of coal gas, so that only one third of the volume of gas was needed to obtain the same lighting power. Compression of the gas gives a further large reduction in volume, so that it was ultimately possible to obtain a gaslight flame that would burn for eight hours from gas compressed by a factor of 32 and stored in a space of $^1/_4$ cubic foot [4]. Portable gas could be connected to isolated street lights for which connection to the mains would be too expensive, and a further advantage was that it could be bought and used as required, without the need for any special structural arrangements.

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[1] *R. Sachtleben*, Die BASF *14*, No. 1, p. 22 (1964).

[2] *P. Bolley*: Das Beleuchtungswesen. Friedrich Vieweg und Sohn, Braunschweig 1862, p. 173.

[3] *Gordon*'s portable gas lamp. Dinglers polytechnisches Journal *12*, 249 (1823); *19*, 161 (1826).

[4] *E. L. Schubarth*: Elemente der technischen Chemie. In Commission bei August Rücker, Berlin 1835, p. 141.

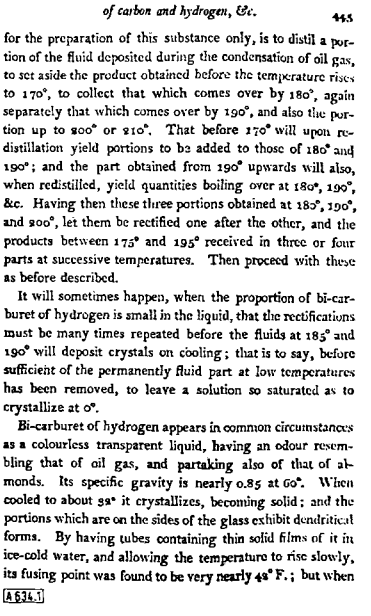
Gordon thus founded the Portable Gas Company in London and, after numerous technical difficulties had been overcome, started the production and sale of portable gas [4]. However, during the introduction and compression of the oil gas by means of a compression pump into a large copper container, from which the portable copper containers were filled with compressed gas, it was observed that an average of some 230 cubic inches of an unknown oily substance separated out from 1000 cubic feet of oil gas, possibly depriving the gas of a large part of its lighting power. Another great difficulty was to regulate the flow of gas from the containers of compressed gas so that it was not too fast initially and not too slow when the container was nearly empty – irregular flow gave rise to very non-uniform flames of varying brightness [4].

The separation of the liquid during the compression of the gas, the importance of this liquid to the lighting power of the gas, and the deposition of liquid on the valves of the gas containers, particularly in winter, led *Gordon* in 1820 to ask *Robert Faraday*, who worked for his Company, whether his brother *Michael* would examine this liquid.

The problem greatly interested *Michael Faraday*, since after his initial experiments with the liquid he thought that he had discovered liquid gas, which did not have to be compressed, and which had a high lighting power [5]. Two years later he isolated butene. The very same liquid that *Faraday* searched for and finally found is nowadays used in non-electric camping lights, which can in fact give a very bright light for many hours from a cartridge of the liquid gas. It was not until 1825 that he had collected sufficiently large quantities of the oil-gas condensate to allow a systematic analytical study of the product.

There is evidently a historical error associated with the discovery of benzene by *Faraday*. *A. W. Hofmann* started his official speech at Berlin (Benzene Festival 1890) with the sentence "The whole thing began with a piece of blocked gas pipe", meaning that benzene, which readily solidifies in winter because of its melting point of 5.5 °C, had separated out of the gas. However, the blockage was due not to benzene, but to condensation water that had frozen in the pipes, which were often badly laid. *Faraday*'s outstanding achievement was the purification of the benzene present in the oil-gas condensate by repeated fractional distillations and crystallizations until a product was obtained that gave the correct melting point of 5.5 °C. Benzene cannot separate out in gas pipes, since even highly enriched benzene deposits contain well over 300 other substances that lower the melting point of the benzene. The method used by *Faraday* for the enrichment of benzene from oil gas by distillation is reproduced in facsimile (Fig. 1).

[5] Entry in Faraday's laboratory journal dated April 17, 1823: "Now search among combustible gases for one becoming a liquid under 8 or 10 or even 20 atmospheres or at common temperature; examine oil-gas products *etc.*"



of carbon and hydrogen, &c. 445

for the preparation of this substance only, is to distil a portion of the fluid deposited during the condensation of oil gas, to set aside the product obtained before the temperature rises to 170°, to collect that which comes over by 180°, again separately that which comes over by 190°, and also the portion up to 200° or 210°. That before 170° will upon redistillation yield portions to be added to those of 180° and 190°; and the part obtained from 190° upwards will also, when redistilled, yield quantities boiling over at 180°, 190°, &c. Having then these three portions obtained at 180°, 190°, and 200°, let them be rectified one after the other, and the products between 175° and 195° received in three or four parts at successive temperatures. Then proceed with these as before described.

It will sometimes happen, when the proportion of bi-carburet of hydrogen is small in the liquid, that the rectifications must be many times repeated before the fluids at 185° and 190° will deposit crystals on cooling; that is to say, before sufficient of the permanently fluid part at low temperatures has been removed, to leave a solution so saturated as to crystallize at 0°.

Bi-carburet of hydrogen appears in common circumstances as a colourless transparent liquid, having an odour resembling that of oil gas, and partaking also of that of almonds. Its specific gravity is nearly 0.85 at 60°. When cooled to about 32° it crystallizes, becoming solid; and the portions which are on the sides of the glass exhibit dendritical forms. By having tubes containing thin solid films of it in ice-cold water, and allowing the temperature to rise slowly, its fusing point was found to be very nearly 48° F.; but when

A 634.1

Fig. 1. Method for the enrichment of benzene from oil gas condensate by distillation (facsimile of *Faraday*'s publication [6]).

The final outcome of *Faraday*'s investigations on the oil gas condensate was summarized by *Schubarth* [4]:

"...eine ölartige Substanz, welche theils farblos ist, theils grün beim reflektirten und gelb-braun beim durchgehenden Licht, specifisches Gewicht 0,821, wie Oelgas riecht, sehr flüchtig ist und sehr leicht kocht, beim Ausgießen wie Champagner braust, sich in Wasser nicht, aber in Alkohol, Aether, den Oelen auflöst, sich leicht mit Schwefelsäure verbindet. Sie ist ein Gemeng von mehreren flüchtigen Oelen, die einander rücksichtlich der Brennbarkeit und Leuchtkraft sehr ähnlich sind, aber durch verschiedne Flüchtigkeit sich unterscheiden. *Faraday* hat deren 3 beschrieben.

1. Bicarburet of hydrogen, (HC)
   Fp +5,5 °C spec. Gewicht bei 15 ° 0,85
   bei 0 ° 0,956
   Siedet bei über 85 °C über.
   Sie besteht aus 92,45 Kohlenstoff und
   7,55 Wasserstoff oder aus
   gleichem Volum Kstdampf und Wstgas.
2. (H_3C_2), die beim Erstarren der vorigen Materie übrig gebliebene Flüssigkeit, wird durch Erkälten nicht fest.
   Spec. Gewicht bei 15,6 °: 0,86
   Siedepunkt 85,5 °, von concentrierter Schwefelsäure stärker angegriffen, als die erstere und besteht aus 89,09 Kohlenstoff und 10,91 Wasserstoff; oder aus 2 Vol. Kstdampf und 3 Vol. Wstgas.
3. (H_4C_2), dritte Flüssigkeit
   Siedepunkt unter 0 °C
   spec. Gewicht bei 12 ° 0,627
   die leichteste aller bekannten Flüssigkeiten.

Die Zusammensetzung ist dieselbe wie die des ölbildenden Gases [*] nur in einem doppelt verdichteten Zustand."

Faraday did not give formulas in the original article, and the discrepancy in the evaluation of the equivalent weights (HC = bicarburet of hydrogen) will be discussed later.

The remarkable feature of *Faraday*'s work is the perseverance that he showed in the analysis of the oil gas concentrate. During the distillation of the crude

[6] *M. Faraday*, Philos. Trans. Roy. Soc. (London) *1825*, I, 440.

[*] Nowadays: ethylene.

product he found that the boiling behavior continuously changed with each repetition of the distillation.

When he isolated a narrow fraction and then redistilled it, he again found that it boiled over a wide range. By critical observation he found that repeated fractionation ultimately led to a fixed boiling point.

Figure 2 shows what was probably one of the first boiling curves, which were reported in digital form. A theoretical boiling curve as found on gas-chromatographic analysis of oil gas condensate with a thin film capillary 100 m long is also shown.

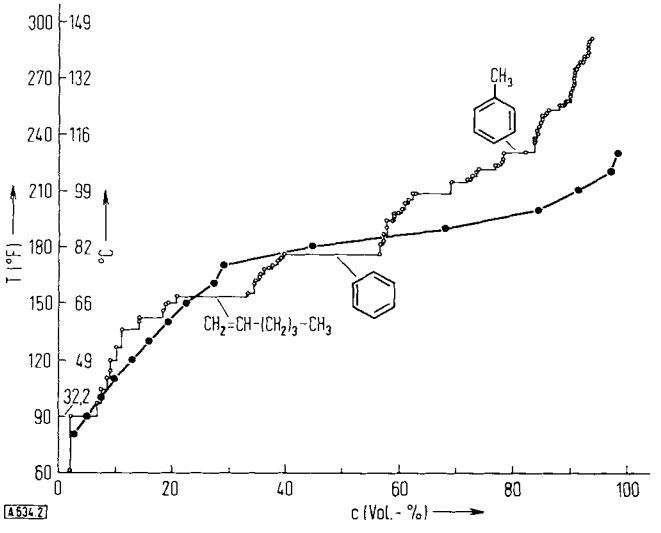


Fig. 2. Boiling curves from *Faraday*'s data (—•—•—) and from the gas-chromatographic analysis (—o—o—).

On repetition of this work on the micro scale, we found that the boiling point increases by 1 °C per drop of distillate in the first few distillations. After many fractionation steps, *Faraday*, isolated a distillate having a constant boiling point of 85 °C. He then used this distillate to determine the melting point and again found that in many cases liquid existed together with solid over a range of from −18 to −10 °C. This seemed too wide a range and by repeated isolation of the crystals at low temperature (pressing out on a press cooled to −18 °C between cooled layers of paper with exclusion of condensation water), he finally obtained constant melting-point benzene of a purity that would be the envy of any modern preparative chemist working under the same conditions.

Faraday also applied an exemplary degree of criticism in the evaluation of the results of his quantitative elemental analysis. His discussion of the error[6] should be read by all those who occasionally forget that measurements are always subject to errors.

Table 1 shows the results obtained by *Faraday* in 1825 together with modern results.

The name "bicarburet of hydrogen" can be explained on the basis of the "proportionals" used at that time. One proportional of C = 6 and one proportional of H_2 = 1, together with the results of the elemental analysis and the error discussion

C:H = 11.44:1 or C:H = 12:1

led to 2 proportionals of carbon and 1 proportional of hydrogen, *i.e.* "bicarburet of hydrogen".

Table 1. Results obtained by *Faraday* in 1825 and values from modern international sources for benzene.

	1825	1968
B.p. (760 torr)	85.3 °C (= 186 °F) [a]	80.10 ± 0.01 °C
M.p.	+ 5.5 °C (= 42 °F) [7] [b]	5.53 ± 0.01 °C [c]
d (15.6 °C)	0.86	d_4^{20} 0.8786 ± 0.0003
Molecular weight	39 (times 2)	78.1147 ± 5×10⁻⁵
Elemental analysis	92.45 C to 7.55 H	92.256 C to 7.744 H

[a] It is difficult even today to calibrate a thermometer in the region of 100 °C, since the barometric pressure is fully effective. Differences of opinion still exist concerning the differences between the temperature reference scales and the magnitude of systematic calibration errors. Moreover, the Fahrenheit scale was extended by linear extrapolation of the fundamental or calibration range of 0—32 ° Fahrenheit, so that systematic errors some distance away from the calibration range are quite understandable.

[b] It is much easier to avoid errors in calibration around 0 °C and around the zero of the Fahrenheit scale (temperature of common salt/ice). This explains the difference in the boiling point found in 1825.

[c] The melting point of benzene is difficult to determine accurately, since dry benzene is strongly hygroscopic. In international comparison experiments arranged recently by IUPAC, the determination of the melting point of benzene gave particularly poor results [7].

3. Re-examination of the Discovery of Benzene

We have tried to retrace *Faraday*'s work with modern analytical methods. The conditions of that period obviously cannot be simulated, since we are now familiar with "bicarburet of hydrogen" or "benzene" (as *Mitscherlich*, 1835, named the substance) or "benzol" (*Liebig*'s name for the mother-substance of what was later to become a large chemical industry). The analyst of today can recognize and characterize an individual substance in a mixture by the "dynamic" method. He no longer has to be a skilful preparative chemist in order to isolate the sample for analysis, as was the case in *Faraday*'s time. The repetition of this work again aroused our esteem for *Faraday*'s achievement when we saw the complexity of the mixture, since it took us days of effort on the micro scale to isolate the high-purity product that had been described so accurately about 140 years ago. (However, the preparative isolation was necessary in our case only because we wished to know what led *Faraday* to describe another substance, which must have overtaxed his measuring and analytical facilities. This will be commented on in detail in Tables 2–4.)

Using the simple apparatus shown in Figure 3, we pyrolyzed 3.3 g of sperm oil in 300 seconds and collected all the products quantitatively. The crude sperm oil, which had already been stored for some years, was continuously pumped into a steel tube at 600 ± 10 °C, and the pyrolysis products were carried into a cold trap by a very weak current of nitrogen. The steel tube was connected to a high current transformer and was subjected to direct electrical heating.

[7] *O. Riedel*, personal communication.

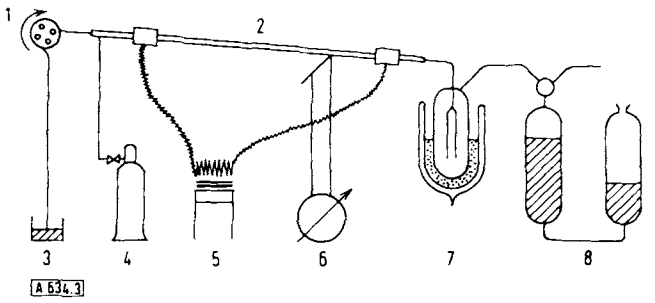


Fig. 3. Pyrolysis apparatus 1: Sleeve pump (0.65 g/min); 1: V2A steel tube (4×0.5 mm, 1 m long, 600 ± 10 °C); 3: sperm oil (3.3 g); 4: nitrogen (8 ml/min); 5: transformer; 6: voltmeter; 7: condensate (at 20 °C: 0.76 g); 8: pyrolysis gas (1654 Ncm³).

A total of 1654 Ncm³ of gas were evolved from 3.3 g of oil. The analysis of the gas is shown in Table 2.

The liquid pyrolysis products, which weighed 0.75 g after deaeration at 20 °C, were distilled in one stage in a microdistillation apparatus up to 121 °C = 250 °F. 1 µl of the yellowish distillate was used for the GC/MS analysis.

A GC/MS analysis is a gas-chromatographic analysis with mass-spectrometric evaluation or mass-spectrometric recordings immediately preceded by gas-chromatographic separation of the products. The gas-chromatographic signals are received by the mass spectrograph in a direct instrumental coupling. A high-efficiency thin film capillary was used for the separation.

In a period of about 20 minutes, a capillary GC/MS combination of this type provides sufficient information to keep several experts very busy for several weeks with its processing and evaluation unless an on-line computer is used. We confined ourselves therefore to the recognition of the main constituents of the liquid sperm-oil pyrolyzates vaporized at temperatures up to 120 °C.

The complete evaluation of the data without the use of a computer would have taken about three months.

Table 2. Analyses of the gaseous pyrolysis products of sperm oil.

	1835 [1] (Vol.-%)	1968 (Vol.-%)
Hydrogen	3—7.7	7.9
Hydrocarbon gas (= saturated flammable gases)	46—50	24
Chlorine absorbable gases (= unsaturated gases)	22.5—38	40
in Detail:		
Oxygen		1.9
Carbon monoxide		18.5
Carbon dioxide		6.8
C_1 Methane		18.8
C_2 Ethane		5.3
Ethylene		30.0
Acetylene		0.3
C_3 Propane		0.5
Propene		7.1
Propadiene		0.03
Propyne		0.24
C_4 *n*-Butane		0.05
1-Butene		0.8
iso-Butene		0.1
trans-2-Butene		0.13
cis-2-Butene		0.08
1,3-Butadiene		1.3
C_5 3-Methyl-1-butene		0.02
Other C_5 compounds		Traces

A rough calculation shows that for the direct use of a computer with programming for structure evaluation, which is still in the very early stages of its development, a computing time of a few minutes should have been enough to accomplish the same work, provided that all the analytical data were stored on magnetic tape and that the mass spectra were evaluated "on line", *i.e.* directly.

The results of the combination analysis (see Fig. 4, chromatogram 1) are summarized in Table 3. In addition to the mass-spectrometric evaluation, substantial gas-chromatographic evaluation was also necessary, since the mass-spectrometric data alone yields remarkably little information in the analysis of olefins.

The pyrolysis condensate having the composition given in Table 3 (see Fig. 4, chromatogram 1) was com-

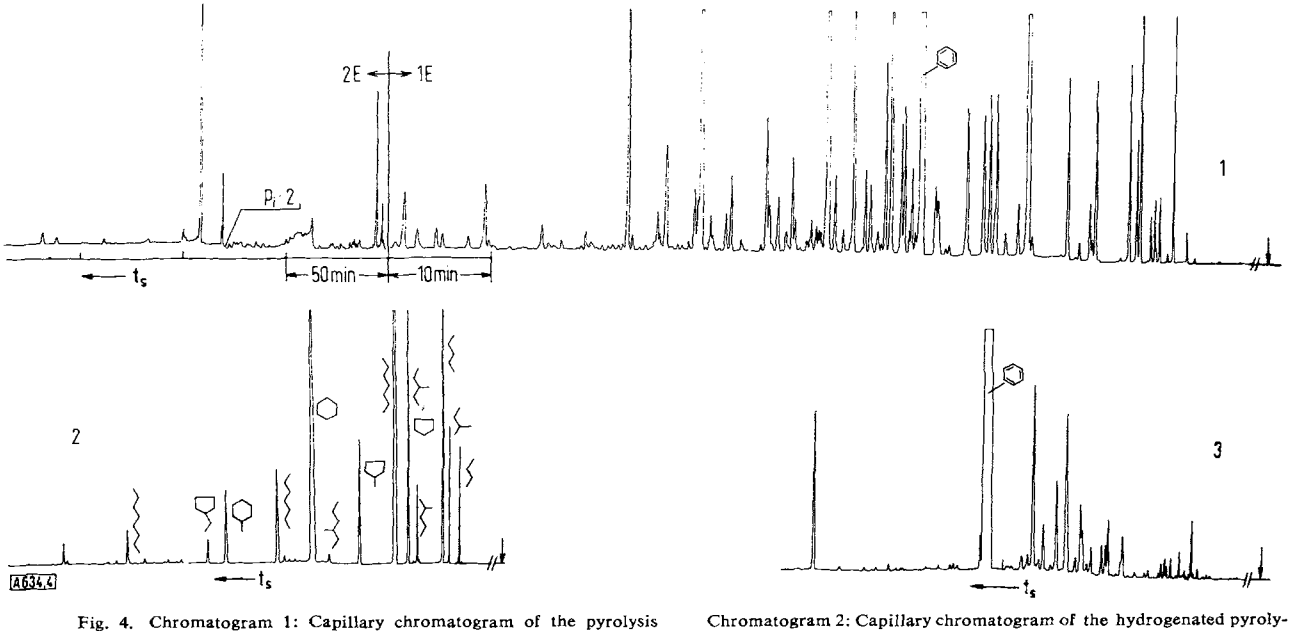


Fig. 4. Chromatogram 1: Capillary chromatogram of the pyrolysis condensate having b.p. 20—120 °C, temperature-programmed and partly pressure-programmed, shown with modified chart drive. Steel thin film capillary, p_i = 2.2 atm N_2.

Chromatogram 2: Capillary chromatogram of the hydrogenated pyrolysis condensate.
Chromatogram 3: Capillary chromatogram of the "hydrocarbon C_2H_3", which was found to be the mother liquor of the crystallizing benzene.

Table 3. Composition of the pyrolysis condensate, determined by gas-chromatographic analysis and GC/MS combination analysis (see Fig. 4, chromatogram 1). Conditions: 100 m thin film capillaries, medium-polarity, polar, nonpolar, are directly coupled to the Varian-Mat CH 4/5 mass spectrometer. A mass spectrum is recorded for each peak at the instant of entry into the ion source. Number of species on medium-polarity capillary in concentrations above 100 ppm: >250; >90 components with retention indices lower than 763 (benzene). Number of species on polar capillary appearing before benzene at a low temperature: > 130. Number of species on nonpolar capillary ≈ 340. Only the hydrocarbons in concentrations higher than 0.5 % were qualitatively identified.

	Conc. (wt.-%)
iso-Butene	0.5
1,3-Butadiene	1.2
1-Pentene	4.5
trans-2-Pentene	0.9
cis-2-Pentene	0.8
1-Ethyl-1-methylcyclopropane	0.7
1,3-Pentadiene	3.2
Cyclopentene	4.3
3-Penten-1-yne	1.8
1-Hexene	12.3
1-Hexyne; 1,5-Hexadiene	1.3
3-Hexene	1.1
n-Heptane	0.7
Cyclohexene	2.1
2,3-Dimethyl-1,3-butadiene	0.8
1,3,5-Hexatriene	3.4
2-Hexen-4-yne	0.5
Benzene	17.0
Heptadiene?	0.6
Toluene	4.4
Separated individual and partially or totally superimposed signals below a total of 0.5 % in concentration.	≈ 38 of the whole.

pletely hydrogenated, the aromatic compounds giving naphthenes. The number of species in concentrations above 100 ppm decreased from 340 to 42; thus the 340 detectable compounds have only about 40 carbon skeletons, by far the most abundant of which are the C_6 structures. This can be seen from Figure 4, chromatogram 2, and from Table 4.

The complexity of the pyrolysis condensate boiling between 20 and 120 °C is interesting. According to tables of CH compounds that have been analytically detected, some 700 components are found in this boiling range. Above a limiting concentration of 100 ppm, we found almost half of all possible compounds. This result is not in conflict with similar investigations, since all the hydrocarbons actually present are found only by carrying the investigations far into the trace range; with a minimum concentration of 1 ppm, it is possible to detect about 80 % of all the possible hydrocarbons and when the limiting concentration of a complete analysis is set even lower, more structures are found than are given in the modern tables. Thus it is evidently not true that *e.g.* gasoline does not contain all the possible saturated hydrocarbons; this is simply a matter of lowering the limiting concentration sufficiently far. The term "complete analysis" is meaningless unless the concentration limit is specified.

The hydrocarbons listed in Table 4 were found in concentrations above 1000 ppm after complete hydrogenation (the Table does not mention that traces of less than 1000 ppm were also detected in the range nonane to decane).

Faraday described two other new hydrocarbons, including the lightest of all liquids known up to 1825, *i.e.* butene ("specific gravity" 28, corresponding to a molecular weight of 56, with the formula 4 proportionals of H_2 and 4 proportionals of C, present-day notation C_4H_8); however, this product was still mixed with the

Table 4. Composition of the hydrogenated pyrolysis condensate.

C-Skeletal structure	Frequency (wt.-%)
iso-Butane	0.6
n-Butane	1.7
iso-Pentane	2.3
n-Pentane	18.7
2,3-Dimethylbutane	0.09
3-Methylpentane + Cyclopentane	7.7
n-Hexane	27.2
Methylcyclopentane	4.3
2-Methylhexane	0.5
2,3-Dimethylpentane	0.1
3-Methylhexane and Cyclohexane	25.1
3-Ethylpentane	0.07
1,3-Dimethylcyclopentane(*cis*- + *trans*-)	0.2
trans-1,2-Dimethylcyclopentane	0.2
n-Heptane	4.4
Methylcyclohexane	3.2
Ethylcyclopentane	0.8
n-Octane	0.6

isomeric butenes. *Faraday* knew that the liquid he was dealing with had a boiling range of −18 to 0 °C, that it was not pure, and that the main component was not C_2H_4 (ethylene, known at that time as "olefiant gas"). This could be deduced from the properties of the chlorinated olefin.

However, the aids available at that time failed *Faraday* in the identification of the "third hydrocarbon". In 1835, this third hydrocarbon was described in *Schubarth*'s "Elemente der technischen Chemie" [4] as C_2H_3, b.p. = 85.5 °C, specific gravity at 15.6 °C = 0.86. It was in fact a solution of about 30 % of C_4 to C_8 hydrocarbons in 70 % of benzene, which remained stable above −18 °C as the mother liquor in the crystallization of benzene. It contains at least 110 components at individual concentrations of more than 100 ppm (see Fig. 4, chromatogram 3). The mother liquor also contains unstable compounds that decompose during the concentration of the solution, and which have not been identified even yet. There is thus good reason for the aim of modern analysis to be an elucidation of the structures of compounds of this type dynamically in concentrations down to the ppb range, and without first isolating the compounds.

It may be concluded from our analytical results and from a comparison with historical analytical values that our distillate and the oil gas condensate from *Gordon*'s portable gas are very similar. If we assume that this is correct, *Faraday* was faced with a mixture containing at least 320 hydrocarbons in concentrations of more than 100 ppm each. Some substances having properties very similar to those of benzene cannot be completely separated from benzene even with the aid of a thin film capillary having a separation number [8] of more than 60. We would have to use a number of separating capillaries connected both in series and in parallel in order to free benzene completely from accompanying substances. Isolation of products that are pure according to their melting points is well nigh

[8] The separation number is in our view the most useful assessment of the separating efficiency of a chromatographic system. In a chromatographic range for which the separation number is *e.g.* 60, a maximum of 60 other signals can be satisfactorily separated (in 4,6 σ separation) between a pair of homologs (*R. Kaiser*, Z. analyt. Chem. *189*, 1 (1962)).

impossible; however, the classical method of preparing the substance is no longer necessary, since, as mentioned previously, pure isolated products are no longer required for the recognition of structures.

The quantitative evaluation of the capillary-chromatographic analysis was carried out after storage of the chromatogram on a magnetic tape by play-back through an automatic electronic direct integrator, which has the properties of a simple minicomputer. Ten minutes after the beginning of the first capillary chromatogram, the directly coupled mass spectrometer recorded the unmistakable mass spectrum of benzene by means of a UV fast recorder. Twenty minutes after a repeated GC recording, the mass spectrum of the signal showed conclusively the presence of toluene. The other main components were identified in the third combination GC/MS run by combined evaluation, and the results were checked by quantitative determination of the hydrocarbons by complete catalytic hydrogenation of the pyrolysis distillate in the form of a structure balance analysis. It is not necessary here to go into details of the apparatus and procedure, which correspond to present-day practice [9].

An interesting historical connection should be mentioned. The production of portable gas was started by *Gordon*, who asked *Faraday* for his assistance. Compressed coal gas was later also sold in portable containers, in order to supply gas to consumers whose homes were not yet connected to gasworks. At the age of 27, the Mannheim goldsmith and jeweller *Friedrich Engelhorn* (1821–1902) founded the firm "Engelhorn und Comp." for the production and sale of portable gas. Three years later, in conjunction with two gas engineers, he founded the "Badische Gesellschaft für Gasbeleuchtung", which installed street lighting in Mannheim. In 1861, *Engelhorn* set up a new company, "Sonntag, Engelhorn und Clemm"; this was the first tar factory in Germany, which produced, not only coal-tar dyes, but also their precursors such as aniline *via* benzene from tar. This Mannheim aniline factory ultimately became the Badische Anilin- und Soda-Fabrik AG., to whose management the author is deeply indebted for their generous support of his analytical investigations.

I am grateful for the idea of this work to Dr. H. Wolter, Völklingen, who has taken a particularly profound interest in the history of Faraday's work. I am also grateful to Dr. W. Benz, who carried out the mass-spectrometric investigations and evaluations, to Dr. E. Frommer for the gas analysis, and to Fräulein L. Arnold, Herr H. Fiedler, Fräulein C. Schneider, and Herr W. Schäfer for the preparation, working-up, and chromatographic analysis of the sperm oil pyrolysis products.

[9] See, for example, *E. Brunner* and *R. Kaiser*, Chemie-Ing.-Techn. *39*, 1418 (1967); *G. Schomburg* and *D. Henneberg*, Chromatographia *1*, 23 (1968).

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The Biosynthesis of Aromatic Amino Acids and its Regulation

BY F. LINGENS [*]

Microorganisms synthesize the aromatic amino acids phenylalanine, tyrosine, and tryptophan, as well as the related compounds p-aminobenzoic acid, tetrahydrofolic acid, p-hydroxybenzoic acid, ubiquinone, vitamin K, and nicotinic acid, by a highly branched route passing through shikimic acid. The biosynthesis is not regulated in the same way in all the organisms studied. The regulation is strongly dependent on the ability of the enzymes involved to be resolved into isozymes, their ability to be inhibited, and their activation, repression, and induction.

1. Introduction

The synthesis of aromatic amino acids in nature starts with intermediates of the carbohydrate metabolism. The main pathway ("shikimic acid route") of this highly branched biosynthetic chain leads to phenylalanine, tyrosine, tryptophan, and *p*-aminobenzoic acid. In some microorganisms, in mammals, and even in humans, tryptophan is used *inter alia* as a starting material for the biosynthesis of nicotinic acid; *p*-aminobenzoic acid is used for the biosynthesis of tetrahydrofolic acid. It has very recently been discovered that vitamin K and ubiquinone are also derived from the main pathway for the biosynthesis of aromatic compounds (see Scheme 1). The single biosynthetic chain described here is subject to biochemical regulation.

The investigations described in this review were carried out mainly on the Enterobacteriaceae *Escherichia coli*, *Aerobacter aerogenes*, and *Salmonella typhimurium*, on yeasts (particularly *Saccharomyces cerevisiae*), and on

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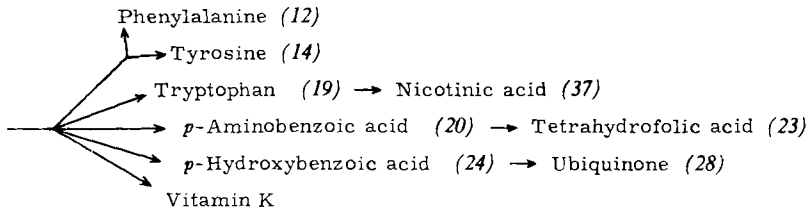


Scheme 1. General scheme of the biosynthetic pathways.

the mold *Neurospora crassa*. It must be pointed out that findings relating to a single organism, particularly in connection with the regulation of biosynthetic processes, cannot be generalized without further investigation. For example, nicotinic acid can be biosynthesized in microorganisms in several different ways; moreover, many microorganisms cannot produce either ubiquinone or vitamin K.

The regulation of biosynthetic chains is a means of ensuring that the end products are formed only as required. The end product of a chain may, for example, inhibit the first enzyme of the chain (negative feedback). The end product may also inhibit the biosynthesis of some or all of the enzymes of the chain (repression).

In a branched biosynthetic chain, it is necessary to regulate the main pathway as well as each individual chain. This is possible *e.g.* if the first step of the main pathway is catalyzed by isozymes, each of which is specifically inhibited by an end product situated beyond the branching point (see Scheme 1). However, this control may also be exerted through a single enzyme, which is inhibited only when all the end products are present at the same time (multivalent negative feedback). A third possibility for regulation in the main pathway is that biosynthesis of the enzyme is suppressed only by the simultaneous presence of end products of several chains (multivalent repression). It would be useful if the end product of one chain in a branched biosynthetic chain not only inhibited the first enzyme of its own chain, but also simultaneously activated the first enzyme of another chain. Multivalent induction, in which an enzyme of one chain is induced by end products of several chains, has also been observed.

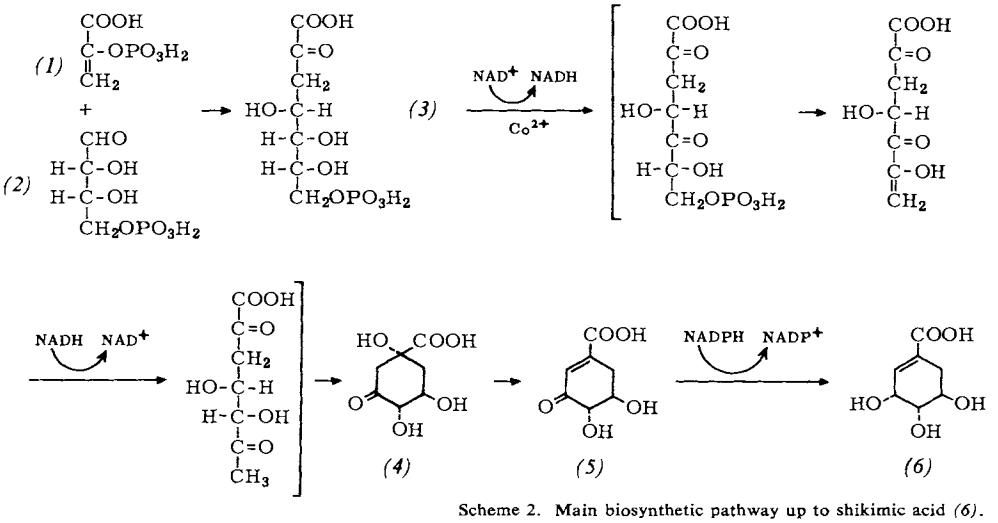
Biochemical deficiency mutants having a suitable genetic block have frequently been introduced into the synthetic chain in order to study biosynthetic processes. (For descriptions of methods, see [1].)

1.1. Definitions

An organism that can grow with CO_2 as its source of carbon is said to be autotrophic; if an organic carbon source is necessary, the organism is heterotrophic. Many microorganisms in nature ("wild strains" = prototrophic forms) synthesize all the compounds that they need to live from a simple organic carbon source and inorganic salts. In a prototrophic organism, the DNA can be changed in such a way by the action of a mutagen that one enzyme disappears (genetic blockage by mutation). The resulting "auxotrophic" forms (biochemical deficiency mutants) also require the end product or one of the compounds of the pathway beyond the genetic block for their growth. A single mutation can also lead to a polyauxotrophic organism, which requires several end products for its growth, owing to mutation in the main stem of a branched biosynthetic chain. Biochemical deficiency mutants cannot grow in media that lack the end product of the broken synthetic path. However, the synthetic chain remains capable of functioning as far as the genetic block; the intermediate product formed in this way is often released into the medium (accumulation).

2. The Main Pathway of the Biosynthesis of Aromatic Amino Acids

The first step in the main pathway is the condensation of phosphoenolpyruvic acid *(1)* with erythrose 4-phosphate *(2)* to form 2-keto-3-deoxyarabinoheptonic acid 7-phosphate *(3)* [2] (see Scheme 2).



Scheme 2. Main biosynthetic pathway up to shikimic acid *(6)*.

[1] *H. Hellmann* and *F. Lingens*, Angew. Chem. *73*, 107 (1961).

[2] *P. R. Srinivasan*, *M. Katagiri*, and *D. B. Sprinson*, J. Amer. chem. Soc. *77*, 4943 (1955).

The enzyme that catalyzes this reaction (DAHP synthetase = PODH lyase: E.C. 4.1.2.15) requires neither a metal ion nor another cofactor [3]. Later investigations showed that in *E. coli* and many other microorganisms this step is catalyzed by isozymes, which all initiate the same reaction and are all characteristically inhibited by the end products of the branched biosynthetic chain.

The second step in the biosynthesis is the conversion of *(3)* into 5,5-didehydroquinic acid *(4)* [4].

This ring closure probably proceeds *via* three intermediates with seven carbon atoms in each. The oxidation at C-5 of *(3)* facilitates the elimination of phosphate in the next step. This is followed by reduction of this carbonyl group to a hydroxyl group, with restoration of the original configuration of *(3)*. The resulting 2,6-diketone cyclizes to give *(4)* [5].

In the third step, *(4)* is dehydrated to form 5,5-didehydroshikimic acid *(5)*. The enzyme involved in this dehydration is highly specific, and does not dehydrate quinic acid to shikimic acid [6]. *(5)* is then reduced to shikimic acid *(6)* (the reductase requires NADPH as the cofactor [7]).

A polyauxotrophic mutant of *E. coli* whose phenylalanine, tyrosine, tryptophan, *p*-aminobenzoic acid, and *p*-hydroxybenzoic acid requirements can be satisfied by shikimic acid alone releases *(5)* into the medium under starvation [8]; this mutant lacks the reductase for the conversion of *(5)* into *(6)*. In polyauxotrophic mutants of *E. coli* [9,10] and *S. cerevisiae* [11] that cannot utilize shikimic acid for growth, shikimic acid has been detected as an accumulated product.

Shikimic acid is phosphorylated with ATP to the 5-phosphate *(7)* [12,13] (see Scheme 3), which then reacts with phosphoenolpyruvic acid to give the 3-enolpyruvyl ether *(8)* of shikimic acid 5-phosphate [14].

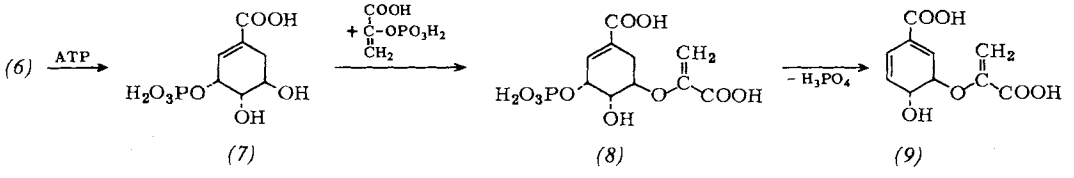
Phosphates frequently cannot be detected as accumulation products, since they are ionized compounds and so do not pass through the cell wall [15]. Moreover, phosphates are readily attacked by "nonspecific" phosphatases, and then cannot be found.

The compound *(8)* was for a long time erroneously regarded as the product at the branching point in the biosynthesis, from which the syntheses of phenylalanine, tyrosine, tryptophan, *etc.*, begin. It was noticeable, however, that *(8)* occurred as an accumulated product (in the dephosphorylated form) only in polyauxotrophic mutants. A product of the branching point, on the other hand, should occur as an accumulated product in mutants that are blocked in the first step after the branch in one of the possible biosynthetic chains. Thus different mutants should give the same accumulated product. This has in fact been found for various *S. cerevisiae* mutants, which accumulated the same branching product [16]. This secondary product of *(8)* was first detected with an *A. aerogenes* mutant, which was dependent on the simultaneous supply of phenylalanine, tyrosine, and tryptophan as a result of several mutations [17,18].

Finally, *(8)* loses phosphoric acid to give the 3-enolpyruvyl ether of *trans*-3,4-dihydroprotocatechuic acid *(9)* (chorismic acid, χωρισμος = separation) [19].

Chorismic acid closes the main stem of the biosynthesis of aromatic amino acids. The five synthetic chains that branch out from this point will now be discussed.

It should be noted that quinic acid has also been postulated as a link in the main chain. This assumption is based on the observation of the activity of this compound as a growth factor for *Aerobacter aerogenes*. This organism can synthesize 5,5-didehydroquinic acid from quinic acid [20,21]. No other microorganism examined so far has this ability. However, quinic acid is not a link in the biosynthetic chain, but serves *A. aerogenes* as an additional source of 5,5-didehydroquinic acid.



(7) (8) (9)

Scheme 3. Main biosynthetic pathway up to chorismic acid *(9)*.

It was particularly difficult to establish the structure of this intermediate, since it is unstable and is released in the dephosphorylated form by suitably blocked mutants.

3. Biosynthesis of Phenylalanine and Tyrosine

The common starting material for the biosynthesis of phenylalanine and tyrosine is prephenic acid *(10)* which is formed enzymatically from chorismic acid *(9)* [22]. The conversion of *(9)* into *(10)*, which is catalyzed by chorismate mutase, may be regarded as a Claisen rearrangement. It can also be effected in the

[3] *P. R. Srinivasan* and *D. B. Sprinson*, J. biol. Chemistry *234*, 713 (1959).

[4] *U. Weiss, B. D. Davis*, and *E. S. Mingioli*, J. Amer. chem. Soc. *75*, 5572 (1953).

[5] *P. R. Srinivasan, J. Rothschild*, and *D. B. Sprinson*, J. biol. Chemistry *238*, 3176 (1963).

[6] *S. Mitsuhashi* and *B. D. Davis*, Biochim. biophysica Acta *15*, 54 (1954).

[7] *H. Yaniv* and *C. Gilvarg*, J. biol. Chemistry *213*, 787 (1955).

[8] *J. J. Salamon* and *B. D. Davis*, J. Amer. chem. Soc. *75*, 5567 (1953).

[9] *B. D. Davis*, J. biol. Chemistry *191*, 315 (1951).

[10] *H.T. Shigeura* and *D. B. Sprinson*, Federat. Proc. *11*, 286 (1952).

[11] *F. Lingens* and *H. Hellmann*, Z. Naturforsch. *13b*, 462 (1958).

[12] *B. D. Davis* and *E. S. Mingioli*, J. Bacteriol. *66*, 129 (1953).

[13] *U. Weiss* and *E. S. Mingioli*, J. Amer. chem. Soc. *78*, 2894 (1956).

[14] *I. G. Levin* and *D. B. Sprinson*, Biochem. biophysic. Res. Commun. *3*, 157 (1960); J. biol. Chemistry *239*, 1142 (1964).

[15] *B. D. Davis*, Arch. Biochem. Biophysics *78*, 497 (1958).

[16] *F. Lingens* and *W. Goebel*, Hoppe-Seylers Z. physiol. Chem. *342*, 1 (1965).

[17] *M. I. Gibson* and *F. Gibson*, Biochem. J. *90*, 248 (1964).

[18] *F. Gibson*, Biochem. J. *90*, 256 (1964).

[19] *H. Morell, M. J. Clark, P. F. Knowles*, and *D. B. Sprinson*, J. biol. Chemistry *242*, 82 (1967).

[20] *B. D. Davis* and *U. Weiss*, Naunyn-Schmiedebergs Arch. exp. Pathol. Pharmakol. *220*, 1 (1953).

[21] *S. Mitsuhashi* and *B. D. Davis*, Biochim. biophysica Acta *15*, 268 (1954).

[22] *H. Plieninger*, Angew. Chem. *74*, 423 (1962); Angew. Chem. internat. Edit. *1*, 367 (1962).

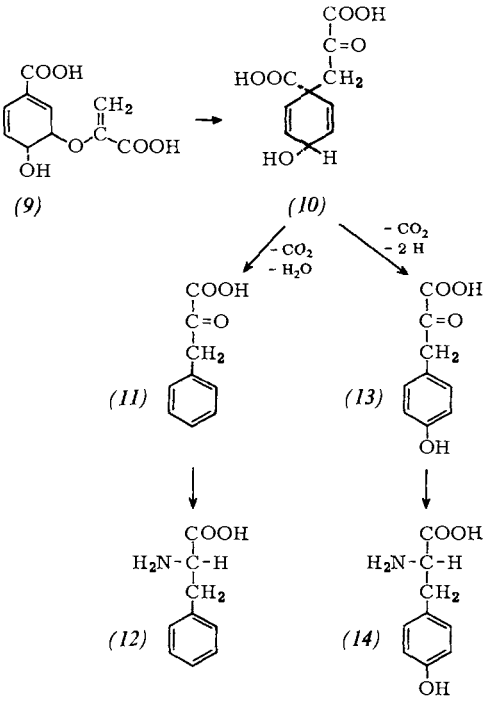
absence of enzyme by careful heating of *(9)* in buffer solutions at pH = 7.0.

Prephenic acid *(10)* is enzymatically aromatized at pH = 7 to phenylpyruvic *(11)* and *p*-hydroxyphenylpyruvic acid *(13)*. The formation of *(11)* is catalyzed by prephenate dehydratase [23].

This reaction proceeds readily in weakly acidic media in the absence of enzyme. This explains why a mutant that lacks prephenate dehydratase, and which accumulates *(10)* under deficiency conditions, can grow readily with the accumulated product after decomposition to form *(11)* if the acidification of the medium is not prevented by continuous addition of alkali [24, 25].

Reductive transamination of phenylpyruvic acid *(11)* leads to phenylalanine *(12)* (see Scheme 4).

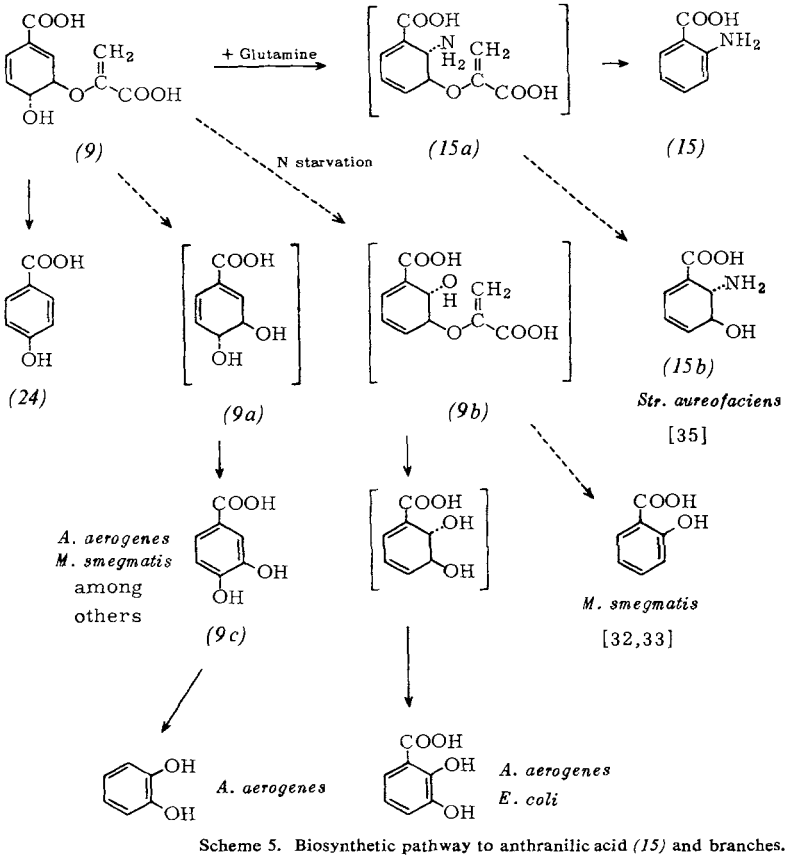
p-Hydroxyphenylpyruvic acid *(13)* is formed from prephenic acid *(10)* with catalysis by prephenate dehydrogenase. This reaction requires NAD as a cofactor [26]. The reductive transamination of *(13)* yields tyrosine *(14)*.



Scheme 4. Biosynthetic pathways to phenylalanine *(12)* and tyrosine *(14)*.

4. Biosynthesis of Tryptophan

The first link in the biosynthetic chain leading to tryptophan is anthranilic acid *(15)* (see Scheme 5). Though the transformation of chorismic acid *(9)* into anthranilic acid is a complex process, this reaction is catalyzed [27,28], at least in *N. crassa* and *S. cerevisiae*, by a single enzyme. The amide nitrogen of glutamine gives the amino group in *(15)* [29]. It might be assumed that this biosynthesis proceeds *via* the 3-enolpyruvyl ether of *trans*-2,3-dihydro-3-hydroxyanthranilic acid *(15a)*;



Scheme 5. Biosynthetic pathway to anthranilic acid *(15)* and branches.

[23] *B. D. Davis*, Federat. Proc. *14*, 691 (1955).

[24] *B. D. Davis*, Science (Washington) *118*, 251 (1953).

[25] *M. Katagiri* and *R. Sato*, Science (Washington) *118*, 250 (1953).

[26] *I. Schwinck* and *E. Adams*, Biochim. biophysica Acta *36*, 102 (1959).

[27] *J. A. DeMoss*, J. biol. Chemistry *240*, 1231 (1965).

[28] *F. Lingens*, *B. Sprössler*, and *W. Goebel*, Biochim. biophysica Acta *121*, 164 (1966).

[29] *P. R. Srinivasan*, J. Amer. chem. Soc. *81*, 1772 (1959).

however, this compound has not yet been detected [16, 30, 31].

In the investigation of the conversion of *(9)* into *(15)*, the formation of phenolcarboxylic acids and phenols has been observed with some microorganisms [34]. The occurrence of large quantities of *p*-hydroxybenzoic acid *(24)* is understandable, since this compound is readily formed, both enzymatically and spontaneously, from *(9)*. The formation of protocatechuic acid *(9c)* could be imagined as resulting from the initial cleavage of the ether linkage in *(9)* to form *trans*-3,4-dihydroprotocatechuic acid *(9a)*, which is then dehydrogenated. Decarboxylation of *(9c)* yields pyrocatechol. If starved of nitrogen, a 3-enolpyruvyl ether of *trans*-2,3-dihydro-2,3-dihydroxybenzoic acid *(9b)* could occur as an analog of the nitrogen compound. The occurrence of this compound would readily explain the formation of salicylic acid (removal of pyruvic acid), as well as the formation of 2,3-dihydroxybenzoic acid (cleavage of the ether linkage and dehydrogenation). *trans*-2,3-Dihydro-3-hydroxyanthranilic acid *(15b)* has been isolated from a *Streptomyces aureofaciens* mutant having a reduced ability to synthesize tetracycline [35]. It may be assumed that this compound is formed by cleavage of the ether linkage in the postulated intermediate *(15a)*.

Cox and *Gibson* [36] very recently showed that 2,3-dihydroxybenzoic acid has an additional growth effect on polyauxotrophic mutants of *E. coli*, but is not a precursor of ubiquinone or vitamin K. However, this compound is evidently also formed in excess of actual requirements, since the accumulation of the serine compound of 2,3-dihydroxybenzoic acid has been observed with *E. coli* [37].

2,3-Dihydro-2,3-dihydroxybenzoic acid was recently detected as an intermediate in the biosynthesis of 2,3-dihydroxybenzoic acid [37a].

N-Pyruvoylanthranilic acid, which is reported to occur as an accumulation product of *A. aerogenes* [38], has been postulated as an intermediate in the conversion of chorismic acid *(9)* into anthranilic acid. *N*-Pyruvoylanthranilic acid has been synthesized [39], but could not be converted into anthranilic acid in enzymatic tests with *S. cerevisiae* extracts [28].

The conversion of *(9)* into *(15)* can be inhibited by glutamine-like substances. No intermediates of the transformation could be detected in inhibition experiments with 6-diazo-5-oxonorleucine. A mutant that normally accumulates anthranilic acid as a result of genetic blocking of the tryptophan biosynthesis chain gives chorismic acid *(9)* and products of the other biosynthetic branches in the presence of 6-diazo-5-oxonorleucine [40]. *(9)* is accumulated in good yield by a series of phe$^-$ and/or tyr$^-$ mutants [*] of *S. cerevisiae* and *E. coli*. The yield can be increased by the addition of diazooxonorleucine if suitably precultured and accumulated [41].

It is interesting to note that chorismic acid can be detected as an accumulation product when diazooxonorleucine is allowed to act on the wild strains of *E. coli* and *S. cerevisiae* [41].

The next step in the biosynthesis of tryptophan is the reaction of anthranilic acid *(15)* with 1-pyrophosphoryl-D-ribose 5-phosphate to give 1-*o*-carboxyphenyl-D-ribosylamine 5-phosphate *(16)* (see Scheme 6). This compound, which had for a long time been formulated as an intermediate [42], was recently also detected enzymatically [43].

The corresponding phosphate-free compound should be expected as an accumulation product with suitably blocked tryptophan-deficient mutants. However, only anthranilic acid is in fact found.

The assumption that 1-*o*-carboxyphenyl-D-ribosylamine could not be detected because of its instability was incorrect; the compound [42] could be recovered unchanged from the culture medium by microorganism in a model experiment [44]. It must therefore be assumed that the unstable primary accumulation product *(16)* breaks down into anthranilic acid and ribose 5-phosphate, which is transferred to the carbohydrate metabolism.

As the biosynthesis proceeds, 1-*N*-(*o*-carboxyphenylamino)-1-deoxy-D-ribulose 5-phosphate *(17)* is formed by an Amadori rearrangement of *(16)*.

Tryptophan-requiring mutants of *A. aerogenes* [45] and *S. cerevisiae* [46] having a genetic block in the next stage of the biosynthetic chain accumulate 1-*N*-(*o*-carboxyphenylamino)-1-deoxy-D-ribulose if starved of tryptophan. This compound and its phosphate *(17)* can also be obtained by synthesis [47].

(17) is cyclized in the next step to form an indole compound *(18)* by dehydration and decarboxylation on the C atom that carried the carboxyl group, as could be shown by the conversion of 4-methylanthranilic acid into 6-methylindole [48]. The C atoms 1 and 2 of the ribulose supply the missing C atoms of the pyrrole ring [49].

The formation of 3-(indol-3-yl)glycerine-1-phosphate *(18)* was detected with enzyme extracts [50]. Tryptophan-requiring mutants of *E. coli* and *Salmonella typhimurium* release 1-indol-3-ylglycerine into the medium [42]; correspondingly blocked mutants of *S. cerevisiae* surprisingly accumulate not

[30] *I. G. Levin* and *D. B. Sprinson*, J. biol. Chemistry *239*, 1142 (1964).

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[37a] *I. G. Young, L. M. Jackman*, and *F. Gibson*, Biochim. biophysica Acta *148*, 313 (1967).

[38] *C. Ratledge*, Nature (London) *203*, 428 (1964).

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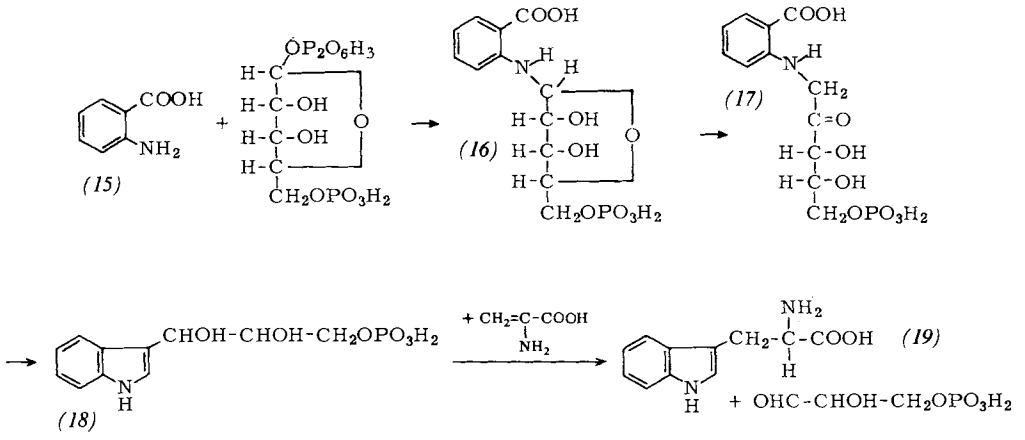
[47] *F. Lingens* and *E. Schraven*, Liebigs Ann. Chem. *655*, 167 (1962).

[48] *C. Yanofsky*, Science (Washington) *121*, 138 (1955).

[49] *C. Yanofsky*, J. biol. Chemistry *217*, 345 (1955).

[50] *C. Yanofsky*, Biochim. biophysica Acta *20*, 438 (1956).



Scheme 6. Biosynthetic pathway to tryptophan *(19)*.

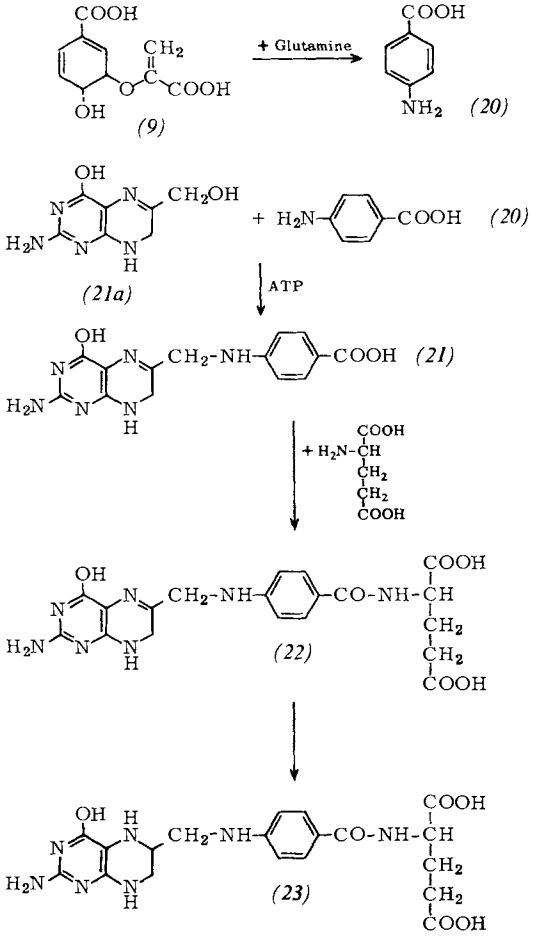
this compound, but 3,3-di(indol-3-yl)-1,2-propanediol[51]. A crude enzyme extract of *S. cerevisiae* converts *(18)* into the 1-phosphate of 3,3-di(indol-3-yl)-1,2-propanediol[51].

3-Hydroxy-3-(indol-3-yl)-2-oxopropyl phosphate was also detected[51]. One might have thought that a biosynthesis of tryptophan could take place *via* this compound with retention of the side chain, as in the biosynthesis of histidine. However, the intermediates tryptophanol phosphate, tryptophanol, and tryptophanal that would be required in this case could not replace tryptophan for a number of microorganisms[52].

The last step of the tryptophan synthesis is the condensation of *(18)* with α-aminoacrylic acid (formed from serine by intramolecular elimination of water), with elimination of glyceraldehyde phosphate to form tryptophan *(19)*. The tryptophan synthetase that catalyzes this reaction consists of two components A and B[53–55], and may be regarded as a multienzyme complex[56]. If part B is absent (owing to mutation), the second part of the reaction does not take place. Tryptophan-requiring mutants of this type accumulate indole if starved of tryptophan.

5. Biosynthesis of *p*-Aminobenzoic Acid and Folic Acid

It has been shown with enzyme extracts from yeast that *p*-aminobenzoic acid *(20)* is formed from shikimic acid 5-phosphate *(7)* with glutamine as the nitrogen donor and NAD[57] (see Scheme 7). Later investigations showed that this biosynthesis also proceeds *via* chorismic acid *(9)*[58]. No intermediates have yet been found in the conversion of *(9)* into *(20)*. Genetic studies[58a] and cross-feeding tests on mutants of *Neurospora*[58b] and of *E. coli*[58c] indicate that an intermediate is formed.



Scheme 7. Biosynthetic pathway to tetrahydrofolic acid *(23)*.

p-Aminobenzoic acid is the starting material for the biosynthesis of folic acid. According to studies by *Brown et al.*, the biosynthesis in *E. coli* proceeds as follows: *p*-Aminobenzoic acid is first condensed with 2-amino-4-hydroxy-6-hydroxymethyl-7,8-dihydropteridine *(21a)* in the presence of ATP to give dihydropteroic

[51] *F. Lingens* and *W. Goebel*, Biochim. biophysica Acta *107*, 183 (1965); *148*, 70 (1967).

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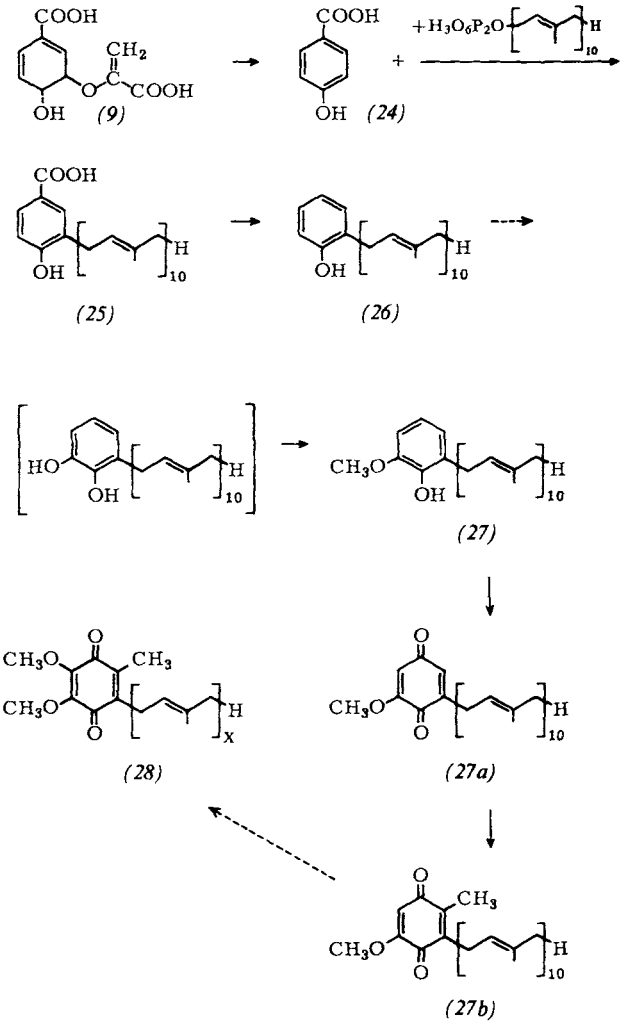
[58b] *S. Hendler* and *P. R. Srinivasan*, Biochim. biophysica Acta *141*, 656 (1967).

[58c] *F. Lingens* and *K. H. Altendorf*, unpublished.

acid *(21)*; *(21)* then reacts with glutamic acid to form dihydrofolic acid *(22)*, which is finally reduced to the biologically active tetrahydrofolic acid *(23)* [59].

6. Biosynthesis of *p*-Hydroxybenzoic Acid and of Ubiquinone

p-Hydroxybenzoic acid *(24)* is formed both enzymatically and spontaneously from chorismic acid *(9)* (see Scheme 8).



Scheme 8. Biosynthetic pathway to ubiquinone *(28)*. In yeast ubiquinone x = 6.

It has been shown in enzyme experiments that for *E. coli*, ^{14}C-shikimic acid is incorporated into ubiquinone. The degree of incorporation is decreased by the addition of *(24)* [60]. This shows that the biosynthesis of ubiquinone can proceed *via* *p*-hydroxybenzoic acid. It has been found with enzyme extracts from *Rhodospirillum rubrum* that *(24)* reacts first with decaprenyl pyrophosphate to form 3-decaprenyl-4-hydroxybenzoic acid *(25)*, which is then decarboxylated to give 2-decaprenylphenol *(26)* [61].

2-Decaprenyl-6-methoxyphenol *(27)* has been isolated as another intermediate in the synthesis of ubiquinone in *Rhodospirillum rubrum* [62,63]. The 3-decaprenylpyrocatechol postulated as an intermediate in the transition from *(26)* to *(27)* has not yet been detected. Other intermediates [*(27a)* and *(27b)*] of the biosynthesis of ubiquinone have recently been detected [63a].

In the discussion of the formation of ubiquinone, it must be borne in mind that *p*-hydroxybenzoic acid *(24)* can be formed, not only from chorismic acid *(9)*, but also from tyrosine. It has been assumed that *(24)* is converted into *p*-hydroxybenzaldehyde, which can also be formed from *p*-hydroxyphenylpyruvic acid by a nonenzymatic reaction. *p*-Hydroxybenzaldehyde is thought to be the starting material both for the quinone ring of ubiquinone and for *p*-hydroxybenzyl alcohol. It should be mentioned that mammals can also synthesize tetrahydrofolic acid *(23)*. The necessary *p*-hydroxybenzoic acid is presumably produced *e.g.* by rats from tyrosine, since there is no chorismic acid available [64]. It is interesting to observe that the protozoon *Tetrahymena pyriformis* can form the benzoquinone ring of ubiquinone from shikimic acid, whereas this organism lacks the enzymes for the synthesis of tryptophan and phenylalanine [65].

7. Biosynthesis of Vitamin K [*]

Davis observed that polyauxotrophic mutants of *E. coli* that depend on the simultaneous supply of phenylalanine, tyrosine, tryptophan, *p*-aminobenzoic acid, and *p*-hydroxybenzoic acid grow better when an unknown sixth factor, which is present in the usual whole medium for bacteria, is also added [66]. This factor is probably a compound that can be converted into vitamin K. It is known from investigations by *Cox* and *Gibson* that vitamin K is formed by the sixth biosynthetic pathway. ^{14}C-Shikimic acid is converted into ^{14}C-vitamin K; the radioactivity in vitamin K could not be reduced by the addition of *p*-hydroxybenzoic acid. In experiments with other substances, 3,4-dihydroxybenzaldehyde and adrenaline were found to be effective [67]. However, it cannot be concluded from this that the two compounds are true intermediates of the biosynthetic chain. *Leistner*, *Schmitt*, and *Zenk* [67a] detected α-naphthol *(29)* as a precursor of vitamin

[59] *G. M. Brown*, *R. A. Weisman*, and *D. A. Molnar*, J. biol. Chemistry *236*, 2534 (1961).

[60] *G. B. Cox* and *F. Gibson*, Biochim. biophysica Acta *93*, 204 (1964); Biochem. J. *100*, 1 (1966).

[61] *R. K. Olsen*, *J. L. Smith*, *G. D. Daves jr.*, *H. W. Moore*, *K. Folkers*, *W. W. Parson*, and *H. Rudney*, J. Amer. chem. Soc. *87*, 2298 (1965).

[62] *R. K. Olsen*, *G. D. Daves jr.*, *H. W. Moore*, *K. Folkers*, and *H. Rudney*, J. Amer. chem. Soc. *88*, 2346 (1966).

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[*] "Vitamin K" here refers to vitamin K_1 and/or K_2.

[66] *B. D. Davis*, J. Bakteriol. *64*, 729 (1952).

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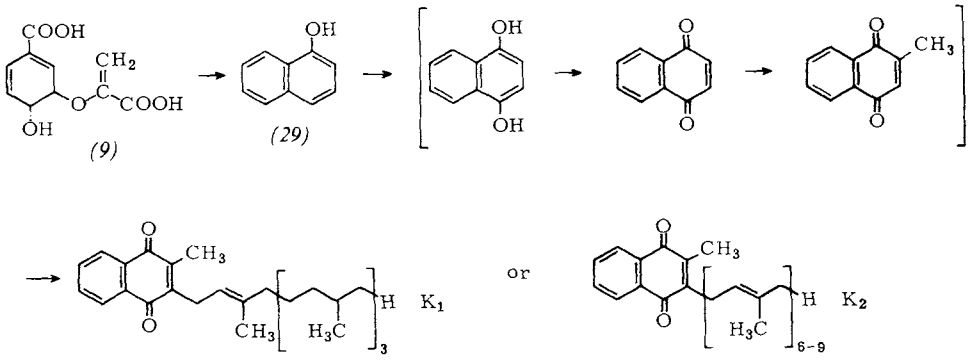


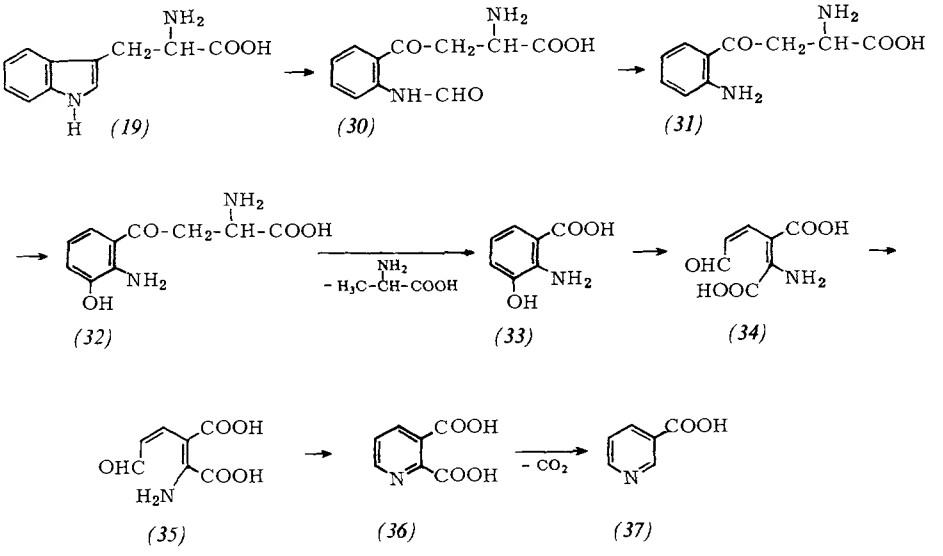
Scheme 9. Biosynthetic pathway to vitamin K.

K_2; these authors postulated other intermediates of the biosynthetic pathway (see Scheme 9).

Davis showed earlier that the sixth factor of the medium could be replaced by pyrocatechol derivatives [68]. *Martius* and *Leuzinger* found that the vitamin K-heterotrophic anaerobic bacterium *Fusiformis nigrescens* converts 1,4-naphthoquinone into 2-methylnaphthoquinone and thence into vitamin $K_{2(45)}$, *i.e.* a vitamin K_2 with 45 C atoms in the side chain. Methionine acts as a methyl donor, but active formate and the β-carbon atom of serine do not [69].

8. Biosynthesis of Nicotinic Acid

The biosynthesis of nicotinic acid is related to the biosynthesis of aromatic amino acids, since the starting material for this synthesis in many organisms is tryptophan [70]. There is also at least one other route, which does not start with aromatic compounds. Some mammals, including man, can synthesize nicotinic acid from tryptophan, so that the definition of a vitamin is not strictly satisfied in this case. The same biosynthetic pathway is followed by fungi, yeasts, and certain phycomycetes [71–73]. In the first step, tryptophan *(19)* is converted into formylkynurenine *(30)*, from which kynurenine *(31)* is formed by cleavage with a formylkynurenine amidase [74]; *(31)* is finally hydroxylated to give 3-hydroxykynurenine *(32)* (see Scheme 10). This is cleaved by kynureninase into 3-hydroxyanthranilic acid *(33)* and alanine [75]. Ring cleavage in 3-hydroxyanthranilic acid *(33)* by a 3-hydroxyanthranilate oxygenase gives 2-amino-3-formylvinylfumaric acid



Scheme 10. Biosynthetic pathway to nicotinic acid *(37)*.

(34) [76, 77]. This compound must be isomerized into 2-amino-3-formylvinylmaleic acid *(35)* before ring closure can take place to give the pyridine system. Quinolinic acid *(36)* is formed, and decarboxylation of *(36)* yields nicotinic acid *(37)*.

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[69] *C. Martius* and *W. Leuzinger*, Biochem. Z. *340*, 304 (1964).

[70] *D. M. Bonner* and *C. Yanofsky*, J. Nutrition *44*, 603 (1951).

[71] *F. Lingens* and *O. Oltmanns*, Z. Naturforsch. *19b*, 1058 (1964).

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[74] *W. B. Jakoby*, J. biol. Chemistry *207*, 657 (1954).

[75] *W. B. Jakoby* and *D. M. Bonner*, J. biol. Chemistry *205*, 699 (1953).

[76] *O. Wiss*, *H. Simmer*, and *H. Peters*, Hoppe-Seylers Z. physiol. Chem. *304*, 221 (1956).

[77] *E. Kuss*, Hoppe-Seylers Z. physiol. Chem. *345*, 195 (1966).

[78] *C. O. Stevens* and *L. M. Henderson*, J. biol. Chemistry *234*, 1188 (1959).

[79] *R. A. Mitchell*, *H. H. Kaug*, and *L. M. Henderson*, J. biol. Chemistry *238*, 1151 (1963).

The 3-hydroxyanthranilate oxygenase was first detected in the liver [78,79]. This enzyme has recently also been detected in *Saccharomyces cerevisiae* [80].

Some authors think it possible that the ring closure is preceded by the decarboxylation, so that the synthesis does not proceed *via* quinolinic acid. However, quinolinic acid exhibits good growth activity for nicotinic acid-deficient mutants of *S. cerevisiae* [71].

Another route for the biosynthesis of nicotinic acid requires aspartic acid and a C_3 compound such as glycerol or glyceraldehyde phosphate as starting materials [81–83]. This route is used with few exceptions by bacteria, as well as by cyanophyceae, green algae, some phycomycetes, and higher plants. It is interesting in this connection to note that the biosynthesis of lysine can also proceed by two routes, *i.e. via* α-aminoadipic acid or *via* α,ε-diaminopimelic acid. A comparison of the results showed that microorganisms that form lysine *via* α-aminoadipic acid synthesize nicotinic acid from tryptophan. When the biosynthesis of lysine proceeds by the α,ε-diaminopimelic acid route, nicotinic acid is generally not formed from tryptophan [73].

9. Regulation of the Biosynthesis of Aromatic Amino Acids

The aromatic amino acids regulate their own biosynthetic pathways by allosteric inhibition, and sometimes also activation, of the following enzymes: 2-keto-3-deoxyarabinoheptonic acid 7-phosphate (DAHP synthetase) [*(1)* + *(2)* → *(3)*], chorismate mutase [*(9)* → *(10)*], prephenate dehydrogenase [*(10)* → *(13)*], prephenate dehydratase [*(10)* → *(11)*], anthranilate synthetase [*(9)* → *(15)*], and *p*-aminobenzoate synthetase [*(9)* → *(20)*] (See Scheme 11).

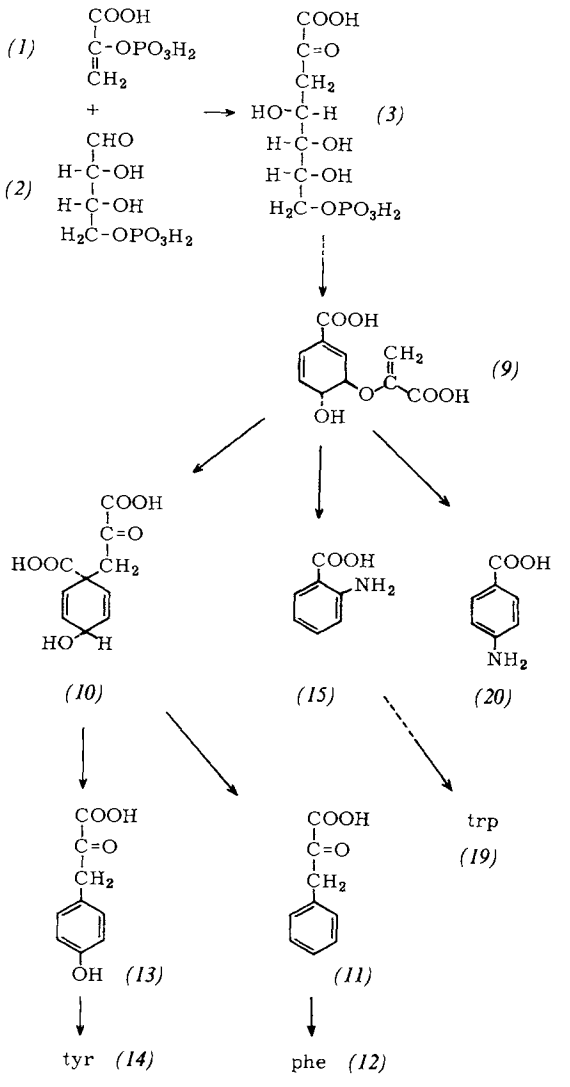
It has not yet been established how the biosynthesis of the vitamins derived from this branched synthetic chain is regulated.

Enzymes whose activities are subject to regulation are allosteric proteins. According to *Monod, Wyman*, and *Changeux* [84], these are oligomers of identical subunits, which are linked by noncovalent bonds. Each subunit has stereospecific sites for the substrate and other ligands (effectors). The oligomer (allosteric protein) occurs in the energetically different states R and T, which are in equilibrium with each other and which differ in the quaternary structure of the protein. The ligands have different affinities for the R and T states, the equilibrium between the two states depending on the concentration of the ligands. This model occurs in two forms:

1. The K system: The effectors and the substrate have different affinities for the R and T states. The effector thus influences the affinity of the enzyme protein for the substrate, and the substrate influences the affinity of the protein for the effector.

2. The V system: In this case the substrate has the same affinity for both states. Consequently the addition of the substrate is not influenced by the effector and *vice versa*. However, the two states differ in their catalytic activity, so that an effector that displaces the equilibrium in favor of the state with the lower catalytic activity inhibits the enzyme.

The investigation of the enzymes for the biosynthesis of aromatic amino acids in microorganisms has not yet progressed to the point where an assignment to these systems can be made in every case. In addition to the allosteric control of the enzymes present, regulation can also be achieved by repression and induction of the biosynthesis of all the enzymes.



Scheme 11. Regulation of the biosynthesis of aromatic amino acids.

Table 1. Inhibiting action of L-phenylalanine and L-tyrosine on enzymes from *A. aerogenes*.

Amino acid added	Inhibition of			
	Chorismate mutase		Prephenate dehydratase	Prephenate dehydrogenase
	P (%)	T (%)	(%)	(%)
L-phe (5×10^{-3} M)	65	4		
(1×10^{-3} M)			100	14
L-tyr (5×10^{-3} M)	16	2	44	
(1×10^{-3} M)				91

[80] *F. Lingens* and *H.-D. Heilmann*, Naturwissenschaften *54*, 369 (1967); *H.-D. Heilmann* and *F. Lingens*, Hoppe-Seylers Z. physiol. Chem. *349*, 223 (1968).

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[83] *M. V. Ortega* and *G. M. Brown*, J. biol. Chemistry *235*, 2939 (1960).

[84] *J. Monod, J. Wyman*, and *J. P. Changeux*, J. molecular Biol. *12*, 88 (1965).

In *Escherichia coli*, the first enzyme in the main chain, DAHP synthetase, consists of three isozymes, one of which is allosterically inhibited and repressed by L-phenylalanine and the other by L-tyrosine. The third enzyme is not subject to allosteric inhibition, but is repressed by L-tryptophan [85–91].

The conversion of chorismic acid *(9)* into prephenic acid *(10)* in *E. coli* and *Aerobacter aerogenes* is catalyzed by two isozymes. Each of these chorismate mutases is combined in a complex with the enzymes prephenate dehydrogenase and prephenate dehydratase, both of which are also inhibited by the end products [92]. Table 1 shows the values of the allosteric inhibition in *A. aerogenes*. The chorismate mutase P and the prephenate dehydratase are incompletely repressed by L-phenylalanine. L-Tyrosine represses one of the two isozymes and the prephenate dehydrogenase.

The enzymes of the tryptophan biosynthesis in *E. coli* and *A. aerogenes* are coordinately repressed by L-tryptophan, and the anthranilate synthetase is completely inhibited [93–95].

Jensen and *Nester* [96–99] have found that in *Bacillus subtilis*, the first step in the main branch is allosterically inhibited by prephenic acid and by chorismic acid, but not by the final amino acids. There is only one DAHP synthetase. The chorismate mutase is not inhibited either by L-tyrosine or by L-phenylalanine; however, these amino acids inhibit the prephenate dehydrogenase and dehydratase. The prephenic acid that accumulates as a result of this inhibition can inhibit the DAHP synthetase. L-Tryptophan acts as a negative effector on the anthranilate synthetase; this can lead to an accumulation of chorismic acid, which also inhibits the DAHP synthetase, though to a smaller extent. L-Phenylalanine, L-tyrosine, and L-tryptophan cause repression of the DAHP synthetase.

A peculiarity is found in the regulation of the biosynthesis of tryptophan in *Pseudomonas putida* [100]. The last enzyme in the chain, the tryptophan synthetase, is induced by its substrate 3-(indol-3-yl)-glycerol-1-phosphate. This enzyme is not affected by L-tryptophan, whereas the other enzymes of the pathway are repressed by this amino acid.

Investigations on *Saccharomyces cerevisiae* have shown [101,102] that L-tyrosine causes allosteric inhibition of the tyrosine-sensitive isozyme of the DAHP synthetase, the chorismate mutase, and the prephenate dehydrogenase. An excess of L-tyrosine in *S. cerevisiae* can be eliminated by induction of degradation to tyrosol. L-Phenylalanine at high concentrations causes inhibition of the phenylalanine-sensitive isozyme of the DAHP synthetase and of the prephenate dehydratase. The biosynthesis of the prephenate dehydratase is also repressed by L-phenylalanine. It is reasonable that an excess of L-phenylalanine should at the same time cause both induction and activation of the prephenate dehydrogenase. The degradation of L-phenylalanine in *S. cerevisiae*, which can serve to eliminate an excess of this amino acid, leads to β-phenylethanol.

It can be shown that L-tryptophan inhibits the first enzyme in its biosynthetic chain, *i.e.* the anthranilate synthetase; the synthesis of this enzyme is repressed by L-tryptophan, which, at the same time causes an increase in the rate of synthesis in another branch of the biosynthetic chain by induction and activation of chorismate mutase. L-Tryptophan is also degraded in *S. cerevisiae*, the product being tryptophol. Simultaneous addition of excesses of L-tryptosine, L-phenylalanine, and L-tryptophan leads not only to the phenomena described, but also to multivalent induction of the *p*-aminobenzoate synthetase, with a consequent release of *p*-aminobenzoic acid into the medium.

Further investigation of the enzymes affected by regulation show that these are allosteric proteins. The two DAHP synthetases, which are inhibited by L-tyrosine and by L-phenylalanine respectively, belong to the V system, while chorismate mutase and prephenate dehydrogenase belong to the K system [102].

The chorismate mutase of *Neurospora crassa* also belongs to the K system of allosteric enzymes, and is activated by L-tryptophan and inhibited by L-tyrosine and by L-phenylalanine. The anthranilate synthetase of *Neurospora* can also be inhibited by L-tryptophan [103]. In a study of the regulation of the biosynthesis of aromatic compounds in *Claviceps paspali*, it was found that an alkaloid-producing strain has an anthranilate synthetase that is not allosterically inhibited by L-tryptophan [104,105]. This evidently ensures that L-tryptophan is produced in sufficient quantities for the syn-

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[86] *K. D. Brown* and *C. H. Doy*, Biochim. biophysica Acta *77*, 170 (1963).

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[88] *C. H. Doy* and *K. D. Brown*, Biochim. biophysica Acta *104*, 377 (1965).

[89] *D. H. Ezekiel*, Biochim. biophysica Acta *95*, 54 (1965).

[90] *C. H. Doy* and *K. D. Brown*, Biochim. biophysica Acta *118*, 157 (1966).

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[92] *R. G. H. Cotton* and *F. Gibson*, Biochim. biophysica Acta *100*, 76 (1965).

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thesis of the alkaloid. *Claviceps paspali* contains three DAHP synthetases, which are inhibited by L-phenylalanine, L-tyrosine, and L-tryptophan respectively. (The tryptophan-sensitive isozyme accounts for most (60 %) of the total activity.) The chorismate mutase, which again belongs to the K system, is inhibited both by L-tyrosine and by L-phenylalanine. This inhibition is eliminated by L-tryptophan, which thus acts as a positive effector. Some tryptophan-like compounds can also activate the chorismate mutase; the latter can be resolved into two isozymes, but only after substantial concentration [106]. The prephenate dehydratase is allosterically inhibited by L-phenylalanine and the prephenate dehydrogenase by L-tyrosine.

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Ternary Nitrides, Phosphides, and Arsenides of Lithium

BY R. JUZA, K. LANGER, AND K. VON BENDA[*]

Ternary phases have been prepared from lithium, another metal, and nitrogen, phosphorus, or arsenic. The ternary compounds, in particular the nitrides, are thermally more stable than the binary compounds. The lithium gives rise to a relatively high polar bonding component. At high temperatures, lithium and the second metal are often randomly distributed among the interstices of the metalloid lattice. The ordering processes that take place with decreasing temperature are investigated by X-ray and magnetic methods and by differential thermal analysis. The phases are classified on a structural basis into seven groups.

1. Introduction

Ternary compounds of lithium with a metal (M) (usually of the first long period) and with nitrogen, phosphorus, or arsenic (X) in various combinations have been prepared and studied. Though work in this field is by no means closed, it has already been found that these compounds can be classified on a crystallochemical basis into a few groups of widely differing natures.

The choice of lithium as the invariable component was decided at the beginning of the experiments by the following considerations:

The strongly electropositive lithium has a low ionization potential, and its compounds are relatively strongly polar. The polar bonding component in Li_3N or Li_3P is greater than in *e.g.* AlN or AlP, or in fact than in any transition metal nitride or phosphide. Thus as we pass from a binary compound of a metal with an element of the nitrogen group to a ternary compound of the same metal containing lithium, the polar bonding component should increase.

The incorporation of lithium was also expected to have special structural consequences. It was known from investigations on $LiFeO_2$ [1] and Li_2TiO_3 [2] that even relatively highly charged ions can be randomly distributed together with lithium ions over the same special position – in this case of the NaCl lattice. This interchangeability despite the large difference in charge is due to the fact that the sizes of the Li ion and of the M^{n+} ions are approximately the same. However, the random distribution of the metals is stable only at high temperatures, and is retained in a metastable state on quenching of the ternary oxides; in the structures that are stable at low temperatures, Li^+ and Fe^{3+} or Ti^{4+} are distributed in a regular manner [3–5].

The single reported observation of a ternary nitride containing lithium – Li_3FeN_2 [6] – was important for

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our present investigation of the chemistry of the metal nitrides. We expected to be able to extend our knowledge of the chemistry of metal nitrogen compounds to the ternary nitrides containing lithium.

Three methods have been used for the *preparation* of ternary *nitrides* of lithium and a second metal (M):

1) nitriding of a mixture of Li_3N + M with N_2 or NH_3;

2) nitriding of an alloy Li_mM;

3) reaction of the binary nitrides Li_3N + M_nN in an atmosphere of N_2.

The reactions were carried out either in a stream of the gas or in a closed vessel, which generally allowed volumetric measurement of the nitrogen absorption. The last method proved particularly useful when the formation of the ternary nitride gave a higher oxidation state of M than that in the binary metal nitride. It was also found useful in some cases to increase the pressure (*e.g.* to 200 atm).

The ternary *phosphides* were prepared from Li_3P with metal and phosphorus or with the metal phosphide (sometimes with addition of phosphorus), and the ternary *arsenides* from Li_3As, metal, and arsenic.

It was often difficult to find a suitable container material for the preparative work. The binary Li compounds are extremely reactive; for example, Li_3N reacts with quartz glass or ceramic materials. On the other hand, phosphorus and arsenic react with metal vessels at high temperatures. Copper or molybdenum vessels were found to be suitable for the preparation of ternary nitrides, and sintered alumina crucibles for the preparation of phosphides or arsenides.

Nearly all the Li compounds investigated are very sensitive to hydrolysis. A technique was developed, therefore, which made possible the preparation and investigation of samples in total absence of moisture and oxygen; all work was carried out under carefully dried protective gas (N_2, Ar).

2. Phases that Can Be Derived from a Binary Lithium Compound

2.1. Phases $(Li,M)_2X$ Derived from the CaF_2 Type

The lithium chalcogenides crystallize in the antifluorite lattice (C1 type). This same lattice or a superstructure of the antifluorite type also occurs in the ternary lithium compounds discussed below, in which the chalcogen is replaced by elements of group V (X = N, P, As). The change in the charge on the nonmetal from −2 to −3 is compensated for by cations of higher charge (M^{n+}) in the cation lattice, assuming that the substance has an electrovalent structure. Compounds of this type have the general formula $Li_{2n-3}M^nX_{n-1}$ (Table 1).

Table 1. Compounds $(Li,M)_2X$ derived from the CaF_2 type. Z = number of formula units in the unit cell, V_M = molar volume.

Compound	Color	Lattice constants (Å)			Z	V_M (cm^{-3})	Distribution Li—M	Ref.
		a	b	c				
LiMgN	Bright red-brown	4.97			4	18.5	statistical	[7]
LiMgP	Brown	6.02			4	32.9	statistical	[9]
LiMgAs	—	6.21			4	36.0	statistical	[10]
LiMgAs	Black	6.05			4	33.3	statistical > 500 °C	[11]
LiZnN	Black	4.88			4	17.5	ordered	[7]
LiZnP	Brown	5.78			4	29.1	ordered	[9]
LiZnAs	Black	5.92			4	31.3	ordered	[9]
Li_3AlN_2	Light gray	9.46			32/2	15.9	ordered	[12]
Li_3AlP_2	Ocher to red-brown	11.47	11.61	11.73	32/2	29.4	ordered	[14]
Li_3AlAs_2	Red-brown to brown	11.87	11.98	12.11	32/2	32.4	ordered	[14]
Li_3GaN_2	Light gray	9.59			32/2	16.6	ordered	[12]
Li_3GaP_2	Brown	11.87			32/2	31.5	ordered	[13]
Li_3GaAs_2	Black	11.96		12.15	32/2	32.7	ordered	[13]
Li_5GeN_3	Yellow-brown	9.61			32/3	16.7	ordered	[15]
Li_5TiN_3	Yellow	9.70			32/3	17.2	ordered	[15]
Li_7VN_4	Gray	9.60			32/4	16.6	ordered	[16, 18]
Li_7MnN_4	Black	9.57			32/4	16.5	ordered	[16]
Li_9CrN_5	Dark brown	—	—	—	—	—	—	[17]

2.1.1. Random Distribution of Metal Atoms

Figure 1 shows the face-centered cubic arrangement of the X atoms in the unit cell of the antifluorite structure, with the tetrahedral and octahedral lattice sites. (The tetrahedral and octahedral coordination are each indicated for one point.) The ternary compounds have a pure antifluorite structure when both metals randomly occupy the "tetrahedral positions" 1–8, while the "octahedral positions" remain unoccupied.

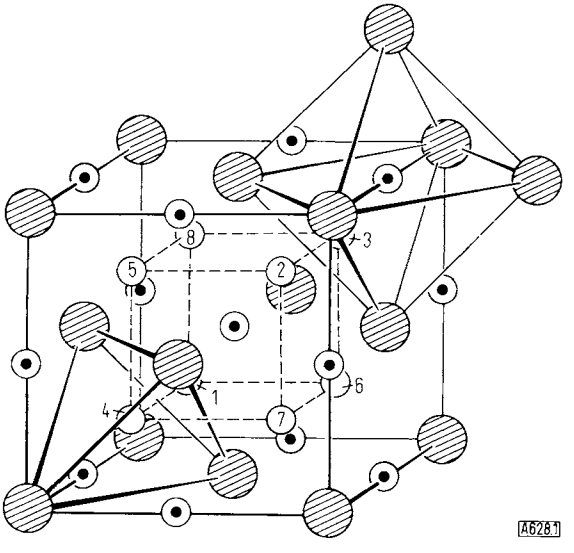

Fig. 1. Unit cell of a face-centered cubic X lattice with the following sites ● = X atoms, ①—⑧ = tetrahedral sites, ⊙ = octahedral sites.

This is the case in LiMgN [7]. This compound is bright red-brown, and when heated to 1100 °C, it decomposes without melting and with volatilization of Li and N_2. Both the color and the decomposition without melting indicate a high ionic bonding component. Estimation by *Pauling*'s method [8] gives 63 % ionic character for an LiN single bond and 55 % for an MgN single bond, *i.e.* the values are roughly the same. The polar component is only slightly lower than in an MgO single bond (73 %). Since the ionic radii of Li^+ and Mg^{2+} are also approximately equal (0.68 Å and 0.66 Å, according to *Ahrens*), the conditions are particularly favorable for a random distribution of the metals. LiMgP [9] and LiMgAs [10] also belong to the pure antifluorite type. However, it is not known in any of these three cases whether the random distribution of the metals is the arrangement that is stable at room temperature.

This series also includes the high-temperature form of the phase LiMnAs [11]. However, the random distribution of lithium and manganese is stable only at temperatures above 500 °C and does not persist on quenching even as a metastable state (cf. Section 2.2.). No other ternary compounds having the composition LiMX and having the pure antifluorite structure are known as yet.

2.1.2. Ordered Distribution of Metal Atoms

In the analogous zinc compound LiZnN [7], the metals are distributed in a regular arrangement. Zinc occupies the tetrahedral positions 1, 3, 5, and 7, and lithium the positions 2, 4, 6, and 8 (Fig. 1). The space symmetry O_h^5 of the lattice with random occupation of the tetrahedral sites is decreased to T_d^2. The zinc and the nitrogen form a zinc blende lattice, and lithium is inserted into the interstices to neutralize the charge. The same is true of LiZnP and LiZnAs [9]. These substances are much more closely packed than the magnesium compounds containing the same element X, though for equal ionic bonding components less dense structures are to be expected because of the greater radius of Zn^{2+}. This closer packing and the deeper color (LiZnN is black) reflect a lower polarity in the zinc compounds.

The structures of the compounds listed in the third section of Table 1 are also closely related to the antifluorite type. The tetrahedral sites in the metalloid lattice which is in principle always cubic close packed, are also occupied in a regular manner. However, since there is less than one M atom per X atom, a highly symmetrical M distribution is possible only on multiplication of the unit cell. Figure 2a shows the distribution of Al in the unit cell of the Li_3AlN_2 structure (space group T_h^7) [12]. The face-centering N atoms of the eight unit cells and the Al atoms are displaced from the ideal positions in such a way that the Al–N distances are about 12 % smaller than the distances from the N atoms to the other tetrahedral sites, in which the lithium is situated. Li_3GaN_2 [12] and Li_3GaP_2 [13] have isotypic crystal structures. In Li_3GaAs_2 [13] there is slight tetragonal distortion, and in Li_3AlP_2 and Li_3AlAs_2 [14] slight orthorhombic distortion of this structure (Table 1).

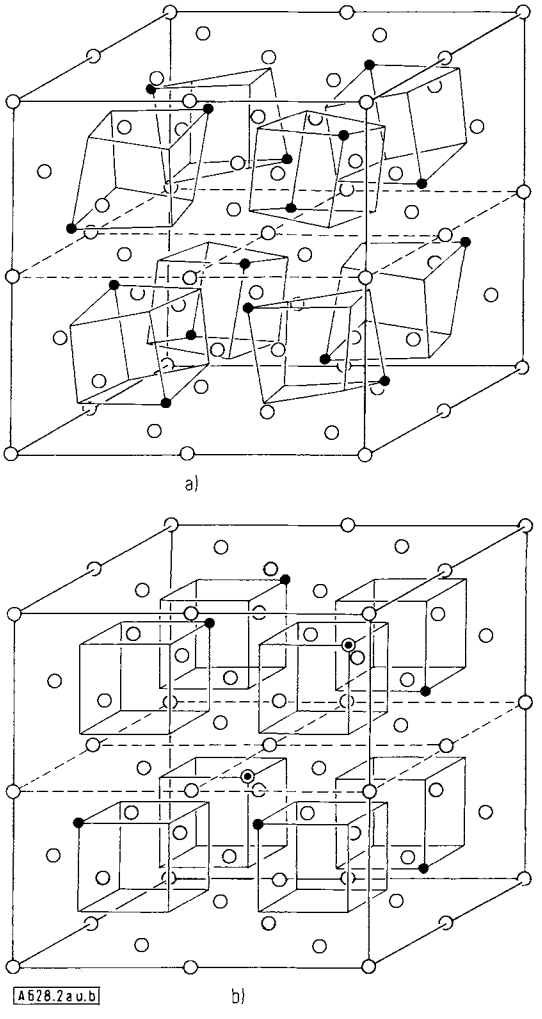

Fig. 2. Distribution of aluminum and vanadium in the structures of Li_3AlN_2 and Li_7VN_4 (lithium occupies the free corners of the "cubes" situated in the octants). a) Li_3AlN_2; O = nitrogen, ● = aluminum. b) Li_7VN_4; O = nitrogen (in the ideal position), ◎ = vanadium in sixfold position, ⊙ = vanadium in twofold position.

Volume considerations as used by *W. Biltz* were frequently found to be useful in the present investigations. For example, Figure 3 shows a plot of the molar volumes of some nitrides, phosphides, and arsenides against the molar volumes of a series of isotypic aluminum compounds (the change from the wurtzite to the zinc blende structure between AlN and AlP has no volume-chemical effect). A deviation from

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linearity points to a change in structure. Li_3AlN_2, Li_3AlP_2, and Li_3AlAs_2 are found to be isotypic. Among the binary lithium compounds, Li_3P, Li_3As, and the high-temperature modification of Li_3Sb are isotypic and crystallize hexagonally in the Na_3As structure (Section 2.4.). Li_3N is much less dense, but its looser packing is lost on formation of the ternary compound Li_3AlN_2.

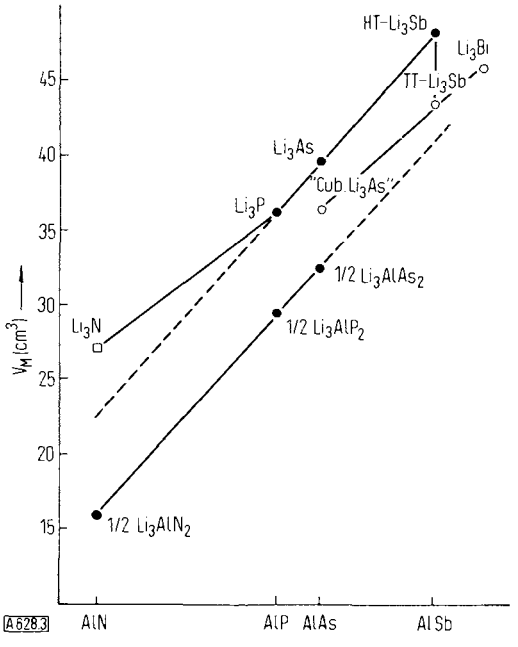

Fig. 3. Molar volumes of Li_3AlX_2 and Li_3X compounds.

The superstructures of the cubic Li_5TiN_3 and Li_5GeN_3 [15] can also be assigned to the Li_3AlN_2 structural type on the basis of intensity calculations if a random distribution of 0.67 M and 0.33 Li over the Al positions shown in Fig. 2a is assumed [15].

Figure 2b shows the distribution of the metals in the structure of the isotypic compounds Li_7VN_4 and Li_7MnN_4, which have cubic structures of space group T_d^4 [16]. For better comparison with the Al compound, the origin was placed in $\frac{111}{888}$ of the actual unit cell in the space group T_d^4. Vanadium occupies one twofold position and one sixfold position; the vanadium ions of the sixfold position form chains with lithium parallel to the three crystallographic axes.

In this connection mention should also be made of Li_9CrN_5 [17] which has been prepared by various methods (preferably from Li_3N and CrN under nitrogen at 240 atm and 600–800 °C). The structure has not yet been established but this compound again appears to have a superstructure of the antifluorite type, since it forms an unbroken series of solid solutions with Li_2O, in which the lattice constant decreases and the superstructure lines disappear as the Li_2O content increases.

The heavier metals of the group V (niobium and tantalum) and group VI (molybdenum and tungsten) triads also give ternary nitrides in which the metals have oxidation states of +5 and +6 respectively [17, 18]. The thermal stability increases with increasing atomic number, while the depth of color decreases, as in the oxygen compounds. The compounds are probably isotypic with one another, but not with Li_7VN_4 and Li_9CrN_5.

It is interesting to note that in the ternary nitrides of the transition metals of groups IV to VII, the metals have a very much *higher oxidation state* in relation to nitrogen than in the binary compounds having highest nitrogen contents, *i.e.* TiN, VN, CrN, and Mn_3N_2 (the high oxidation states were verified by measurement of the nitrogen absorption during the reaction, by redox titration, and by total analysis). In the Li–Cr–N system, CrN actually reacts with Li_3N under argon to form Cr_2N and Li_9CrN_5 [17]; thus the partial pressure of nitrogen over the ternary compound of chromium in the oxidation state +6 is lower than over CrN.

One might have expected that highly charged M ions (V^{5+}, Mn^{5+}) would give distinctly *anionic structural groups* comparable to the VO_4^{3-} groups of the orthovanadates. This is not so, since the resulting structures would then have been much more complicated and not so closely related to the antifluorite type. On the other hand MN_4 tetrahedra in the superstructures of the compound with M = Al, Ga, Ti, V, and Mn already differ appreciably from LiN_4 tetrahedra. This can be seen even in the Al compounds in which the AlN_4 tetrahedra are much more closely packed than the LiN_4 tetrahedra. In the case of the vanadium compounds, the parameters are not yet known with sufficient accuracy to yield any detailed information. These compounds probably occupy an intermediate position between pronouncedly complex compounds and pure atom-ion lattices. Moreover, the high negative charge of the supposed complex and the large number of cations would scarcely be paralleled anywhere else.

Some information about the nature of the bonds between the transition metal and the nitrogen would be desirable in this connection. The transition metal and the lithium are practically equivalent in the structure; the percentage of transition metal ions *e.g.* in Li_7VN_4 is low. On the basis of the electronegativities the predominating LiN bonds are strongly polarized. The polarity of the VN bond, or of the transition metal-nitrogen bond in general, cannot be estimated at present.

2.2. Phases (Li, M, □)$_3$X Derived from the Li_3Bi Type

Li_3Bi has a cubic structure of the filled antifluorite type, in which the octahedral sites of the face-centered cubic Bi lattice are occupied as well as the tetrahedral sites 1–8 (Fig. 1). This type also occurs as the low-

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temperature form of Li_3Sb, but has not been observed in Li_3As and Li_3P. However, ternary phases of this cubic type have been found in the systems Li–Mn–As[11], Li–V–As, Li–V–P, Li–Ti–As, and Li–Ti–P[19]; thus this lattice can be stabilized by the replacement of lithium by transition metals. Fig. 4 shows the arsenide phases in a section of the ternary diagram of the Li–M–As system (the thick portions of the lines and the shaded areas indicate the regions of homogeneity).

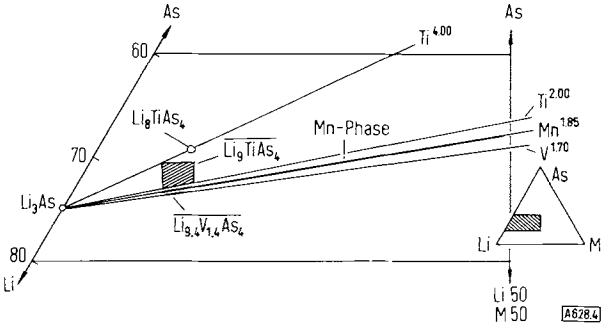

Fig. 4. Ternary cubic phases in the systems Li–Ti–As, Li–V–As, and Li–Mn–As (atom-%).

Since the transition metals M are incorporated in oxidation states higher than +1, vacancies appear in the structure as the M content increases. The phases will therefore be denoted by the formula $(Li,M,\square)_{12}X_4$, taking into account the fact that the unit cells contain four X, or eight times this. As in the compounds discussed in Section 2.1. a random or a regular distribution of Li and M is also possible in the ternary phases of the Li_3Bi type; both have been observed. According to all the investigations carried out so far, the M-atoms always occupy the tetrahedral sites, and disordered distribution between tetrahedral and octahedral sites has never been observed. Another characteristic feature is that at room temperature, the random distribution is stable or metastable only in phases having low M contents and in which the oxidation state of the transition metal is low.

In the ternary system containing *manganese* high-temperature X-ray patterns have established a single-phase range at 530 °C from $(Li_{9.8}\ Mn_{1.2}\square_1)As_4$ to $(Li_{4.6}Mn_4\square_{3.4})As_4$ (Fig. 4). This single-phase range may be regarded as corresponding to a solid solution between LiMnAs, which crystallizes in the antifluorite structure (Section 2.1.), and the hypothetical cubic Li_3As, with the Li_3Bi lattice. The cubic form of the normally hexagonal Li_3As (Section 2.4.) is stabilized by the incorporation of manganese, with simultaneous appearance of vacancies in the cation lattice. The lattice constant of the cubic form of Li_3As (about 6.22 Å) can be extrapolated from Figure 5; Figure 3 shows that this Li_3As modification would be too close-packed, but fits in with the trend of the cubic form of Li_3Sb and Li_3Bi.

In the cubic high-temperature phase $(Li, Mn,\square)_{12}As_4$ the initially randomly distributed Li and M atoms

[19] *K. Langer* and *R. Juza*, Z. anorg. allg. Chem., in press.

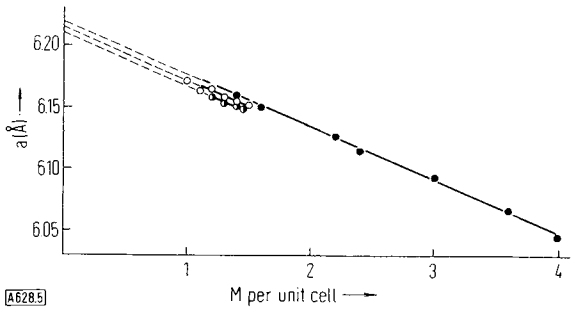

Fig. 5. Lattice constants of the cubic phases (Li, M, $\square)_{12}As_4$.
O M = $Ti^{2.00}$ (800 °C; quenched), ◑ M = $V^{1.70}$ (750 °C; quenched), ● M = $Mn^{1.85}$ (525 °C; high temperature diffraction patterns, recalculated for 20 °C by thermal expansion coefficient).

assume regular arrangements at low temperatures to give four other phases, whose homogeneity ranges are shown in Figure 6 (the diagram was obtained from the results of high-temperature X-ray analysis as well as by investigation of samples that had been tempered to equilibrium at 60 °C; the ordering processes in rapidly cooled samples are too slow at room temperature to reach the equilibrium state).

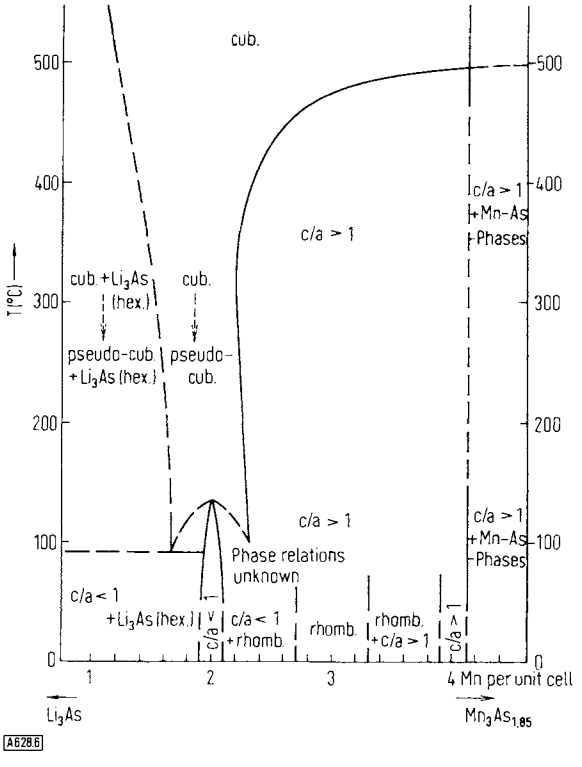

Fig. 6. Subsolidus diagram of the section Li_3As–$Mn_3As_{1.85}$.

This diagram is valid for the pseudobinary section Li_3As–$Mn_3As_{1.85}$. Samples in which the oxidation state of the manganese differs from +1.85 were not obtained in a homogeneous state at 60 °C. This is interesting, since Mn^{2+}, with its half-filled 3d shell, has a relatively stable electron configuration. However, a maximum oxidation number of +1.88 is also found for manganese in the Mg–Mn–As system[20].

The first step in the *ordering process* that occurs with falling temperature, at all Mn contents between 1.6 and 4 Mn per

[20] *R. Juza* and *R. Kroebel*, Z. anorg. allg. Chem. *331*, 187 (1964).

cell, is an accumulation of the Mn in every second layer of tetrahedral sites perpendicular to one of the crystallographic axes *e.g.* in sites 1, 4, 6, and 7 (Fig. 1). The tetrahedral sites 2, 3, 5, and 8 then contain only lithium. Further Li occupy some of the four octahedral sites. The space symmetry O_h^5 for a random distribution decreases to D_{4h}^7.

At *low Mn contents* in the cell (less than 2.2 Mn per 4 As), the lattice dimensions remain the same. The unit cell is still cubic, though the symmetry of the Mn arrangement becomes tetragonal, *i.e.* a "pseudocubic phase" occurs (Fig. 6). For a composition $(Li_{8.3}Mn_2\square_{1.7})As_4$, the state of order of the manganese distribution in the "pseudocubic phase" is not yet optimal. The "pseudocubic phase" changes rapidly at 136 to 140 °C into a "tetragonal phase $c/a < 1$" ($c/a = 0.978$), in which the Mn, according to the intensity calculation, are very probably arranged in chains along the *c* axis, *e.g.* in positions 1 and 4 (Fig. 1). It is found in general that the strongest contraction always takes place in the direction of densest occupation by Mn.

At *higher Mn contents* (more than 2.2 Mn per cell), the lattice contracts in the first step of the rearrangement process to form the "tetragonal phase $c/a > 1$", as a result of the accumulation of Mn in every second layer of tetrahedral sites in the a_1a_2 plane. At the composition $(Li_{4.6}Mn_4\square_{3.4})As_4$, the Mn distribution has achieved its maximum order in the "tetragonal phase $c/a > 1$", since with 4 Mn per cell, every second layer of tetrahedral sites normal to the *c* axis (positions 1, 4, 6, and 7) is fully occupied by Mn.

This is not so for $(Li_{6.45}Mn_3\square_{2.55})As_4$, since in this case 3 Mn and 1 Li are randomly distributed among the positions 1,4,6, and 7 in the "tetragonal phase $c/a > 1$". At low temperatures, therefore, another ordered phase having an orthorhombic unit cell is formed ($a = 5.92_8$ $b = 6.12_9$, $c = 6.20_0$ Å). It has not been fully established how the Mn are arranged in this phase, particularly since a superstructure of the cell mentioned probably occurs.

The three low-temperature phases centered around 4, 3, and 2 Mn per cell are separated at 60 °C by two-phase regions. At less than about 1.9 Mn per cell, hexagonal Li_3As and the ordered phase with 2 Mn per cell occur as phase separation products of the "pseudocubic phase".

Manganese(II) compounds generally have a high *paramagnetic susceptibility* owing to the presence of five unpaired electrons in the half-filled 3d shell. On the other hand, interaction between the spin moments of the Mn ions can lead to antiferromagnetism. MnO is the classic example of the occurrence of antiferromagnetism[21]; below the Néel temperature (127 °K) the paramagnetic susceptibility shows a marked decrease, and the compound passes into the antiferromagnetic state. Neutron diffraction measurements showed that MnO, which crystallizes in the NaCl lattice, then has a magnetic superstructure: it contains two cation sublattices. The spin moments of the Mn^{2+} ions are parallel to one another in one of the cation sublattices, but antiparallel to the spin moments in the second cation sublattice[22].

The ternary Li–Mn–As phases should be paramagnetic, and this paramagnetism should depend on the "*dilution*" of Mn^{2+} ions by diamagnetic ions (Li^+, As^{3-}); an increase in susceptibility was in fact found with increasing dilution[23]. Moreover, the increasing order and the decrease in the Mn–Mn distances with fall in temperature should affect the susceptibility at a given dilution.

The *temperature-dependence* of the susceptibility, and at the same time its dependence on the degree of order of the lattice and on the MnMn distances, will be discussed with the aid of two series of experiments (cf. Fig. 7):

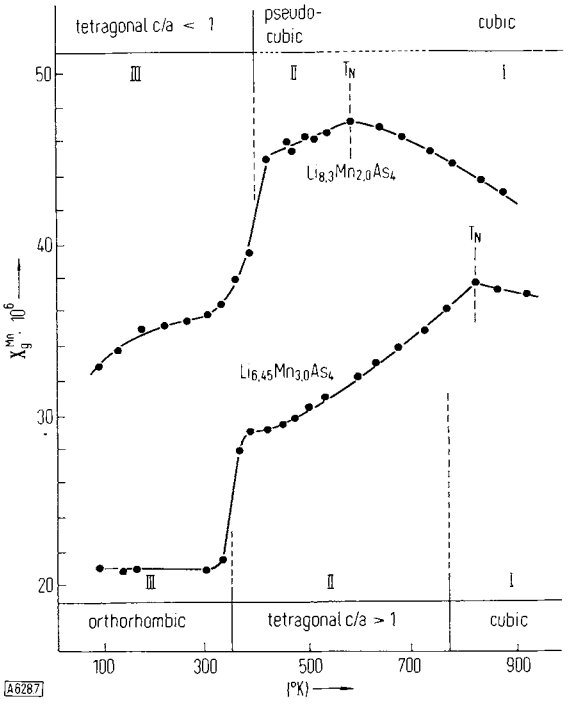

Fig. 7. Gram susceptibility of manganese as a function of temperature for the compositions $(Li_{8.3}Mn_2\square_{1.7})As_4$ and $(Li_{6.45}Mn_3\bullet_{2.55})As_4$.

The cubic high-temperature phase with *low Mn content* $(Li_{8.3}Mn_2\square_{1.7})As_4$ shows the expected increase in magnetic susceptibility with falling temperature at high temperatures in the range of random distribution of Li and Mn; this increase in susceptibility obeys the Curie-Weiss law. The susceptibility found is only about 50 % of the value calculated for free Mn^{2+} ions. The paramagnetic Curie temperature is strongly negative; there is thus spin coupling between the Mn ions. The shortest possible MnMn distance (3.06_5 Å) is only relatively rarely realized, owing to the random distribution of 2 Mn over eight possible positions. When the temperature falls below T_N, the susceptibility decreases. This is the range in which the "pseudocubic phase" with preferential arrangement of the Mn in layers normal to the *c* axis occurs. The shortest possible MnMn distance remains 3.06_5 Å. The point at which the susceptibility begins to decrease has to be regarded as the Néel temperature. A second strong decrease in susceptibility corresponds to the transition into the "tetragonal phase $c/a < 1$" (MnMn distance = 3.02 Å within the Mn chains).

In the phase having a *higher Mn content*, $(Li_{6.45}Mn_3\square_{2.55})As_4$ the region in which the paramagnetism obeys the Curie-Weiss law ends at a higher temperature; the shortest possible MnMn distance, which is 3.04 Å, is somewhat smaller than in the compound having a lower manganese content. An antiferromagnetic phase evidently occurs in the region of the "tetragonal phase $c/a > 1$" (Mn in planes normal to the *c* axis; shortest MnMn distance = 3.01_0 Å). The Néel temperature is about 50 °C higher than the temperature at which the cubic → "tetragonal $c/a > 1$" transition was detected by X-ray methods. This is probably because the change in the lattice dimensions is preceded by a pseudocubic preordering of the Mn (as above at 2 Mn per cell), which was not detected in the X-ray studies. As was mentioned earlier, the antiferro-

[21] *H. Bizette, C. F. Squire,* and *B. Tsai,* C. R. hebd. Séances Acad. Sci. *207,* 449 (1938).

[22] *W. L. Roth,* Physic. Rev. *110,* 1333 (1958).

[23] *R. Juza, H. D. Trapp,* and *H. Seidel,* Z. anorg. allg. Chem., *356,* 273 (1968).

magnetic compound must have two cation sublattices with antiparallel spin directions. However, these can be detected and described only by neutron diffraction studies. A second decrease in susceptibility corresponds to the transition to the orthorhombic phase. The MnMn distance in this phase (2.96 Å) is smaller than in any other phase. The magnetic susceptibility is only about 10 % of the value expected for free Mn^{2+} ions, and is independent of the temperature. The orthorhombic phase probably exhibits a Pauli paramagnetism, which is associated with the occurrence of collective electrons resulting from the small metal-metal distances.

The cubic high-temperature phase discussed at the beginning of this section, with random distribution of lithium and manganese over the tetrahedral sites and more or less complete occupation of the octahedral sites by other lithium atoms, corresponds to a ternary *vanadium phase* [19] (Fig. 4), which is homogeneous for compositions between $(Li_{10}V_{1.2}\square_{0.8})As_4$ and $(Li_{9.6}V_{1.4}\square_1)As_4$ on quenching from 750 °C. This range may be regarded as corresponding to solid solutions of the sample having the highest vanadium content with Li_3As (up to 0.67 mole). The oxidation state of the vanadium is again found to be slightly lower than +2. The increase in the number of lattice vacancies in the $(Li, V, \square)_{12}As_4$ phase, as in the cubic Mn phase, leads to contraction of the lattice. The lattice constants (Fig. 5) exhibit parallelism with those of the cubic manganese phase, and so suggest derivation from the hypothetic cubic Li_3As phase. The ternary $(Li,V,\square)_{12}As_4$ phase corresponds to the ternary phosphide $(Li_{9.8}V_{1.2}\square_1)P_4$, though no variation of composition has been found for the latter. In contrast to the samples having low manganese contents, *e.g.* $(Li_{9.4}Mn_{1.4}\square_{1.2})As_4$, there is no evidence of any slow decomposition of the vanadium phases at room temperature into hexagonal Li_3As or Li_3P and ordered phases having higher vanadium contents. The analogs of the manganese-rich phases are not formed in the systems Li–V–As and Li–V–P, or in the systems Li–Ti–As and Li–Ti–P, which will be discussed subsequently.

The ternary arsenides and phosphides of *titanium* differ from the corresponding phases of manganese and vanadium in that the titanium occurs in these substances in variable oxidation states.

In the Li–Ti–As system, the phase having the cubic unit cell and a random distribution of Li and Ti was found in the shaded region in Figure 4. The tie-line Li_3As–"Ti_3As_2" (Ti has an oxidation number of +2), for which the lattice constants are plotted in Figure 5, in this case forms only the lower limit of the phase range, which widens toward the As corner. This is due to the observed increase in the As content of the phase, which corresponds to an increase in the number of metal vacancies in relation to the unit cell of the structure. The resulting contraction of the cell indicates a continuous increase in the oxidation number from +2 to about +3.5. $(Li_9Ti_1\square_2)As_4$ may be regarded as the characteristic composition of this phase. Moreover, when the oxidation number of Ti is +4, a compound $(Li_8Ti_1\square_3)As_4$ having a superstructure with the eightfold unit cell of the basic structure occurs.

Similar phases have been found in the system Li–Ti–P. The phase having the small unit cell is again centered on the composition $(Li_9Ti_1\square_2)P_4$ with Ti^{III}; the oxidation number of the titanium can vary between +2.5 and +3.5. Solid solutions are not formed with Li_3P. The phase corresponds in this respect to the ternary vanadium phosphide. The phase with Ti^{IV} and the superstructure again has the composition $(Li_8Ti_1\square_3)P_4$.

The ternary titanium arsenides and phosphides occupy a position intermediate between the corresponding phases of vanadium and manganese in the Li_3Bi-type on the one hand and the ternary arsenides and phosphides of the main group metals (*e.g.* Al and Ga) in the antifluorite-type on the other. The maximum oxidation number is reached in the ternary phases of titanium, as in the compounds derived from the antifluorite type; on the other hand, these phases correspond to the phases derived from the Li_3Bi type, owing to the presence of lithium in some of the octahedral sites and owing to the phases with low oxidation numbers.

2.3. Solid Solutions $(Li,M)_3N$ Derived from Li_3N

Cu_3N is endothermic (ΔH = 17.8 kcal) and decomposes rapidly even at 450 °C [24]. The nitrides of nickel and of cobalt are only slightly more stable [25]. However, all three metals absorb nitrogen in a fast reaction in mixtures with Li_3N at 600–700 °C and at a nitrogen pressure of only 1 atm [26]. The nitride formed is stabilized as a solid solution in Li_3N. In the structure of Li_3N [27] (Fig. 8), the nitrogen ions, which predominantly determine the cell dimensions, have a primitive hexagonal arrangement. The compound thus has a relatively bulky structure, as can be seen from its high molar volume (Fig. 3). Lithium occupies a twofold and a onefold position; the latter is characterized by the shortest metal-nitrogen distance.

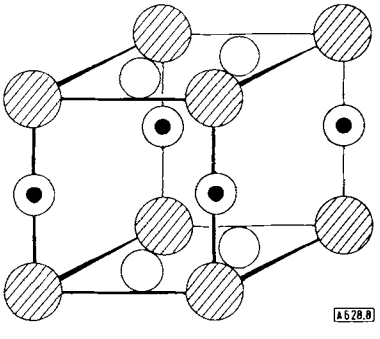

Fig. 8. Unit cell of Li_3N. ● = nitrogen, ○ = lithium in twofold position, □ = lithium in onefold position.

The replacement of lithium by heavy metals (the heavy metals mentioned are randomly substituted for lithium in the onefold position) leads in all three cases to a marked shortening (up to 9 %) of the *c* axis, a slight increase in the *a* axis, and a large decrease in the volume of the unit cell. Solid solutions having maximum heavy metal content are: $(Li_{2.4}Co_{0.5})N$, $(Li_{2.4}Ni_{0.6})N$, and $(Li_{2.7}Cu_{0.3})N$.

[24] *R. Juza* and *H. Hahn*, Z. anorg. allg. Chem. *241*, 172 (1939).

[25] *P. H. Emmet*, *S. B. Hendriks*, and *S. Brunauer*, J. chem. Soc. (London) *52*, 1456 (1930).

[26] *W. Sachse* and *R. Juza*, Z. anorg. allg. Chem. *259*, 278 (1949).

[27] *E. Zintl* and *G. Brauer*, Z. Elektrochem. angew. physik. Chem. *41*, 102 (1935).

Li_3N is the most strongly salt-like of all metal nitrides. Co_3N and Ni_3N are interstitial compounds having predominantly metallic properties. Cu_3N has a coordination lattice with a strongly ionic component. The incorporation of the heavy metals into the host lattice of Li_3N evidently levels the large differences in the character of transition metal-nitrogen bonding in the binary compounds.

2.4. Phases $(Li,M)_3As$ Derived from the Hexagonal Li_3As

It was of interest to know whether the lithium in the hexagonal Li_3As could be replaced by copper in the same way as in Li_3N. In the ternary system Li–Cu–As (Fig. 9), there is a single-phase region above 560 °C, which extends from Li_3As to Li_2CuAs; at room temperature, on the other hand, one finds only Li_3As and Li_2CuAs, with no miscibility of the two phases.

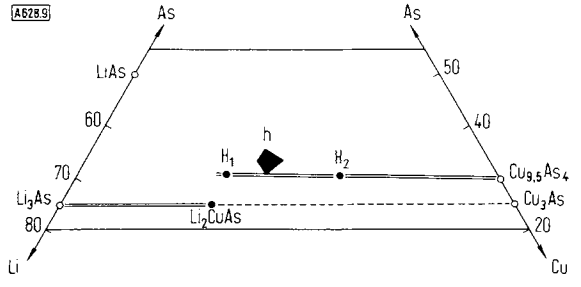

Fig. 9. Ternary phases in the system Li–Cu–As (atom-%). Double line: single phase at 650 °C; shaded points and area: ternary phases at room temperature.

Li_3As crystallizes in the hexagonal Na_3As structure [28] (DO_{18} type, D^4_{6h}; Fig. 10: the triple elementary cell is shown). The arsenic is approximately hexagonal close packed. The lithium occupies fourfold and twofold positions. At 560 °C, the lithium in the twofold position can be progressively replaced by copper. This position is completely occupied by copper at the composition Li_2CuAs. It is interesting to note that the twofold position is situated in the center of an equilateral triangle of arsenic *i.e.* in a triangular site; copper also occurs in triangular sites in other compounds. Moreover, this position has the smallest metal arsenic distance in the lattice. No similar solid solutions or compounds Li_2MAs (M = transition metal) have been found in the systems examined by us.

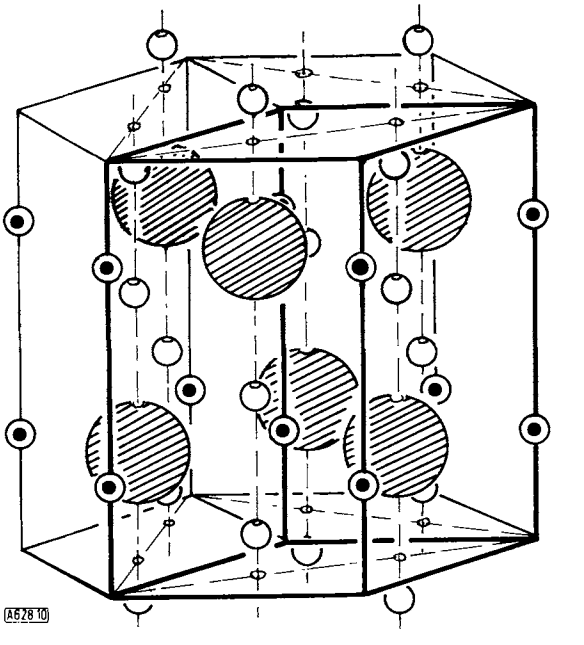

Fig. 10. Structure of Li_3As (Na_3As type according to *Brauer* and *Zintl*). ⊚ = arsenic, ⊙ = lithium in twofold position, O = lithium in fourfold position.

[28] *G. Brauer* and *E. Zintl*, Z. physik. Chem., Abt. B *37*, 323 (1937).

Mansmann[29] showed that a twofold Cu position in the structure given by *Steenberg*[30] for β-Cu_3As (cf. Section 3.3.) must be corrected. The structure thus becomes anti-isostructural with LaF_3 as corrected by *Mansmann*[31]. *Mansmann* also showed that in Na_3P, which, according to *Brauer* and *Zintl*[28], crystallizes in the Na_3As structure given by these authors, the lattice constant *a* must be increased by a factor of $\sqrt{3}$. Thus Na_3P also has a corrected anti-LaF_3 unit cell, and is isotypic with β-Cu_3As.

According to *Brauer* and *Zintl*, Li_3As is isotypic with Na_3P. The larger cell found for Na_3P cannot be detected for Li_3As by X-ray methods, owing to the unfavorable ratio of the atomic numbers. Thus it is not certain whether Li_3As crystallizes in the structure shown in Figure 10 or in the structure found by *Mansmann* for Na_3P, Cu_3As, and LaF_3. Li_2CuAs does not crystallize with the larger cell, but as shown in Figure 10; this can be stated with certainty because of the high scattering power of Cu.

Mention should now be made of the *changes* in the *molar volume* and in the lattice dimensions that are

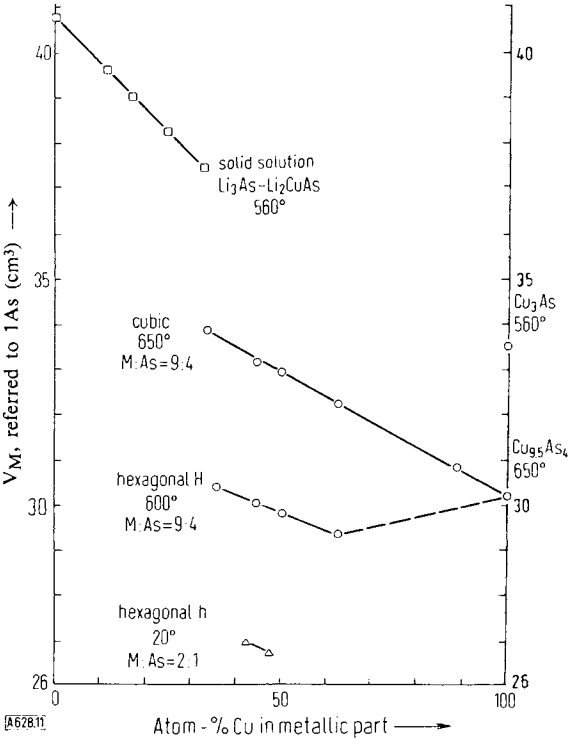

Fig. 11. Molar volume of lithium copper arsenides (calculated from the X-ray densities).

[29] *M. Mansmann*, Z. Kristallogr., Kristallgeometr., Kristallphysik, Kristallchem. *122*, 399 (1965).

[30] *B. Steenberg*, Ark. Kem., Mineralog. Geol., Ser. A *12*, No. 26 (1936–1938).

[31] *M. Mansmann*, Z. Kristallogr., Kristallgeometr., Kristallphysik, Kristallchem. *122*, 375 (1965).

characteristic of all the substitutions of lithium by heavy metal discussed here. As is shown in Figure 11, the molar volume (based on one As atom) decreases on incorporation of copper; the lattice constants along the Cu–As layer (*a* axis) are considerably shortened and the lattice dilates slightly along the *c* axis.

Comparison of these and similar contractions with the bonding radii for metallic and for ionic bonds respectively leads to agreement with a predominantly metallic bonding state, but not with predominantly ion bonding. From the point of view of polar bonding it is necessary to take into account a strong polarization of electrons in the layers occupied by copper and arsenic which shortens the interatomic distances as well as weaker bonding perpendicular to the layers due to the lithium situated between the layers.

3. Phases that Can Be Derived from a Transition Metal Compound

3.1. Solid Solutions $(Fe,Li)_2As$ Derived from the Cu_2Sb Type

The binary phases Fe_2As [32], Mn_2As [33], and Cr_2As [34] crystallize in the tetragonal system, and are isotypic with Cu_2Sb [32] (C 38 type) in the space group D_{4h}^7. The metalloid atoms in this lattice have in principle a face-centered cubic arrangement, with the metal atoms situated in the interstices (Fig. 12). This structure is related to the antifluorite type, but has a lower symmetry; the bonding in phases having this structure is predominantly intermetallic.

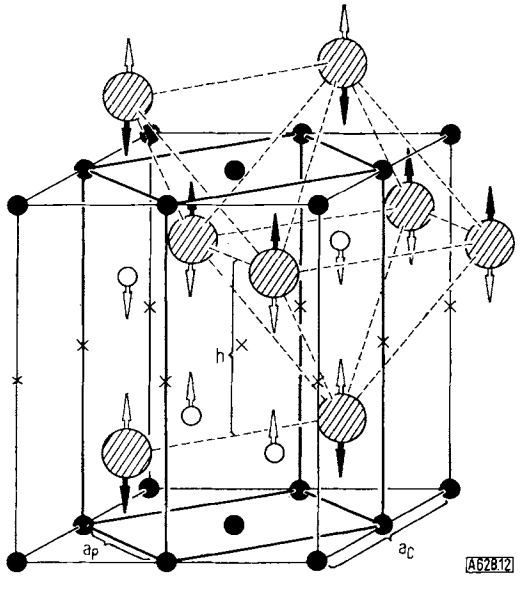

Fig. 12. Cu_2Sb type (unit cell shown in thick lines) and its relationship to the antifluorite type. ● = metalloid (X), ● = metal in distorted tetrahedral coordination (z = 0), ○ = metal in distorted octahedral coordination.

The actual translation unit of this lattice is the P cell indicated by thick lines. The axial relationships between this and the large C cell are $c_P = c_C$, $a_P\sqrt{2} = a_C$. The C cell has the same number of formula units and fundamentally the same structure as the unit cell shown in Figure 1; the origin of its coordinates are situated at $^1/_4$, $^1/_4$, $^1/_4$, *i.e.* at the point 1 in Figure 1. (The face centered X-arrangement in Figure 1 appears here as the "X-tetrahedra" situated in the C-cell.) However, the X lattice in the Cu_2Sb type is tetragonally distorted by about 15 % along the *c* axis in relation to the true face-centered cubic arrangement (axial ratio $c/a > \sqrt{2}$); the X-atoms (ideal position $z_X = 0.75$) are displaced slightly in the direction of the white arrows. As in the low-temperature form of the LiMnAs phase, there are close packed $(MX_{4/4})_\infty$ polyhedral layers in the a_1a_2 plane. The coordination of X around the transition metal in these layers at the level $z = 0$ is not truly tetrahedral (symmetry T_d), but tetragonal bisphenoidal (symmetry S_4); the coordination polyhedron is a tetrahedron that is stretched parallel to the *c* axis. The bisphenoidal sites (crosses in Fig. 12) at the level $z = 0.5$ are unoccupied. The second metal atom enters the position that would be the octahedral site in a true cubic close packed X lattice. Since this position in D_{4h}^7 has a free *z* parameter, the coordination in this case is 1+4+1. The lattice on the whole has a layer character, which results in increased cleavage of the crystals perpendicular to the *c* axis.

A ternary solid solution $(Fe, Li)_2As$[35] is derived from the binary Fe_2As phase of this structure (Fig.13).

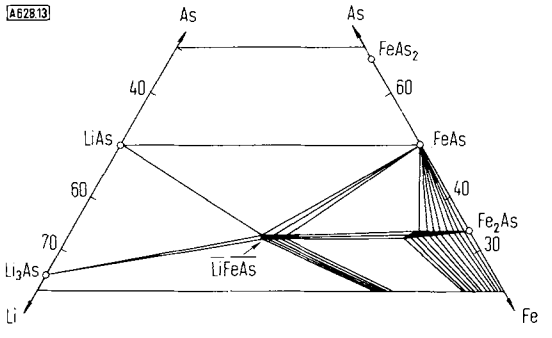

Fig. 13. Phases in the system Li—Fe—As (atom-%; samples quenched from 800 °C).

On the join (Fe + Li):As = 2:1, on which the solid solution has the composition $(Fe_{2-x}Li_x)As$, x can be equal to 0.25. This gives a substitution solid solution, in which up to 25 % of the Fe in the "octahedral position" is replaced by Li; the random incorporation of Li leads to an expansion of the lattice by about 1.7 % without alteration of the c/a ratio. The As parameter ($z_{As} = 0.735$ in Fe_2As) changes only very slightly or not at all, while the As atoms are still displaced (in accordance with the white arrows in Fig. 8) from the ideal positions (at $z_{As} = 0.75$).

In addition to the substituting lithium, a certain further quantity of lithium can be incorporated into this solid solution in the bisphenoidally distorted "tetrahedral sites" (at $z = 0.5$). Solid solutions of the composition $(Fe_{2-x}Li_{3/2x})As$ (Fe_2As–Li_3As section) are homogeneous up to the composition $(Fe_{1.75}Li_{0.38})As$, and have distinctly larger lattice constants than $(Fe_{2-x}Li_x)As$ for equal substitution x. Similar solid solutions may be formed by Mn_2As.

[32] *M. Eleander, G. Hägg,* and *A. Westgren,* Ark. Kem., Mineralog. Geol., Ser. B *12*, No. 1 (1936–1938).

[33] *H. Nowotny* and *F. Halla,* Z. physik. Chem., Abt. B *36*, 322 (1937).

[34] *H. Nowotny* and *O. Årstad,* Z. physik. Chem., Abt. B *38*, 461 (1938).

[35] *R. Juza* and *K. Langer,* Z. anorg. allg. Chem., in press.

3.2. Compounds LiMX Derived from the Cu_2Sb Type

When the degree of substitution of Li for Fe in the Fe_2As structure is greater than 25 %, the ternary phase LiFeAs (cf. Fig. 13) occurs in the Li–Fe–As system in addition to the Fe_2As solid solution [35]. In this phase the "octahedral position" is completely occupied by lithium. The transition from the Fe_2As solid solution to the ternary compound is accompanied by a change in the arsenic parameter from $z < 0.75$ to $z > 0.75$ ($z_{As} = 0.76$ in $Li_{1.1}FeAs$). The As atoms are now displaced in the direction of the black arrows (Fig. 12). LiCoAs and LiFeP [35] have similar structures, in which the arsenic or phosphorus parameter is again 0.76. The three compounds are stable down to room temperature and have been obtained in homogeneous form only with a small excess of metal. (*e.g.* (Li + Fe):As = 2.1:1); thus the experimental result shows that the oxidation number of the transition metal is again slightly less than +2.

LiFeAs is involved in reactions with the binary substances $FeAs_2$, FeAs, LiAs, and Li_3As between 800 and 500 °C, which have not yet been studied in detail. Another characteristic of this compound is that to a small extent it can form solid solutions with the Fe_2As solid solution described above (limiting compositions on quenching from 800 °C: $Li_{1.1}FeAs$–$Li_{0.1}Fe_{1.2}As$).

No corresponding solid solution LiFeP–Fe_2P has been found, probably because Fe_2P crystallizes in a special hexagonal lattice [36]. The situation is more complicated in the system Li–Co–As, since the ternary phase $LiCo_3As_2$ [35], which has not yet been extensively studied, occurs between LiCoAs and the binary boundary phase Co_2As, which is not isotypic with Fe_2As [37].

Cr does not give a phase analogous to LiFeAs, LiFeP, and LiCoAs. However, it was possible to obtain a series of solid solutions $Li_{1.1}Fe_{1-x}Cr_xAs$ with $0 < x < 0.5$ [35], from which the cell dimensions of the pure Cr phase could be extrapolated.

It is interesting to *compare* the binary and ternary substances having the common feature of layers of transition metal at $z = 0$ surrounded by arsenic in a tetrahedral or distorted tetrahedral arrangement.

Figure 14 shows plots of the dimensions of the P cells and two quantities that characterize the properties of the $(MAs_{4/4})_\infty$ layers against the atomic number of the transition metal. h (cf. Fig. 12) is the distance between the $(MAs_{4/4})_\infty$ layers, and s is the tetragonal bisphenoidal stretching of the coordination tetrahedra [*]. The extrapolated data are plotted for the hypothetical LiMX phase in the case of chromium. The transition from the binary to the ternary compound is indicated in each case by an arrow. The change on formation of the $(Fe, Li)_2As$ solid solution (which is not shown) is very small, but is in the same sense.

It can be seen from Figure 14 that very close packing of the layers in the a_1a_2 plane of the ternary Cr phase would give a relatively large distance between the layers. This is probably why the structure becomes unstable when the layer contains only chromium.

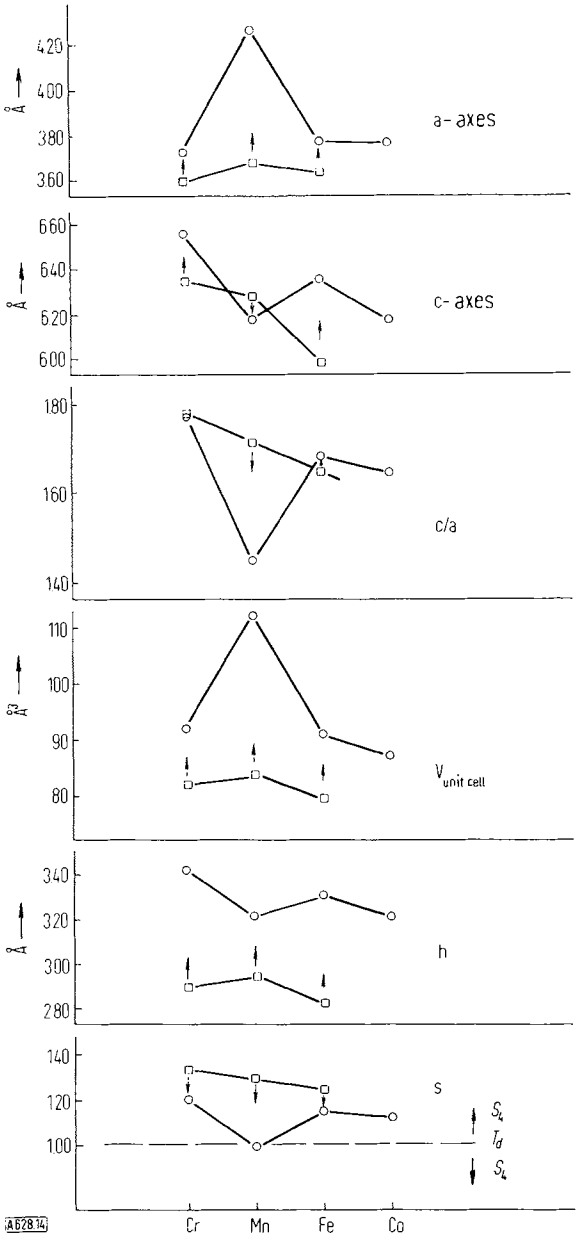

Fig. 14. Relationship between the crystallographic properties of M_2As phases in the Cu_2Sb type and of LiMAs phases (cf. text). □ = M_2As, O = LiMAs.

The cell dimensions of the ternary compounds of chromium, iron, and cobalt decrease continuously. The manganese compound does not comply with this continuity; while the cell dimensions of the binary compound Mn_2As are only slightly greater than those of its neighbors, the ternary compound LiMnAs occupies a special position. This difference in behavior can be correlated with the difference in the positions occupied by lithium; the intensity calculation for the compound LiMnAs (c/a = 1.024 for the C-lattice) shows that lithium is situated in the tetrahedral sites (z = 0.5). In the phases LiFeAs and LiCoAs, on the other hand, the lithium is situated in the o tahedral sites. Since the X-ray determination of the positions is subject to some uncertainty owing to the low scattering power of lithium, a consideration of distances is also

[36] *S. Rundqvist* and *F. Jellinek*, Acta chem. scand. *13*, 425 (1959).

[37] *R. D. Heyding* and *L. D. Calvert*, Canad. J. Chem. *35*, 449 (1957).

[*] The quantity s is the c/a ratio of the prism that can be circumscribed about the tetragonally distorted coordination "tetrahedra" around the transition metal. It is found from the lattice constants of the P cell and the arsenic parameter: $s = 2\bar{z}_{As} \cdot \frac{c}{a}\sqrt{2}$.

useful as a further indication of the difference in the behavior of lithium. The arrangement of Li (in tetrahedral sites in the manganese compound and in octahedral sites in the other compounds) leads in every case to Li–As distances of 2.67 Å. If the lithium were situated in the octahedral sites of the manganese compound, the Li–As distance would be 3.01 Å *i.e.* it would be much too large [35].

A valuable aspect for bond-theory treatment of the phases is apparent from Fig. 14: the distortion of the tetrahedral field around the transition metal in the $(MAs_{4/4})_\infty$ layer is reduced on removal of the transition metal from the "octahedral position" of the M_2As phases. This leads, in the case of manganese with its half-filled 3d shell, to a true tetrahedral coordination. The distance *h* between the tetrahedral layers always increases.

3.3. Phases $(Cu,Li)_{9.5}As_4$ Derived from $Cu_{9.5}As_4$

Whereas the behavior of Li_3As toward Cu_3As (Section 2.4.) is relatively simple, the behavior of the copper arsenides toward Li_3As is very complex. One might expect Cu_3As to form a complete range of solid solutions with Li_3As, since β-Cu_3As changes at 450 to 460 °C into a high-temperature modification of Na_3As type. However, no such complete series of solid solutions occurs. The curve of the molar volume of the Li_3As–Li_2CuAs solid solutions (Fig. 11) cannot be extrapolated to the molar volume of Cu_3As. The variation of the lattice constants makes it even clearer that a series of solid solutions cannot exist.

In addition to Cu_3As, there is another copper arsenide having a higher arsenic content. This is "Cu_5As_2", which according to our investigations has the composition $Cu_{9.5}As_4$. A high-temperature modification of this phase crystallizes in the cubic system with one formula unit $Cu_{9.5}As_4$ in the unit cell [38]. On rapid cooling, it changes into an orthorhombic low-temperature modification at 315 °C. This modification has two formula units in the unit cell, and its structure is closely related to that of the high-temperature modification [38].

$Cu_{9.5}As_4$ leads to several ternary phases, whose structures, though related, differ according to composition and temperature (640 °C, 600 °C, 20 °C). Copper in the cubic $Cu_{9.5}As_4$ phase can be replaced by lithium at 640 °C (cf. Fig. 9); this replacement can be continued up to a composition $Li_6Cu_3As_4$, with simultaneous expansion of the cubic unit cell. Since the structure of the cubic $Cu_{9.5}As_4$ is not yet accurately known, nothing can be said about the nature of the replacement of copper by lithium. Another single-phase range extending approximately from $Li_3Cu_6As_4$ to $Li_6Cu_3As_4$ is formed at 600 °C; this phase (H) crystallizes in the hexagonal system with a large unit cell. The solid solution H breaks down at room temperature into the boundary phases $Li_{5.8}Cu_{3.2}As_4$ (H_1) and $Li_{3.4}Cu_{5.7}As_4$ (H_2). The phase H also gives the phase LiCuAs (h) at room temperature. This phase is also hexagonal, but has a small unit cell. Samples having compositions in the LiCuAs phase range (Fig. 9) thus have three modifications, *i.e.* a cubic modification at high temperatures, a hexagonal modification with a large unit cell (H) at medium temperatures, and a hexagonal modification with a small unit cell (h) at room temperature. It can be seen from Figure 11 that the packing in these phases becomes increasingly close in the order mentioned. Geometrical relationships between the lattice constants and similar X-ray intensities point to the existence of a structural relationship, which has not yet been elucidated. There is no simple structural relationship between these phases and the LiMX phases derived from the Cu_2Sb-type (Section 3.2.).

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4. Concluding Remarks

Ternary compounds of lithium with elements of the nitrogen group have not yet been very extensively studied. Many articles on ternary oxides of lithium have been published, but none of them contains information that enables parallels to be drawn with the nitrogen compounds. It is more likely that such parallels exist for the ternary compounds of lithium with the heavier chalcogens, about which much less is known [39–42]. The only analogy known is the close relation between magnetic properties of the Li–Mn–As phases and of the solid solutions resulting from the substitution of manganese by lithium in MnSe [43,44]. However, it was important to us that it was possible to follow consistently the points mentioned in the introduction regarding the new nitrogen, phosphorus, and arsenic compounds. We expect that exhaustive investigation of a number of phases will provide interesting disclosures concerning bonding in these phases.

We are grateful to the Deutsche Forschungsgemeinschaft and to the Fonds der Chemischen Industrie for their support of these investigations.

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Photochemical Synthesis of Substituted 5*H*- and 7*H*-Benzocycloheptenes[1]

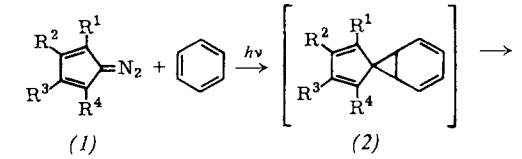
By *H. Dürr* and *G. Scheppers*[*]

Dedicated to Prof. A. Steinhofer on the occasion of his 60th birthday

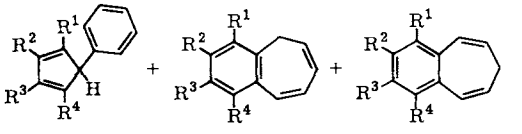
Photolysis of 5-diazocyclopentadienes in olefins leads, *via* the intermediate cyclopentadienylidenes, to the formation of spiroheptadienes by addition, or to the formation of alkenylcyclopentadienes by insertion[2].

We have found that the spironorcaradienes *(2)* that are expected to be formed by the pyrolysis of 5-diazocyclopentadienes *(1a)–(1d)* in benzene are not stable but rearrange[3] under the reaction conditions. Alongside the phenylcyclopentadienes *(3)*, 5*H*- and/or 7*H*-benzocycloheptenes *(4)* and *(5)* are formed by a reaction, which, to the best of our knowledge, is a new type of rearrangement reaction. The product isolated depends upon the substituents R^1–R^4 (see Table).

The compounds were identified IR- and NMR-spectroscopically; *(5a)* was also identified chemically by hydrogenation to 1,2,3,4 - tetraphenyl - 6,7,8,9 - tetrahydro - 5*H* - benzocycloheptene[4a], which proved to be identical in all respects[5] with a compound formed by reaction of cycloheptyne[4b] and tetraphenylcyclopentadienone.



(1) *(2)*



(3) *(4)* *(5)*

	R^1	R^2	R^3	R^4	Yields (%) of (3)	(4)	(5)	M.p. (°C) (3)	(4)	(5)
(a)	C_6H_5	C_6H_5	C_6H_5	C_6H_5	5	0	52	254	—	243
(b)	C_6H_5	H	H	C_6H_5	0	0	18–21	—	—	117–119
(c)	Cl	Cl	Cl	Cl	16–17	16–17	0	39–40	78–80	—
(d)	*o*-Phenylene		*o*-Phenylene		0	45–50		—	90–100	

Procedure:

A solution of 1.00 g (2.60 mmole) of *(1a)* in 200 ml of distilled benzene was irradiated in an N_2 atmosphere for one hour with a Philips high-pressure mercury vapor lamp (HPK 125, λ = 280 nm, Pyrex filter). After removal of solvent by distillation, the residue was chromatographed twice on silica gel with benzene/petroleum ether (b.p. 60–90 °C) (1:9). The first fraction to leave the column contains *(5)*. The presence of compounds *(3a)* and *(5a)* in the eluate is confirmed by thin layer chromatography, as well as IR and NMR spectroscopy.

(4a): IR (KBr): 3030 (s), 2970 (s), 1630 (w), 1435 (m) cm^{-1}; NMR ($CDCl_3$): δ = 2.49 ppm (t, 2H, 7 Hz); 5.6–6.1 ppm (t, 2H, 7 Hz); 6.41 ppm (d, 2H, 9.5 Hz); 6.90 and 7.20 ppm (20 H).

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Oxidation Products of Phosphorin

By *K. Dimroth, K. Vogel, W. Mach*, and *U. Schoeler*[*]

Dedicated to Prof. A. Steinhofer on the occasion of his 60th birthday

Solutions of 2,4,6-triphenylphosphorin and other arylated phosphorins in benzene become deep blue when shaken with conc. $HClO_4$ or H_2SO_4. They are decolorized by addition of water or aqueous sodium acetate solution. When the colorless solutions thus obtained are treated with strong acids, also with nonoxidizing acids such as trifluoroacetic acid, they become blue again.

Since the first blue coloration occurs only with oxidizing acids it must be concerned with an oxidation reaction and not merely with protonation of the phosphorus. Once oxidation has occurred, the oxidation product is converted by nonoxidizing acids into the blue salt which yields the colorless, non-protonated product on treatment with bases. Several products, which could not yet be separated, are formed in the oxidation.

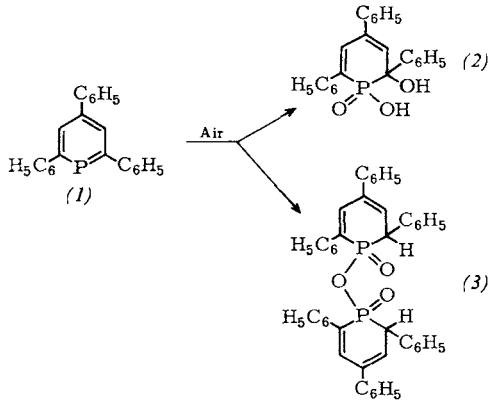
Pure products are obtained if a solution of 2,4,6-triphenylphosphorin in benzene is left exposed to the air for a considerable time. After *ca.* ten days colorless crystals separate. A further product is obtained on evaporation of the mother liquor. The first compound has m.p. 162–165 °C and composition $C_{23}H_{19}O_3P$, and its structure is probably *(2)*. Osmometric molecular-weight determination gives values indicating association. With trifluoroacetic *(2)* at once gives a blue color.

(2), UV: λ_{max} = 250 nm, $\varepsilon = 1.3\times10^4$ (in acetonitrile);
IR: 2600 to 2800 cm^{-1} and 940 to 970 cm^{-1} (P–OH), 1174 cm^{-1} (P=O) in KBr, 3612 cm^{-1} (C–OH) in CCl_4;
NMR: singlet at –6.6 ppm (1 H, COH); –10 to –11 ppm (broad, 1 H, P–OH); band complex at –7.8 to –7 ppm (17 H, aromatic and olefinic).

The second compound is soluble in benzene, has the composition $C_{46}H_{36}O_3P_2$, melts at 225 °C, and reacts with trifluoroacetic acid only slowly and with blue coloration. It may have structure *(3)*.

(3), UV: λ_{max} = 264 nm, $\varepsilon = 2.9\times10^4$ (in acetonitrile);
NMR: quartet at –3.4 ppm (2 benzyl-H); $J_{P\text{-}CH}$ = 27 Hz, $J_{Ha/Hb}$ = 5 Hz; band complex at –7.8 to –6.8 ppm (34 H, aromatic and olefinic);
Molecular weight (mass spectrometric) = 698.

Compound *(3)* quickly exchanges deuterium with deuterated solvents, the NMR signal at −10.5 ppm disappearing.

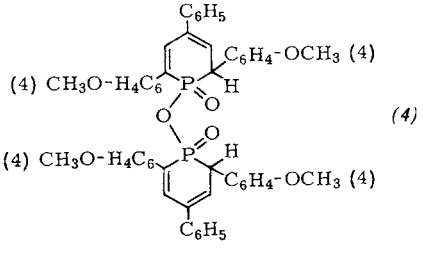


(1) *(2)* *(3)*

A compound of m.p. 195 °C analogous to *(3)*, and to which we ascribe structure *(4)*, was obtained from 2,6-bis-(4-methoxyphenyl)-4-phenylphosphorin.

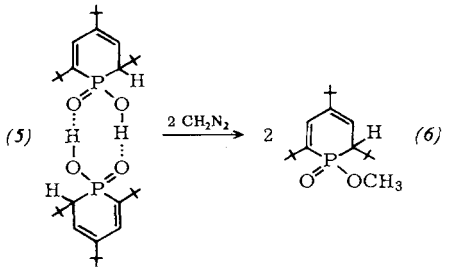
(4), UV: $\lambda_{max} = 240$ nm, $\varepsilon = 8.3 \times 10^4$ (in methanol);

NMR: quartet at −3.3 ppm (2 benzyl-H), $J_{P-CH} = 28$ Hz, $J_{Ha/Hb} = 5$ Hz; singlet at −3.70 ppm (6 H,O−CH_3), singlet at −3.72 (6 H, O−CH_3); band complex at −7.5 to −6.5 (30 H (aromatic and olefinic);
Molecular weight (mass spectrometric) = 820 (± 5); further fragments at *m/e* = 400 and 384, of which the second peak is to be ascribed to 2,6-bis-(4-methoxyphenyl)-4-phenylphosphorin.



(4)

If 2,4,6-tri-*tert*-butylphosphorin is oxidized under similar conditions, a colorless crystalline product $C_{17}H_{31}O_2P$, m.p. 203 °C, is formed. Osmometric and mass-spectrometric studies show that it is dimeric, and on the basis of the NMR data we assign to it the structure *(5)*.



(5) *(6)*

(5), UV (in *n*-hexane): $\lambda_1 = 237$ nm, $\varepsilon = 2925$, $\lambda_{max} = 275$ nm, $\varepsilon = 4075$;

IR (in CCl_4): P−OH: 2600–2900 cm^{-1}, 2200–2400 cm^{-1}, P−OH: 940 cm^{-1}, P−O: 1170 cm^{-1};

NMR (in $CDCl_3$): singlet $\delta = -12.2$ ppm (1 H); quartet $\delta = -6.63$ ppm, J_1 (P−CH) = 36.5 Hz, $J_2 = 2.0$ Hz (1 H); octet $\delta = -5.92$ ppm, J_3 (P−CH) = 22 Hz, $J_4 = 6$ Hz, $J_2 = 2$ Hz (1 H); quartet $\delta = -2.15$ ppm, J_5 (P−CH) = 24 Hz, $J_4 = 6$ Hz (1 H); singlet $\delta = -1.34$ ppm (9 H); singlet $\delta = -1.15$ ppm (9 H); singlet $\delta = -1.10$ ppm (9 H).
Molecular weight (mass spectrometric): 298 (monomer), 595 ± 1 (dimer).

The same product is obtained on treating 2,4,6-tri-*tert*-butylphosphorin with bromine water, hydrogen peroxide in acetone, or nitric/sulfuric acid at 0 °C. With diazomethane in ether/methanol, colorless crystals (m.p. 51 °C, composition $C_{18}H_{33}O_2P$) are obtained, whose structure is assigned by NMR.

(6), UV (in cyclohexane): $\lambda_1 = 247$ nm, $\varepsilon = 3300$; $\lambda_2 = 278$ nm, $\varepsilon = 3460$;

IR (in CCl_4): P−O−C: 1040 cm^{-1}; P=O: 1220 cm^{-1};

NMR: Quartet $\delta = -6.52$ ppm (1 H); J_1 (P−CH) = 36 Hz, J_2 (H−H) = 2 Hz; octet $\delta = -5.75$ ppm (1 H); J_3 (P−CH) = 23 Hz, J_4 (H−H) = 7 Hz; J_2 (H−H) = 2 Hz; doublet $\delta = -3.54$ ppm (3 H); J_5 (P−CH) = 11 Hz; quartet $\delta = -2.00$ ppm (1 H); J_6 (P−CH) = 23 Hz; $J_4 = 7$ Hz; singlet $\delta = -1.29$ ppm (9 H); singlet $\delta = -1.10$ ppm (9 H); singlet $\delta = -1.08$ ppm (9 H).
Molecular weight (mass spectrometric) = 312.

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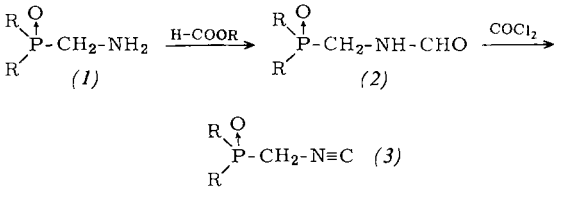
Phosphinylmethyl Isocyanides

By *N. Kreutzkamp* and *K. Lämmerhirt* [*]

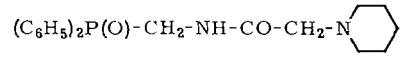
Dedicated to Prof. H. Böhme on the occasion of his 60th birthday

The *P,P*-diphenyl- (R = C_6H_5) and *P,P*-dibenzyl- derivatives (R = $CH_2-C_6H_5$) of the previously unknown phosphinylmethyl isocyanides *(3)* have been prepared. These represent the first examples of such derivatives and were obtained from the corresponding *N*-phosphinylmethylformamides *(2)* by means of the Ugi reaction [1]. The formamides *(2)*

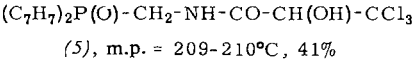


(1) *(2)* *(3)*

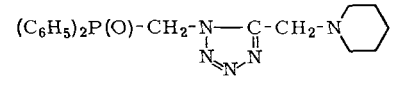
are obtainable in quantitative yields from the amines *(1)* and ethyl formate.



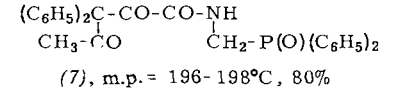
(4), m.p. = 115-116°C, 60%



(5), m.p. = 209-210°C, 41%



(6), m.p. = 163°C, 67%



(7), m.p. = 196-198°C, 80%

The phosphinylmethyl isocyanides *(3)* are relatively stable, colorless, odorless, solid substances, which afford the otherwise unobtainable tertiary phosphine oxides when subjected to either the Passerini or Ugi reactions. Compounds *(4)–(7)* represent examples of the oxides thus obtainable.

Procedure:

Phosphinylmethyl isocyanides: 10.8 ml of a 20 % solution of phosgene in toluene is added dropwise at 15–20 °C, with stirring, to a solution of 5.2 g of *N*-diphenylphosphinylmethylformamide and 6.6 ml triethylamine in 30 ml methylene chloride. The reaction mixture is concentrated by evaporation under vacuum and the residue thus obtained is boiled several times with fresh portions of benzene. The combined benzene solutions are then concentrated and *P,P*-diphenylphosphinylmethyl isocyanide precipitates out (m.p. 146–148 °C on recrystallization from benzene; yield 80 %).

P,P-Dibenzylphosphinylmethyl isocyanide (m.p. 143–144 °C) can be obtained from *N*-dibenzylphosphinylmethylformamide in 72 % yield by using the same procedure.

N-(*P,P*-Diphenylphosphinylmethyl)piperidinoacetamide *(4)*: A mixture of 10 ml methanol, 1.7 g piperidine, 2 ml 10 N HCl, and 2 ml 40 % formaldehyde solution is prepared under ice-cold conditions. 4.8 g *P,P*-diphenylphosphinylmethyl isocyanide is added in small portions. The resulting mixture is allowed to stand for 72 hours at 20 °C and finally evaporated under vacuum. The oily residue is taken up in hydrochloric acid, extracted twice with methylene chloride, and the aqueous phase rendered alkaline. Extraction with methylene chloride then affords the required compound as an oil, which solidifies on rubbing with ether and which can be recrystallized from benzene.

1 - Diphenylphosphinylmethyl - 5 - piperidinomethyltetrazole *(6)*: An ice cold solution of 1.7 g piperidine in 20 ml of acetone is prepared and treated successively with 2 ml 40 % formaldehyde solution, 5 ml 12.5 % hydrochloric acid, 1.3 g sodium azide in 10 ml H_2O, and 4.8 g *P,P*-diphenylphosphinylmethyl isocyanide. The mixture is stirred for an hour at 20 °C, saturated with potassium carbonate, and then extracted with acetone. On evaporation of the acetone extract there remains an oil which solidifies on rubbing with ether. The crystals thus obtained can be recrystallized from ethanol.

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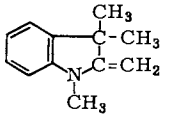
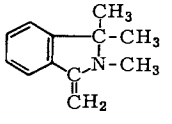
1,1,2-Trimethyl-3-methyleneisoindoline

By *A. Fabrycy* and *A. Kosmider* [*]

1,3,3-Trimethyl-2-methyleneindoline *(1)*, normally referred to as Fischer's base, has long been known.



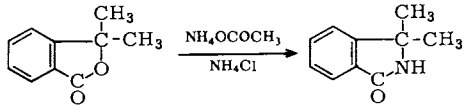
(1)



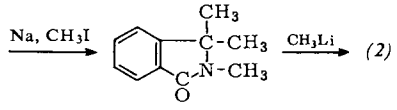
(2)

We have now synthesized 1,1,2-trimethyl-3-methyleneisoindoline *(2)* that is isomeric with *(1)*.

We have obtained 3,3-dimethyl-1-isoindolinone *(4)* [1] by the action of a mixture of ammonium acetate and ammonium chloride on dimethylphthalide *(3)* in an autoclave for 24 h at 400 °C/130 atm, the yield being 65 %. In contrast to other phthalides [2] the compound *(3)* does not exchange its O for N under milder conditions.



(3) *(4)*



(5)

1,1,2-Trimethyl-3-methyleneisoindoline *(2)* is a basic liquid that darkens in air; its structure was confirmed by elemental analysis and IR and NMR spectra.

With *p*-dialkylaminobenzaldehyde compound *(2)* forms red dyes that have good light- and wash-fastness on polyacrylonitrile fibers.

Experimental:

Dimethylphthalide *(3)* (200 g), ammonium acetate (300 g), and ammonium chloride (150 g) are heated in a 1-liter autoclave for 24 h at 380 °C; the pressure rises to 120–130 atm. After cooling, the semisolid brownish-black mass is rubbed three times with warm ethyl methyl ketone (total 800 ml), and the extract is filtered. The filtrate is washed with water (200 ml), treated with active charcoal, dried over Na_2SO_4, and concentrated to 250 ml. After cooling to −20 °C, the 3,3-dimethyl-1-isoindolinone *(4)* that crystallizes out is filtered off and washed with a little ethyl methyl ketone. Further amounts of the product can be obtained from the filtrate by evaporation to half its volume. Recrystallized from benzene the substance has m.p. 161 °C; the yield is 98 g (65 %).

The isoindolinone *(4)* (80.5 g, 0.5 mole), finely cut sodium (12.5 g), and anhydrous benzene (1.3 liter) are heated under reflux with stirring for 3–7 h (the time depends on the state of division of the sodium). After cooling the solid material is filtered off [no unchanged *(4)* can be recovered from the filtrate] and suspended in anhydrous benzene (500 ml). Methyl iodide (150 g) in benzene (200 ml) is added dropwise with stirring and warming (reflux condenser) during 8 h. The resulting mixture is heated for a further 2 h, cooled, and filtered, and the unreacted methyl iodide and the solvent are distilled off (water-bath). The residual yellow viscous liquid is distilled in a vacuum. 2,3,3-Trimethyl-1-isoindolinone *(5)* distils at 135–136 °C/3 torr; m.p. 35–36 °C; yield 61 g (70 %).

The isoindolinone *(5)* (17.5 g, 0.1 mole) in ether (100 ml) is added dropwise to a solution of methyllithium (from 2.5 g = 0.5 mole of Li) in ether (100 ml) at 15 °C and the whole is boiled for 1 h, then after cooling treated with water (100 ml). The ethereal layer is washed with water, dried over Na_2SO_4, and freed from solvent. On subsequent vacuum distillation the base *(2)* distils at 84–86 °C/3 torr; $n_D^{20} = 1.5719$; yield 14.7 g (85 %). Its perchlorate forms colorless crystals that melt at 197–198 °C.

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The Coordination Behavior of Triphenylsilanide[1]

By *Th. Kruck, E. Job,* and *U. Klose*[*]

π-Cyclopentadienyl- and CO-stabilized neutral complexes containing a covalent metal-silicon bond have been prepared in recent years for various transition metals. These are non-polar compounds of the types $Y_3Si-M(CO)_n$ (M = Mn or Co), $(\pi\text{-}C_5H_5)(CO)_3M-SiY_3$ (M = Cr or Mo), and $(\pi\text{-}C_5H_5)_2Zr(Cl)SiY_3$ (Y = alkyl, aryl, and halogen)[2], synthesized by replacement of an H or halogen atom attached to the complexed metal by the SiY_3 group by means of Y_3Si-X [X = H or $N(CH_3)_2$] or $LiSi(C_6H_5)_3$. We now report on the first metal complexes in which a silanide donor ligand, $:SiY_3^{\ominus}$, is attached to a transition metal atom by a coordinate bond.

Triphenylsilanide was the first of many possible combinations to be examined for ability to act as a σ donor. The $Si(C_6H_5)_3^{\ominus}$ ion is not only isoelectronic with the commonly used complexing ligand triphenylphosphine, but it also contains free 3d orbitals in the central atom, which allow metal → silicon back-bonding. Owing to its negative charge it should be a stronger donor than the phosphine ligand, and it therefore seemed to us that π acceptors would also have to be attached to the metal to stabilize the M–Si bond.

We therefore allowed $LiSi(C_6H_5)_3$ (which is readily obtainable by reduction of hexaphenyldisilane with lithium) to react with tetracarbonylnickel[3] (molar ratio 1:3) in tetrahydrofuran (THF). Above about −20 °C, the reaction led initially to a deep green, soluble intermediate, which has not yet been examined in any detail. Above about 0 °C vigorous evolution of CO takes place and the intermediate is converted within a few minutes into the monosubstituted carbonyl anion, triphenylsilanidotricarbonylnickelate(0)[4]:

$$Ni(CO)_4 + Si(C_6H_5)_3^{\ominus} \rightarrow [(C_6H_5)_3SiNi(CO)_3]^{\ominus} + CO$$

The lithium salt $Li[(C_6H_5)_3SiNi(CO)_3]\cdot 2\,THF$ can be precipitated from the orange solution with hexane. It crystallizes as light yellow needles, which are unstable in air, melt at 99 to 101 °C, and decompose with darkening of their color above about 110 °C. It dissolves very readily in water and in polar organic solvents, less readily in benzene, and not at all in aliphatic hydrocarbons. The anion is surprisingly stable in water, so that precipitation reactions are possible with bulky univalent cations. The light yellow $[N(CH_3)_4][(C_6H_5)_3SiNi(CO)_3]$ is obtained as shining leaflets, which sinter with decomposition at 200 °C.

The ionic constitution of these substances is confirmed by such precipitation reactions, by conductivity measurements, and by their diamagnetic behavior. The IR spectrum [ν_{CO} = 2003 (A_1) and 1936 cm^{-1} (E), solid in KBr] indicates that the anion has the expected distorted-tetrahedral structure (C_{3v} symmetry).

The much greater reactivity of triphenylsilanide as compared with triphenylphosphine is rather surprising. This high reactivity is also seen in the substitution of pentacarbonyliron at only 25–30 °C when this compound is treated in a similar manner with $LiSi(C_6H_5)_3$ (molar ratio 3:1) in THF. The reaction again leads smoothly to the light yellow lithium salt of the monosubstituted anion $[(C_6H_5)_3SiFe(CO)_4]^{\ominus}$ whose IR spectrum [ν_{CO} = 2007 (A_1), 1906 (A_1), and 1880 cm^{-1} (E), solution in THF, or 2002, 1925, 1891, and 1825 cm^{-1}, solid in KBr] clearly points to a trigonal-bipyramidal structure having symmetry C_{3v}. The triphenylsilanidotetracarbonylferrate(0) is unstable in the presence of an excess of $LiSi(C_6H_5)_3$, at least at room temperature; it decomposes with loss of an $Si(C_6H_5)_3^{\ominus}$ ion:

$$[(C_6H_5)_3SiFe(CO)_4]^{\ominus} + Si(C_6H_5)_3^{\ominus} \rightarrow [Fe(CO_4)]^{2\ominus} + (C_6H_5)_3Si-Si(C_6H_5)_3$$

The strong long-wave shift of the C–O stretching frequencies of the silanide complexes in relation to those of the isosteric compounds $Ni(CO)_3P(C_6H_5)_3$ (ν_{CO} = 2070 and 2000 cm^{-1} [5]) and $Fe(CO)_4P(C_6H_5)_3$ (ν_{CO} = 2051, 1978, and 1945 cm^{-1} [6]) is in agreement with the anionic character of the new ligand, which leads to a high negative charge on the metal, and hence to considerable M → CO back-bonding.

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[1] Metal complexes with anionic silicon compounds. Part I.

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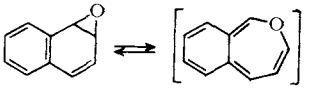
1,2-Naphthalene Oxide

By *E. Vogel* and *F.-G. Klärner*[*]

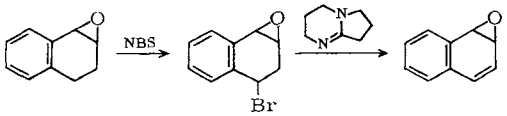
In order to gain a better understanding of arene oxide-oxepin equilibrium systems, it was desirable to have "frozen-in" arene oxides available for purposes of comparison. 8,9-Indan oxide and 9,10-tetralin oxide[1] have recently been prepared and it is found that the tri- and tetramethylene chains that function as brackets in these molecules restrict arene oxide-oxepin isomerization to such a degree that the oxepin form is no longer detectable by spectroscopic methods.



(1) *(2)*

We suspected that the previously unknown 1,2-naphthalene oxide *(1)* would prove to be another fixed arene oxide. Judging by the results obtained with benzonorcaradiene[2,3], it was to be expected that the rearrangement of *(1)* to the isomeric oxepin *(2)* would be relatively strongly endothermic, owing to the loss of benzene resonance, and that *(2)* would be formed at most as a short-lived intermediate in an inversion process[3].

The synthetic route to 1,2-naphthalene oxide that we envisaged involved the introduction of a double bond into 1,2-dihydronaphthalene oxide *(3)*[4]. On reaction with *N*-bromosuccinimide, compound *(3)* yields a bromide *(4)*, m.p. 94–95 °C, the NMR spectrum of which shows the bromine substituent to be in the benzylic position. However, the configurative relationship of the substituent to the epoxide ring remains unsettled. Whereas earlier attempts to dehydrohalogenate *(4)* to 1,2-naphthalene oxide with various bases had been unsuccessful[5], the use of 1,5-diazabicyclo[4.3.0]-non-5-ene[6] (0 °C, tetrahydrofuran) led to the desired product.



(3) *(4)* *(1)*

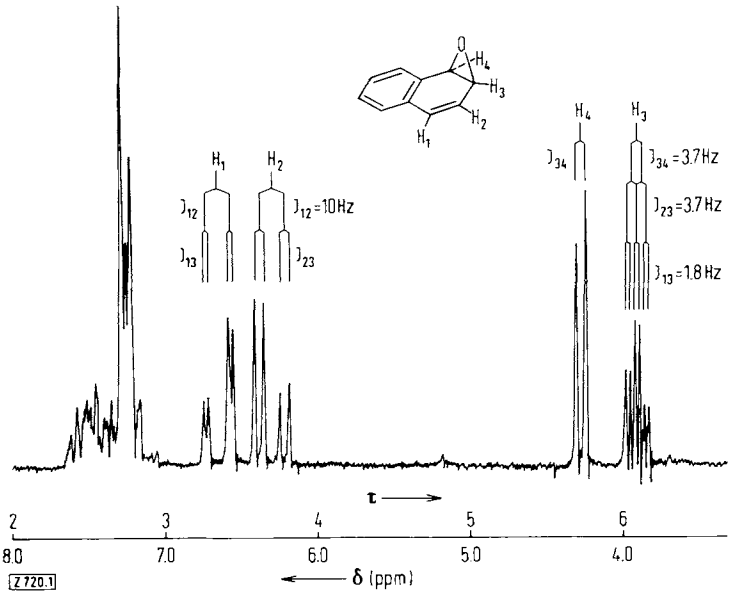


Figure 1. ^{1}H—NMR spectrum of 1,2-naphthalene oxide (in CCl_4; 60 MHz; tetramethylsilane as internal standard). No absorption beyond $\tau = 6.2$.

1,2 Naphthalene oxide is obtained as a colorless crystalline compound that in the solid state rapidly rearranges – sometimes with explosive violence – to α-naphthol.

The presence of 1,2-naphthalene oxide follows unequivocally from the NMR spectrum reproduced in Figure 1. If the isomeric oxepin derivative *(2)* were present, then the signals corresponding to the protons H^3 and H^4 would appear at lower field strengths and, furthermore, the absorption due to H^4 would be a singlet. The electronic spectrum of the oxide [maxima at 220 (ε = 17600), 268 (8850), and 304 nm (1570) in dioxane] is remarkably similar to that of benzonorcaradiene[2]. This finding rules out the possibility that 1,2-naphthalene oxide is in equilibrium with a significant concentration of the isomeric oxepin *(2)*, which is doubtless colored.

Compound *(1)* is relatively stable in solution (ether). In the presence of catalytic amounts of a protic or a Lewis acid it spontaneously isomerizes to α-naphthol. Attempts to convert *(1)* into the known *trans*-1,2-dihydronaphthalene-1,2-diol[7] have been unsuccessful.

The fact that a number of authors have recently invoked 1,2-naphthalene oxide and other arene oxides as intermediates in enzymatic oxygenations of aromatic compounds[7,8] seems a further justification for the publication of these results.

Synthesis of 1,2-Naphthalene Oxide

a) *4-Bromo-1,2-epoxy-1,2,3,4-tetrahydronaphthalene (4)*

N-Bromosuccinimide (7.12 g, 40 mmole) and α,α'-azoisobutyrodinitrile (0.1 g) are added to a solution of 1,2-epoxy-1,2,3,4-tetrahydronaphthalene *(3)* (5.84 g, 40 mmole) in CCl_4 (75 ml). Once the reaction has been started by quickly heating the mixture to boiling, no more heat has to be supplied. Succinimide and unreacted *N*-bromosuccinimide are filtered off and the filtrate is concentrated under vacuum until the bromide *(4)* begins to precipitate. On cooling to −10 °C, the main part of *(4)* crystallizes out in almost pure form; a further crop of *(4)* is obtained by working up the mother liquor. Recrystallization from ether/ethyl acetate (5:1) affords 2.1 g of *(4)* (23 % yield) having m.p. 94–95 °C (decomp.).

b) *1,2-Naphthalene Oxide (1)*

1,5-Diazabicyclo[4.3.0]non-5-ene (400 mg, 3.2 mmole) is added dropwise, with stirring at 0 °C under an N_2 atmosphere, to 4-bromo-1,2-epoxy-1,2,3,4-tetrahydronaphthalene *(4)* (450 mg, 2 mmole) in tetrahydrofuran (5 ml). The reaction mixture is stirred for 12 h at 0 °C and then allowed to stand for a further 12 h at this temperature. The tetrahydrofuran is evaporated off at 0 °C under vacuum and the residue is treated first with 15 ml of pentane and then with 2 ml of water. The aqueous phase is extracted once again with 15 ml of pentane and the combined pentane solutions are washed three times with dilute KOH and dried over K_2CO_3. On cooling to −80 °C, *(1)* crystallizes out as colorless needles, yield 240 mg (83 %). It is not possible to determine the exact melting point of *(1)* because it rearranges rapidly to α-naphthol.

In order to prevent the occurrence of acid catalysis during the preparation, all glass apparatus is washed with concentrated ammonia.

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Perchlorobutatriene and Perchloro-[4]radialene

By *B. Heinrich* and *A. Roedig* [*]

The remarkable thermal instability of perchloroallene[1] in conjunction with observations carried out on the dimerization of perchlorobutenyne[2] prompted us to synthesize perchlorobutatriene *(4)*. The synthesis was accomplished by

reaction of β,β-dichloroacrolein with trichloromethyllithium[3] in tetrahydrofuran at −120 °C, treatment of the carbinol *(1)* (m.p. 78 °C) with PCl_5 at 60 °C, and dehydrochlorination of the *sym*-hexachlorobutene *(3)* with potassium *tert*-butoxide in light petroleum (fraction 50–70 °C) at room temperature.

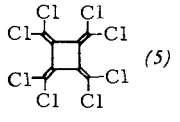
$$Cl_2C{=}CH{-}CHO \xrightarrow{CCl_3Li} \underset{(1)}{Cl_2C{=}CH{-}CHOH{-}CCl_3} \xrightarrow{PCl_5}$$

$$\underset{(2)}{Cl_2C{=}CH{-}CHCl{-}CCl_3} + \underset{(3)}{CCl_3{-}CH{=}CH{-}CCl_3} \rightarrow \underset{(4)}{Cl_2C{=}C{=}C{=}CCl_2}$$

The first reaction step proceeds almost quantitatively. On replacement of OH by Cl in compound *(1)*, the main product is compound *(2)* (b.p. 58–60 °C/0.1 torr), which, however, may be separated easily from *(3)* (m.p. 83.5 °C, yield of pure product 25 %). A subsequent allyl rearrangement *(2)* → *(3)* does not take place. The colorless crystalline compound *(4)* (m.p. 59–60 °C) that is obtained from *(3)* in 43 % yield can be sublimed without losses at 12 torr (bath temperature 55 °C) and is surprisingly stable compared to perchloroallene and to perfluorobutatriene[4], which in the liquid state explodes at temperatures above −5 °C. In CCl_4, it adds chlorine quantitatively to form perchlorobutadiene.

Apart from the strong C=C absorption at 1601 cm^{-1}, the extremely simple IR spectrum (KBr) of compound *(4)* shows only a split band at 855–880 cm^{-1} and a further weak band at 748 cm^{-1}. Its UV spectrum is characteristic of butatrienes[5,6]; the maxima (256 nm, log ε = 4.25, and 292 nm, log ε = 4.99) are merely displaced toward longer wavelengths as a result of chlorine substitution.

When heated for several hours at 100 °C in aprotic solvents, compound *(4)* yields, alongside small amounts of an explosive polymeric product, a colorless dimer (m.p. 164 °C, yield 50 %) that is not identical with any of the known


(5)

compounds C_8Cl_8[2,7] derived from perchlorobutenyne. The structure *(5)* is indicated by *inter alia* the following criteria:

a) the analogous behavior of other butatrienes[8] and cumulenes[9], which dimerize photochemically or thermally to [4]radialenes,

b) the UV spectrum, whose general form and maxima (232 nm, log ε = 4.30, 298 nm, log ε = 4.32, 312 nm, log ε = 4.27, 342 nm, log ε = 3.91) are very similar to those seen in the spectrum of tetramethylenecyclobutane[10], apart from the red shift caused by chlorine substitution, and

c) the dipole moment of 0.2 D, which within the range of application of the Debye theorem is to be regarded, to a first approximation, as zero.

Compound *(5)* is thermally stable at temperatures above 200 °C and does not rearrange to any of the perchlorobutenyne dimers. Our results thus refute the otherwise reasonable assumption that the formation of these C_8Cl_8 isomers could proceed *via* the intermediates *(4)* and *(5)*.

Perchlorobutatriene (4)

Compound *(3)* (20 g) is stirred for 70 h with potassium *tert*-butoxide (30 g) in anhydrous petroleum ether with exclusion of air. The mixture is centrifuged and the separated supernatant liquid is treated with a further 5 g-portion of potassium *tert*-butoxide and stirred for another 50 h. The solution remaining on removal of the solids is concentrated under vacuum and the crude product thus obtained is taken up in methanol (60 ml), filtered, and frozen out by cooling to −70 °C. Recrystallization is from a little ethanol, with gentle warming. All the mother liquors are evaporated to dryness under vacuum, the residue is sublimed and recrystallized, and then united with the preliminary charge. After drying over P_2O_5 under vacuum and sublimation at 11 torr (bath temperature 55 °C), 6.0 g (41.5 %) of colorless coarse crystals (m.p. 59–60 °C) is obtained.

Perchloro-[4]radialene (5)

Compound *(4)* (500 mg) is dissolved in anhydrous carbon tetrachloride (0.5 ml) and, after addition of a trace of hydroquinone, heated in a tube to 100 °C for 65 h. Carbon tetrachloride (2 ml) is added to the solution, which is then separated from insolubles by centrifugation. The solvent is removed under vacuum and the resulting residue is recrystallized twice from light petroleum (b.p. 50–70 °C). After sublimation at 0.01 torr (bath temperature 120–130 °C), 242 mg (48.5 %) of colorless crystals (m.p. 164 °C) is obtained.

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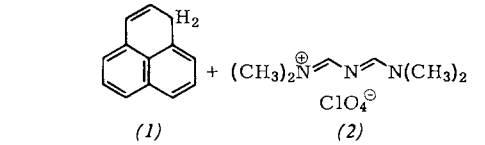
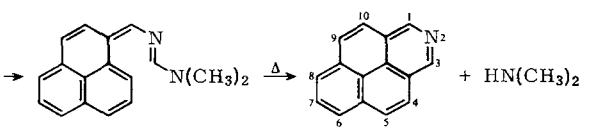
2-Azapyrene

By *R. Kirchlechner* and *Ch. Jutz* [*]

The reaction of phenalene *(1)*[1] with 3-dimethylamino-2-azapropenylideneammonium perchlorate *(2)*[2] and sodium methoxide in pyridine leads to the orange colored amine *(3)*, which on heating undergoes ring closure to 2-azapyrene *(4)*. Only one other monoazapyrene, thebenidine (4-azapyrene)[3], has previously been reported.


(1) *(2)*


(3) *(4)*

2-Azapyrene *(4)*, pale yellow crystals, m.p. 162–165 °C, partly decomposes both on melting and on sublimation in vacuum. (Methyl iodide derivative, m.p. 281–284 °C; picrate, m.p. 280 °C.) Its UV spectrum (in ethanol) resembles that of pyrene: λ_{max} = 375 nm (log ε = 4.01); 370 (3.48); 356 (3.83); 332 (4.83); 316.5 (4.61); 304 (4.25); 294 (sh) (3.89); 270.5 (4.53); 260 (4.52); 240 (4.99).

Solutions of *(4)* in organic solvents display an intensive blue fluorescence and in aqueous mineral acids a blue-green fluorescence. In the NMR spectrum ($CDCl_3$) a singlet occurs at $\tau = 0.87$, which is ascribed to the protons H-1 and H-3 (the neighboring protons to the ring nitrogen); the remaining protons show a characteristic split multiplet with main signals at $\tau = 2.05$, 2.18, 2.38, and 2.50. In trifluoroacetic acid *(4)* is protonated and H-1 and H-3 give rise to a doublet, $J = 6$ Hz, at $\tau = 0.53$. The multiplet of the remaining ring protons occurs well downfield at $\tau = 1.43$, 1.53, 1.60, 1.67, and 1.80. IR spectrum (KBr disk): 1618, 1582, 1534, 1449, 1412, 1377, 1351, 1250, 1238, 1208, 1180, 1134, 1071, 1052, 1013, 971, 884, 840, 820, 808, 804, 750, 709, 683 cm^{-1}.

Procedure:

A mixture of 332 mg (2 mmole) phenalene *(1)* and 475 mg (2.1 mmole) 3-dimethylamino-2-azapropenylideneammonium perchlorate *(2)* in 25 ml of water-free pyridine is treated, under purified nitrogen, with 2.2 mmole of sodium methoxide. The resulting mixture is stirred for 6h and then boiled under reflux for a further 10h. The pyridine is distilled off under vacuum and the residue taken up in a little methylene chloride and passed through a short Al_2O_3 column (activity grade III), The residue obtained on evaporating the eluate is dissolved in 20 ml 4 N HCl (with warming if necessary), filtered, and neutralized whilst hot with aqueous ammonia. 2-Azapyrene separates out as fine needles, yield 250 mg (61 %). On recrystallization from a methanol/water mixture the 4-azapyrene recovered has m.p. 162–165 °C.

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A New Method for the Introduction of Nitrile Groups

By *D. vor der Brück*, *A. Tapia*, *R. Riechel*, and *H. Plieninger* [*]

Reaction of nucleophilic heterocycles (XH) with ethoxycarbonyliminotriphenylphosphorane *(1)* [1] and BF_3-ether leads to the formation of nitriles, as well as triphenylphosphine oxide, sometimes in very good yield.

$$XH + (C_6H_5)_3P{=}N{-}CO_2C_2H_5 + BF_3{\cdot}(C_2H_5)_2O \xrightarrow{THF} X{-}C{\equiv}N + (C_6H_5)_3P{=}O + C_2H_5OH$$

(1)

The following compounds have been obtained in this way:
Pyrrole-2-carbonitrile, yield 45 %.

Ethyl-3-cyano-2,4-dimethylpyrrole-5-carboxylate, m.p. 177 °C, yield 46 %.

3-Ethyl-2,4-dimethylpyrrole-5-carbonitrile, m.p. 134 °C, yield 57 %.

2,3,4-Trimethylpyrrole-5-carbonitrile, m.p. 139 °C, yield 50 %.

Indole-3-carbonitrile, m.p. 181 °C, yield 65 %.

2-Ethoxy-1-methylindole-3-carbonitrile, m.p. 126 °C, yield 96 %.

Reaction of 3,4-dimethyl-2,5-dihydropyrrol-2-one yields 2-ethoxy-3,4-dimethylpyrrole-5-carbonitrile in 15 % yield (m.p. 90 °C).

In the case of acid-sensitive compounds this synthesis appears to be more favorable than nitrile synthesis by way of cyanates [2].

Procedure:

Ethoxycarbonyliminophosphorane (1.5 mmole) and BF_3-ether (1.5 mmole) are dissolved in *ca.* 50 ml of tetrahydrofuran, 1 mmole of the heterocyclic compound is added, and the mixture boiled under reflux for about 4 hours. The solvent is then evaporated off under vacuum and the resulting residue chromatographed on silica gel, or aluminum oxide, with ether/petroleum ether. The triphenylphosphine oxide remains on the column.

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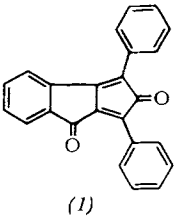
[1] *H. Staudinger*, Helv. chim. Acta *2*, 635 (1919); *L. Horner* and *A. Gross*, Liebigs Ann. Chem. *591*, 117 (1955).

[2] *D. Martin* and *S. Rackow*, Chem. Ber. *98*, 3662 (1965).

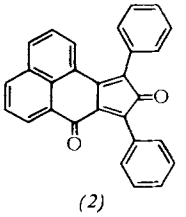
Synthesis of 1,3-Diphenyl-2,8-dihydrodibenz[*e*,*h*]-azulene-2,8-dione

By *W. Ried* and *J. Ehret* [*]

Condensations of diketones with dibenzyl ketone are well known [1,2]. The corresponding reactions with triketones lead to the formation of the "ketocyclones" *(1)* [3] and *(2)* [4], which possess a further carbonyl group vinylogous to the carbonyl function of the cyclopentadienone. These compounds are of value for the synthesis of substituted fluorenones [3], pentalenes [5], benzanthrones [4], and other ring systems [6].

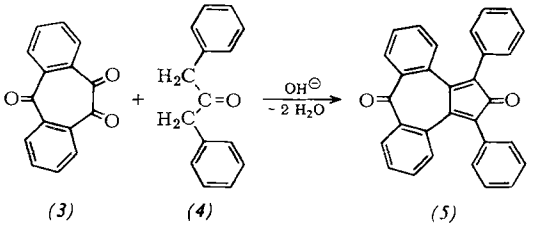


(1)



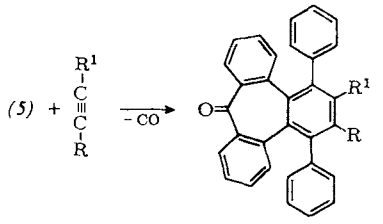
(2)

The "ketocyclones" *(1)* and *(2)*, in which the cyclopentadienone system is condensed with a five- or six-membered ring, finds its continuation in the 1,3-diphenyl-2,8-dihydrodibenz[*e*,*h*]azulene-2,8-dione *(5)* with a condensed seven membered ring. Compound *(5)* can be formed from 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene-5,10,11-trione *(3)* and dibenzyl ketone *(4)* in 50–60 % yield, the otherwise observed benzilic acid type rearrangement to anthraquinone [7] taking place only to a small extent.



(3) *(4)* *(5)*

When crystallized from ethanol, *(5)* forms shining violet crystals m.p. 248–249 °C. Diels-Alder reactions of *(5)* with dienophilic agents afford the tribenzocycloheptenes *(6a)* to

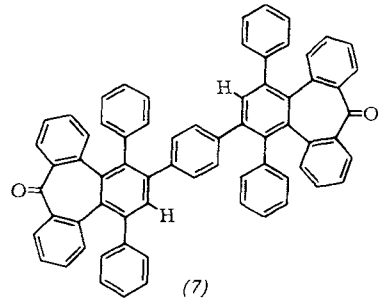


(6)

	R	R^1	M.p. (°C)	Yield (%)	Recrystallized from
(6a)	$-CO_2CH_3$	$-CO_2CH_3$	251	45	dry ethanol
(6b)	$-CO-C_6H_5$	$-CO-C_6H_5$	302–303	65	benzene
(6c)	$-C_6H_5$	$-CH_3$	260–261	50	dry ethanol
(6d)	$-C_6H_5$	$-C_6H_5$	379–380	45	benzene

(6d), of which *(6d)* has already been synthesized by another method [8].

Compound *(5)* reacts with 1,4-diethynylbenzene to form *(7)* [m.p. 429–430 °C, from xylene] and with 2,2′-diethynylbiphenyl [9] to form *(8)* [m.p. 388–389 °C, from xylene].



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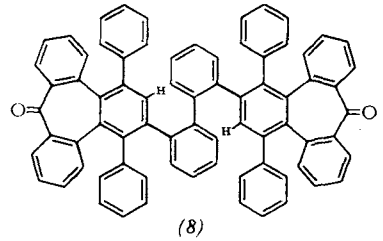

(8)

Procedure:

a) Synthesis of *(5)*: 2.36 g (0.01 mole) of *(3)* and 2.10 g (0.01 mole) of *(4)* are dissolved in 200 ml water-free ethanol at room temperature. 1.75 ml 10 % methanolic KOH is added dropwise, and with vigorous stirring, to the ice-cold solution. The resulting mixture is allowed to stand for 48 hours at a temperature of 6–8 °C. The crystals of *(5)* that separate out are filtered off under suction and recrystallized from water-free ethanol or acetonitrile (Yield 50–60 %).

b) Synthesis of *(6a)–(6d)*, *(7)*, and of *(8)*: Molar quantities of *(5)* and an acetylenic compound are heated, in β-decalol if the latter is not liquid, for several hours until evolution of gas ceases, extensive decoloration taking place.

The reaction mixture is then cooled, diluted with ethanol, and the precipitate filtered off by suction. The crude product is then recrystallized (using the respective solvents given above for the compounds *(6a)–(6d)*, *(7)*, and *(8)*).

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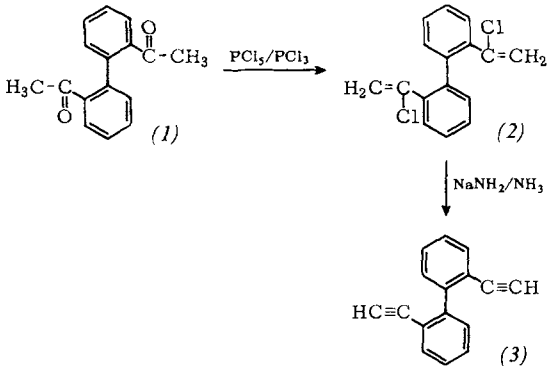
Synthesis of 2,2′-Diethynylbiphenyl and its Reaction with Cyclopentadienone Derivatives

By *W. Ried* and *V. B. Saxena* [*]

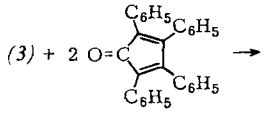
The hitherto unknown 2,2′-diethynylbiphenyl *(3)* is of interest as a starting material for photoreactions and thermochemical reactions. It can be synthesized as follows:



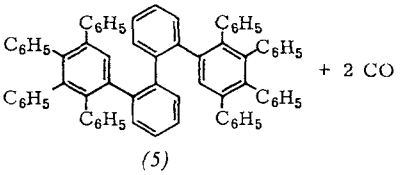
(1) (2) (3)

2,2′-Diacetylbiphenyl *(1)* [1] reacts with PCl_5/PCl_3 at 40 °C, giving 2,2′-bis(1-chlorovinyl)biphenyl *(2)*, from which 2 moles of HCl are removed on reaction with $NaNH_2$ [2] in liquid NH_3. The product *(3)* crystallizes as colorless leaflets and melts at 49 °C.

Both ethynyl groups of *(3)* react with cyclopentadienone derivatives, *e.g.* *(4)*, at elevated temperature, with evolution of CO and formation of polyphenylenes, *e.g.* *(5)* (colorless crystals, m.p. 235 °C).



(4)



(5)

Synthesis of 2,2′-Diethynylbiphenyl (3)

2,2′-Diacetylbiphenyl (6 g, 0.025 mole) and PCl_5 (20 g, 0.1 mole) are heated in PCl_3 (50 ml) at 40 °C for 48 h with stirring, then the mixture is evaporated in a vacuum and the

residue is treated with ice. The aqueous suspension is extracted with benzene (about 300 ml), and the organic phase is at once chromatographed on acid Al_2O_3. Benzene (1000 ml) is used for elution. After evaporation of the solvent the residue is taken up in ether, and the solution is decanted at once into a suspension of $NaNH_2$ prepared from sodium (6 g) and iron(III) nitrate (0.3 g) in liquid ammonia (400 ml) at −40 °C. The mixture is stirred for 2 h at −40 °C. Ammonium chloride (15 g) is added to decompose the excess of sodium amide, and the ammonia is allowed to evaporate overnight. The mixture is then hydrolyzed with dilute sulfuric acid, and the organic component is extracted into ether. After evaporation of the ether the residue is chromatographed in benzene on acid Al_2O_3. The eluate is evaporated and the residue is kept at −30 °C for 2 days. Yield: 1.2 g (*ca.* 25 %) of colorless leaflets, m.p. 49 °C.

Reactions of Cyclopentadienone Derivatives with 2,2'-Diethynylbiphenyl

1 mole of *(3)* and 2 moles of the cyclopentadienone derivative are heated in a small volume of 2-decalol under nitrogen until gas evolution ceases and decoloration is almost complete (several hours). After cooling, the product is filtered off and recrystallized from ethyl acetate or *o*-dichlorobenzene.

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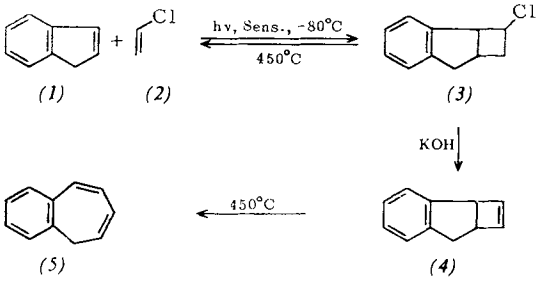
A Simple Synthesis of Benzocycloheptene

By *W. Metzner* and *K. Morgenstern* [*]

In the presence of photosensitizers, indene *(1)* adds on 1,2-dichloroethylene with formation of 1,2-dichloro-1,2,2a,7b-tetrahydrocyclobuta[*b*]indene [1]. Extension of this reaction to vinyl chloride *(2)* suggested itself as a simple means of synthesizing the hitherto difficultly accessible [2] benzocycloheptene *(5)*.

Irradiation (Philips HPK 125 W, pyrex filter glass) of *(1)* and benzophenone in liquid *(2)* at −80 °C resulted in the formation of the adduct *(3)* (yield 69 %) as a mixture of two stereoisomers (molar ratio 10:1; b.p. 82–86 °C/0.8 torr). Attempts to convert *(3)* into *(5)* [4] by thermal elimination of HCl [3] led to fission into the starting materials of the photoreaction.



However, compound *(3)* is dehydrohalogenated to the hitherto unknown 2a,7b-dihydrocyclobuta[*b*]indene *(4)* (yield 60 %; b.p. 43–45 °C/0.3–0.5 torr; $n_D^{20} = 1.5642$) when treated with KOH/triethylene glycol at 230 °C. Thermal valence isomerization [5] of *(4)* leads to the formation of *(5)* in 83 % yield [4].

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Synthesis of *N-tert*-Butyloxycarbonyl- and *N-tert*-Amyloxycarbonylamino Acids

By *B. Rzeszotarska* and *S. Wiejak* [*]

N-tert-Butyloxycarbonylamino acids (BOC-amino acids) and the less frequently used *N-tert*-amyloxycarbonylamino acids (AOC-amino acids) are particularly suitable for the synthesis of peptides. However, their syntheses involve preparative difficulties that are connected with the instability of *tert*-alkyl chloroformates, the well-known disadvantage of the azide method and of the several-step synthetic route.

Recently we described a method [1] for the introduction of the benzyloxycarbonyl amino-protecting group by means of benzyl 8-quinolyl carbonate. By an analogous procedure we have now prepared the *tert*-butyl and *tert*-amyl 8-quinolyl carbonates and obtained BOC- and AOC-amino acids by their reaction with amino acids.

Procedure:

A solution of *tert*-butyl or *tert*-amyl chloroformate (prepared according to reference [2]) is added dropwise at −60 °C to a solution of 8-hydroxyquinoline and triethylamine (molar ratio 1:1) in tetrahydrofuran, which is also cooled to −60 °C. The mixture is allowed to stand for 24 h at −25 °C and for 24 h at 20 °C and the solvent is then evaporated off under vacuum. The residue is dissolved in ethyl acetate and the resulting solution is washed first with water, then with ice-cold 0.1 N HCl, and once more with water. It is finally dried over $MgSO_4$ and the solvent is evaporated off. The mixed carbonates, which are obtained in *ca.* 70 % yield, crystallize out of an alcohol/water solution. *tert*-Butyl 8-quinolyl carbonate melts 69.5–72 °C (softening temperature 67 °C) and *tert*-amyl 8-quinolyl carbonate melts at 46–46.5 °C. Both substances can be stored almost indefinitely at room temperature.

A solution of the amino acid (0.5 mmole in 0.55 ml of 1 N NaOH) is mixed with a solution of the *tert*-alkyl 8-quinolyl carbonate (0.75 mmole) in dimethylformamide (0.9 ml) and the mixture is heated to 70 °C (water-bath temperature) for 1.5 h. The solvents are evaporated off under vacuum, the residue is dissolved in water, and 8-hydroxyquinoline and unreacted carbonate are removed by extraction into ethyl acetate. The aqueous solution is acidified with 4 N HCl and

Derivative	Yield (%)	M.p. of crude product
BOC-L-Ala	96	80.5–82
BOC-Gly	98	84.5–86.5
BOC-L-Pro	92	131–133.5
BOC-L-Val	91	72–75
AOC-Gly	98	80–83
AOC-L-Try	86	121–123
AOC-L-Ser	95	oil

extracted into ethyl acetate. On evaporation of the solvent, the BOC- or AOC-amino acid crystallizes out in almost pure form.

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[1] *B. Rzeszotarska* and *G. Palka*, Bull. Acad. Polon. Sci. Ser. Sci. chim. *16* [1] (1968), in press.

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tert-Butyl Fluoroformate, a New Reagent for Peptide Syntheses

By *E. Schnabel, H. Herzog, P. Hoffmann, E. Klauke,* and *I. Ugi*[*]

The *tert*-butoxycarbonyl group (BOC) is nowadays frequently used in peptide chemistry for the protection of amino groups. Synthesis of BOC-amino acids[1] is, however, rather laborious. We therefore sought a convenient and generally applicable reagent for introduction of the BOC group – a reagent that could also be stored. *tert*-Butyl fluoroformate *(1)*[3] is obtained from carbonyl chloride fluoride[2] and *tert*-butyl alcohol at *ca.* −25 °C:

$$(CH_3)_3COH + ClCOF \xrightarrow{-HCl} (CH_3)_3COCOF$$
(1)

The ester *(1)* distills unchanged in a vacuum (b.p. −8 to −7 °C/1.9 torr; + 4 °C/15 torr; $n_D^{10} = 1.3591$; $\nu_{CO} = 1830$ cm^{-1}) and may be stored for months at 0 °C to room temperature, depending on its purity. It reacts rapidly (within 1 to 4 h) with α-amino acids at low temperatures (*e.g.*, below 0 °C) at pH 8 to 10, with formation of BOC-α-amino acids. Yields are usually 85–95 %, even when crude ester *(1)* is used.

tert-Butyl Fluoroformate

370 g of *tert*-butyl alcohol is placed in a 2-liter three-necked flask fitted with a stirrer, a thermometer, and a reflux condenser (−60 °C). 595 g of carbonyl chloride fluoride is condensed in at a bath temperature of approximately −70 °C. Part of the *tert*-butyl alcohol dissolves. The contents of the flask are then warmed. When the temperature of the mixture reaches −40 °C distinct refluxing sets in (condenser temperature below −45 °C) and weak evolution of hydrogen chloride starts. After 1½ h the temperature is allowed to rise slowly (over a period of 3 h) to −10 °C, the excess of carbonyl chloride fluoride being removed by allowing the temperature of the reflux condenser to increase and condensing the vapor in a downward low-temperature condenser. Above *ca.* −30 °C evolution of hydrogen chloride becomes distinctly faster and at −20 °C is rapid. At this temperature a clear colorless solution is formed. The solution is stirred at −10 °C until evolution of hydrogen chloride ceases (5–6 h). After short degassing (at *ca.* 200 torr) the crude solution can be used as reagent. Its content of *tert*-butyl fluoroformate amounts to about 60 %, the remainder being mainly *tert*-butyl alcohol. The pure ester can be obtained by distillation. Very similar results are obtained if the reaction is carried out in trichlorofluoromethane as solvent or in presence of isobutene as hydrogen chloride acceptor.

Synthesis of BOC-serine

5.3 g of serine is slurried in a mixture of 10 ml of dioxane and 10 ml of 4 N NaOH and, after cooling to −15 °C, 5 ml of the crude solution of *tert*-butyl fluoroformate is added. The mixture is stirred for 2 h at room temperature, its pH being continuously adjusted to 8.5, then it is filtered and the filtrate is extracted with 30 ml of ether. After acidification with citric acid and addition of sodium chloride to saturation, the solution is extracted four times with 30 ml portions of ethyl acetate. The ethyl acetate extracts are combined, washed five times with 10 ml of saturated sodium chloride solution and twice with water. The solvent is then distilled off, leaving a syrupy residue (9.3 g, 90 %) that crystallizes on standing.

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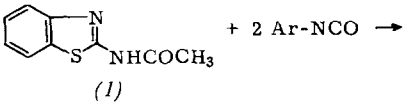
[3] We propose the abbreviation BOCF for compound *(1)*.

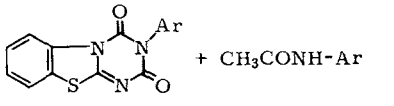
Synthesis of Anellated 1,3,5-Triazine-2,4-diones

By *U. v. Gizycki* and *G. Oertel*[*]

2-Acetylaminobenzothiazole *(1)* reacts with aryl isocyanates in the presence of pyridine (3 h, 140 °C) to give 2-arylbenzothiazolo[3,2-*a*][1,3,5]triazine-1,3-diones *(2)*.

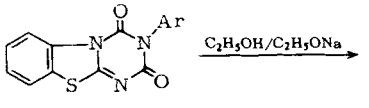


(1)

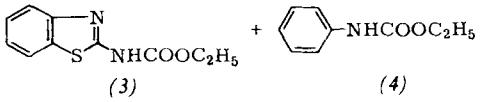


(2)

	Ar	Yield (%)	M.p. (°C)
(2a)	C_6H_5	75	272–274
(2b)	*p*-ClC_6H_4	90	289–293 (decomp.)
(2c)	*m*-ClC_6H_4	87	265–269 (decomp.)
(2d)	*m*-,*p*-$Cl_2C_6H_3$	92	279–282
(2e)	*p*-$NO_2C_6H_4$	87	281–283



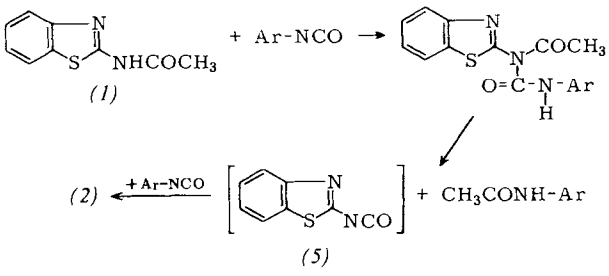
(2a)



(3) *(4)*

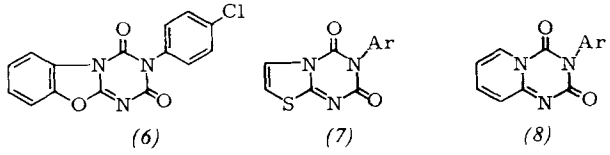
The structure of the products is confirmed by elemental analysis, the mass-spectrometrically determined molecular weight, the position of the carbonyl band in the IR spectrum (double band at 1680 and 1740 cm^{-1}), and by the reaction of *e.g. (2a)* with alcohol to form the urethanes *(3)* and *(4)*.

The formation of *(2a)–(2e)* can be regarded as a 1,4-dipolar cycloaddition of the isocyanatobenzothiazole *(5)*, which occurs as intermediate, to the aryl isocyanate that is present in excess.



(1) *(2)* *(5)*

2-Acetylaminobenzoxazole, 2-acetylaminothiazole, and α-acetylaminopyridine react in a manner analogous to *(1)*, thereby forming 2-(4-chlorophenyl)benzoxazolo[3,2-*a*][1,3,5]-triazine-1,3-dione *(6)*, 2-arylthiazolo[3,2-*a*][1,3,5]triazine-1,3-dione *(7)*, or 2-arylpyrido[1,2-*a*][1,3,5]triazine-1,3-dione *(8)*, respectively.



(6) *(7)* *(8)*

	Ar	Yield (%)	M.p. (°C)
(6)		50	300–305 (decomp.)
(7a)	C_6H_5	53	259–263 (decomp.)
(7b)	*p*-ClC_6H_4	84.5	257–263 (decomp.)
(7c)	*m,p*-$Cl_2C_6H_3$	63	238–241 (decomp.)
(8a)	C_6H_5	63	above 210 (decomp.) [a]
(8b)	*p*-ClC_6H_4	74	234 (decomp.)

[a] Measured in a sealed tube.

It is possible to use the free 2-amino heterocycles in place of the 2-acetylamino compounds; however, at least 3 moles of aryl isocyanate are then required and diarylureas are formed as by-products instead of arylacetamides.

Because of the great variability of the starting materials, the above synthesis of 3-aryl-*s*-triazine-2,5-diones will probably find a wide range of application.

Procedure for the synthesis of (2):

A mixture of 2-acetylaminobenzothiazole *(1)* (1 mole), aryl isocyanate (2.5 mole), and anhydrous pyridine (2.5 mole) is heated to 135 °C for 3–4 h, and then taken up in anhydrous ether (500 ml if experiment is conducted on a 0.1 molar scale). After 30 min, the mixture is filtered under suction. The crude crystals, which are usually pale yellow, are washed thoroughly with ether and alcohol; if necessary, they can be recrystallized from glycol monomethyl ether acetate with addition of activated charcoal. The same general procedure can be used for the synthesis of *(6)–(8)*.

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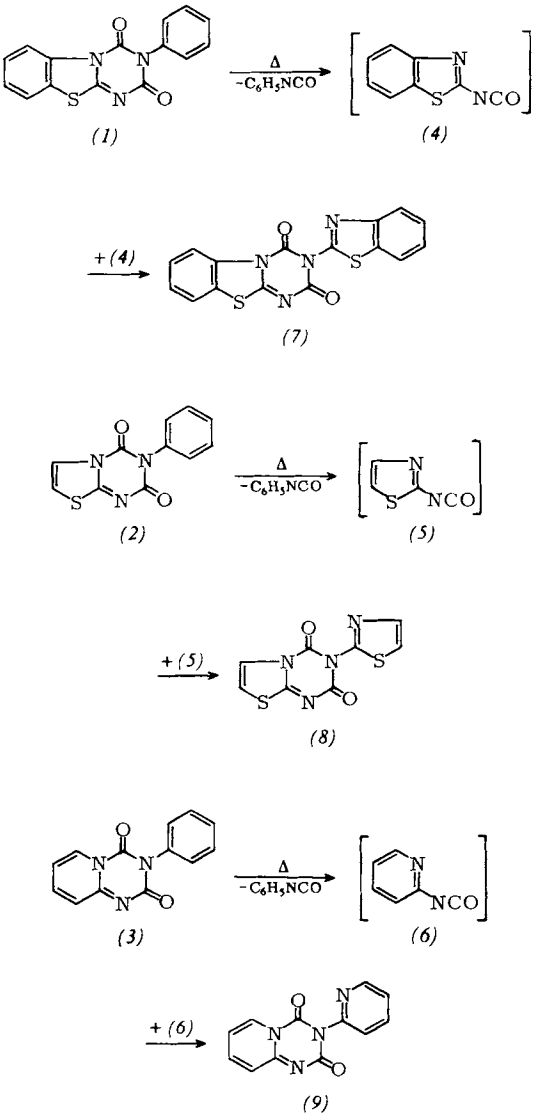
Anellated 1,3,5-Triazine-2,4-diones as Dimers of Heterocyclic Isocyanates

By *U. v. Gizycki* and *G. Oertel* [*]

When the anellated 3-phenyl-1,3,5-triazine-2,4-diones *(1)–(3)* [1] are heated, they lose phenyl isocyanate quantitatively. The heterocyclic isocyanates *(4)*, *(5)*, and *(6)* that are formed in this reaction cyclodimerize to give the crystalline compounds 2-(2-benzothiazolyl)benzothiazolo[3,2-*a*]-[1,3,5]triazine-1,3-dione *(7)*, m.p. above 305 °C (decomp.), 2-(2-thiazolyl)thiazolo[3,2-*a*][1,3,5]triazine-1,3-dione *(8)*, m.p. above 230 °C, or 2-(2-pyridyl)pyrido[1,2-*a*][1,3,5]triazine-1,3-dione *(9)*, m.p. 243–245 °C.



(1) *(4)* *(7)* *(2)* *(5)* *(8)* *(3)* *(6)* *(9)*

The tendency of isocyanates of types *(4)* to *(6)* to undergo cyclodimerization is known in the case of 2-isothiocyanatopyridine, which is also isolable only as a dimer of type *(9)* (S instead of O) [2]. On the other hand, the iminoalkyl isocyanates that are formed when dialkyl amidines are treated with phosgene are isolated only as the monomers [3].

The dimers *(7)* to *(9)* are well crystalline, colorless to pale yellow compounds whose IR spectra show characteristic double bands in the carbonyl region between 1680 and 1705 and 1730 and 1750 cm^{-1}. The NMR spectrum of compound *(8)* contains two four-line systems at δ = 7.15; 7.25; 7.7; 7.8 ppm and δ = 7.82; 7.85; 7.89; 7.92 ppm.

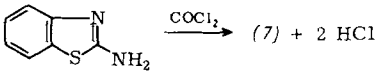
Thermolysis of compounds *(1)* to *(3)* follows the general pattern for anellated 3-aryl-1,3,5-triazine-2,4-diones of this type.

Procedure for the thermolysis and isolation of the products:

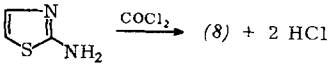
The starting materials *(1)–(3)* are heated to 300 °C at 0.2 torr for 1 h in a suitable distillation apparatus (*e.g.* round bottom flask, column, condenser, receiver); phenyl isocyanate collects in the receiver, which is cooled to −78 °C. The reaction products *(7)–(9)*, which are deposited in the apparatus, may be recrystallized from benzene/acetonitrile. Compound *(9)* can be separated from starting material that has also sublimed over by fractional crystallization from benzene/acetonitrile, *(9)* being more readily soluble than the impurities in this solvent system.

Since compounds *(7)* to *(9)* are to be regarded as dimeric isocyanates their preparation may be carried out according to one of the usual methods of preparing isocyanates, *e.g.*:

1) Reaction of 2-aminobenzothiazole *(10)* or 2-aminothiazole *(11)* with phosgene at −10 °C followed by heating the reaction mixture to 110 °C in chlorobenzene. Compound *(7)* or *(8)* is formed in 71 or 21 % yield respectively.

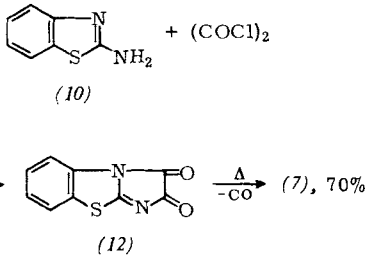


(10)

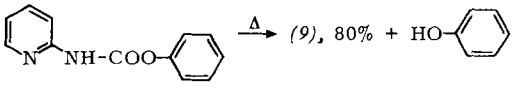


(11)

2) Reaction of *(10)* with oxalyl chloride (5 h, 70 °C, in benzene) and thermolysis of the crude product *(12)*.



3) Thermolysis of phenylurethanes. Compound *(9)* can be obtained particularly easily by this method.



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New Synthesis of *P,P*-Diphenyl-*N,N*-bis(trimethylsilyl)phosphinamide

By *O. Schmitz-DuMont* and *W. Jansen*[*]

A suspension of the potassium salt of diphenylphosphinamide[1] in anhydrous ether reacts with trimethylsilicon chloride to form *P,P*-diphenyl-*N*-trimethylsilylphosphinamide *(1)*.

$$(C_6H_5)_2PNHK + ClSi(CH_3)_3 \rightarrow KCl + (C_6H_5)_2PNH{-}Si(CH_3)_3 \quad (1)$$

The resulting ethereal solution is filtered to remove KCl and evaporated to dryness. The residue is recrystallized from liquid NH_3. Compound *(1)* is obtained, in 60 % yield, as strongly doubly refracting, colorless needles, m.p. 41–42 °C, that are readily soluble is ether, dioxane, and benzene, but difficultly soluble in liquid NH_3 at −70 °C. IR spectrum in KBr: $\bar{\nu}$ (N–H) = 3230 cm^{-1} and $\bar{\nu}_{as}$ (Si–N–P) = 908 cm^{-1}. The structure

$$(C_6H_5)_2P[Si(CH_3)_3]{=}NH$$

is ruled out by the absence of the P=N band, which would appear at about 1300 cm^{-1}, and by the reaction of *(1)* with sulfur to form

$$(C_6H_5)_2P(S)NH{-}Si(CH_3)_3$$

[IR spectrum in $CHCl_3$: $\bar{\nu}$ (N–H) = 3355 cm^{-1}, $\bar{\nu}_{as}$(Si-P-N) = 908 cm^{-1}].

In liquid ammonia, compound *(1)* reacts with potassium amide to give the ether-soluble potassium salt *(2)*.

$$(C_6H_5)_2PN[Si(CH_3)_3]K \quad (2)$$

When an ethereal solution of this salt is treated with trimethylsilicon chloride it yields the bis(trimethylsilyl) compound *(3)*.

$$(C_6H_5)_3PN[Si(CH_3)_3]_2 \quad (3)$$

In compound *(3)*, both trimethylsilyl groups are bonded to the nitrogen atom. The structure

$$(C_6H_5)_3P[Si(CH_3)_3]{=}BN{-}Si(CH_3)_3$$

can be discounted since the P=N bands are not present in the IR spectrum and compound *(3)* reacts with sulfur to give

$$(C_6H_5)_3P(S)N[Si(CH_3)_3]_2$$

Compound *(3)*, which has also been obtained by another method[2], can be crystallized by dissolution in a small amount of benzene and subsequent passage of NH_3 at −20 °C. It forms colorless doubly refracting platelets, m.p. 49–50 °C, is readily soluble in ether, benzene, and chloroform but less so in liquid NH_3. Instead of one Si–N–P vibration at 908 cm^{-1}, the IR spectrum (in KBr) shows two very strong bands at 864 and 918 cm^{-1}, which can be assigned to the asymmetric vibrations of Si–N–P and Si–N–Si.

The recently reported[3] lithium salt

$$(tert\text{-}C_4H_9)_2PN[Si(CH_3)_3]Li$$

reacts differently from *(2)* to yield.

$$(tert\text{-}C_4H_9)_2P[Si(CH_3)_3]{=}N{-}Si(CH_3)_3.$$

Clearly the lone pair of electrons that is present on the phosphorus atom in the potassium salt *(2)* is involved to such an extent in the resonance system of the two phenyl groups that it is no longer available for the bonding of $(CH_3)_3Si^+$ to the phosphorus atom.

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Preparation of Orotic Acid from 4-Chloromethyluracil

By *P. Rambacher* and *N. Kaniss*[*]

The attempted oxidation of readily accessible 4-methyluracil to orotic acid[1] by means of potassium hexacyanoferrate(III) gave the desired product only in poor yield. Oxidation of uracil-4-aldehyde[2] is also of little practical importance because the aldehyde itself is not readily available. However, if hydrogen peroxide is allowed to react, in alkaline solution, with 4-chloromethyluracil *(2)*, which can be easily prepared from urea and γ-chloroacetoacetyl chloride *(1)*, orotic acid is obtained in good yield.

4-Chloromethyluracil (2): A solution of *(1)*, which is prepared by passing chlorine (35.5 g) into a solution of diketene (38.5 ml) in trichloroethylene (125 ml) at 20 °C[3], is added over a period of 45 min to a solution of urea (30 g) in acetic anhydride (200 ml) that contains pyridine (41 ml) at 20 °C. The reaction mixture is stirred for 12 h, and on subsequent cooling with ice 29 g of a coarse crystalline product is precipitated. After recrystallization from 225 ml of glacial acetic acid 23.5 g of 4-chloromethyluracil is obtained. Contrary to values given by other workers for the melting point of 4-chloromethyluracil[4,5], the product we obtained melts at 240 °C with decomposition.

Orotic Acid: Compound *(2)* (8 g) is added over a period of 3 min to a solution of NaOH (12 g) in water (100 ml) and 35 % hydrogen peroxide (20 ml), the temperature being kept below 50 °C. The reaction mixture is stirred for 30 min and then allowed to run into a mixture of conc. hydrochloric acid (74 ml) and water (200 ml), whereupon orotic acid is precipitated (yield 6.5 g). The orotic acid obtained is practically pure and crystallizes with one mole of water. The product of the above synthesis is identical with that prepared from oxaloacetic ester and urea[6] or thiourea[7].

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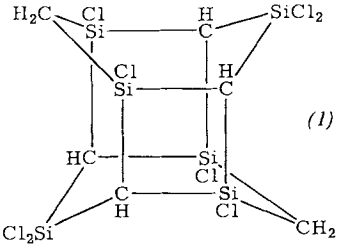
A Carbosilane $Si_6Cl_8C_6H_8$ with an Asterane Structure

By *G. Fritz*, *R. Haase*, and *H. Scheer*[*]

The compound $Si_6Cl_8C_6H_8$ *(1)* was isolated from the products of pyrolysis of CH_3SiCl_3. It is formed alongside 2,2,4,4,6,6,8,8-octachloro-2,4,6,8-tetrasilabicyclo[3.3.0]oct-1(5)-ene *(2)*[1].

The mass spectrum of *(1)* shows the molecular ion having the lowest isotopic masses at m/e = 527.67428 (the formula $Si_6Cl_8C_6H_8$ gives a molecular weight of 532 calculated for the lowest isotopic masses). The ^1H–NMR spectrum of *(1)* contains a resonance line at 94 Hz and a second one at 115 Hz in an intensity ratio of 1:1; these are ascribed to CH protons. Si–CH_3 can be ruled out on the basis of the positions of these signals. The number of protons in *(1)* could be determined ^1H–NMR spectroscopically by carrying out measurements on a mixture of known proportions of *(1)* and octamethylcyclotetrasiloxane and integrating the area of the signals arising from the protons in this mixture. Compound *(1)* contains two sets of four equivalent protons which are present in two CH_2 groups and four CH groups. According to their chemical properties, the eight chlorine atoms in compound *(1)* are all bonded directly to silicon atoms. The structure 1,3,3,5,7,9,9,11-octachloro-1,3,5,7,9,11-hexasilapentacyclo[6.4.0.0^{2,7}.0^{4,11}.0^{5,10}]dodecane *(1)* is in agreement with all experimental results.



(1)

Procedure:

Vaporized CH_3SiCl_3 is pumped by means of a circulating pump through a quartz tube heated to 700 °C, unreacted CH_3SiCl_3 being recirculated to the reaction zone. After 30 days, 2 to 3 liters of a mixture containing numerous silicon compounds is present[2]. On removal of Cl_3Si-CH_2-$SiCl_3$ and $(Cl_2Si–CH_2)_3$ by distillation, a mixture of colorless crystals is precipitated, which consists mainly of *(2)* and *(1)*. Compound *(2)* can be removed from the crystalline product by dissolution in diethyl ether, in which *(1)* is only difficultly soluble. When a saturated solution of *(1)* in CCl_4 at *ca.* 70 °C is allowed to cool slowly to room temperature, *(1)* crystallizes out as highly refractive white crystals, which sublime at 210 °C ($p_{atmospheric}$, N_2 atmosphere).

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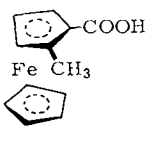
The Absolute Configuration of [2.2]Paracyclophanecarboxylic Acid

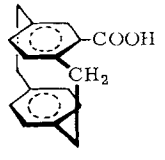
By *H. Falk* and *K. Schlögl*[*]

[2.2]Paracyclophanecarboxylic acid *(2)*[1] as well as metallocenecarboxylic acids, such as methylferrocene-α-carboxylic acid *(1)*[2], can be obtained in optically active form because of their special molecular geometry.

The closely related topology of the environment of the carboxyl group in the acids *(1)* and *(2)* enabled us to determine the absolute configuration of *(2)*, this being the first example of a planar chiral compound[3] with known absolute configuration.



(+)-*(1S)*-*(1)*



(+)-*(S)*-*(2)*

Kinetic resolution of the anhydride of racemic *(1)* with (−)-α-phenethylamine (in dry pyridine at 0 °C) affords the dextrorotatory acid in 6.5 % optical yield[4,5]; the absolute configuration of (+)-*(1)* has been established as (1*S*)[2] by two independent methods[6]. Analogous results were also obtained for other methylmetallocene-α-carboxylic acids[5]. Reaction of the anhydride of racemic [2.2]paracyclophanecarboxylic acid with (−)-phenethylamine yielded also the dextrorotatory carboxylic acid: $[\alpha]_D^{20} = +6.2°$ (*c* = 1 in $CHCl_3$). Optical yield: 3.9 %. The very similar topology of the reaction areas both in *(1)* and in *(2)* ought to determine the result of the kinetic resolution. Hence, the arrangements $COOH/CH_3$ and $COOH/CH_2$ in (+)-*(1)* and (+)-*(2)*, respectively, have the same chiralities, and (+)-*(2)* and its subsequent products[1] should consequently have the absolute configuration (*S*)[3].

In the case of *(2)*, as with the methylmetallocene-α-carboxylic acids[2,5], the salt formed from the (+)-acid and (−)-phenethylamine is the lesser soluble in ethanol. Two consecutive crystallizations afforded a salt ($[\alpha]_D^{20} = +97°$; *c* = 0.5 in $CHCl_3$), from which optically pure acid (+)-*(2)* could be isolated: $[\alpha]_D^{20} = +164°$ (*c* = 0.5 in $CHCl_3$); ref.[1] gives +160° (*via* the brucine salt).

Optically active acetyl[2.2]paracyclophane *(3)* ($[\alpha]_D^{20} = +65°$, *c* = 0.5 in $CHCl_3$) was obtained from (+)-*(2)* by reaction of the acid chloride with $Cd(CH_3)_2$.

Additional information as to the absolute configuration of *(2)* may be gained from ORD and CD studies on the ketone *(3)* and the acid *(2)*, but mainly from chemical correlations. These problems are now under investigation.

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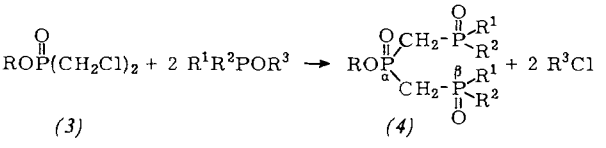
Preparation and Properties of Bis(phosphonylmethyl)phosphinates and Bis(dihydroxyphosphonylmethyl)phosphinic Acid[1]

By *Ludwig Maier*[*]

Bis(hydroxymethyl)phosphinic acid *(1)* can be chlorinated with $SOCl_2$[2] or PCl_5[3] to give bis(chloromethyl)phosphinyl chloride *(2)* in excellent yield.

$$(HOCH_2)_2P(O)OH + 3\ SOCl_2 \rightarrow (ClCH_2)_2P(O)Cl + 3\ HCl + 3\ SO_2$$
(1) *(2)*

Esterification of *(2)* with alcohols in the presence of a tertiary amine leads to good yields of bis(chloromethyl)phosphinates *(3)*, which undergo a Michaelis-Arbusov reaction when heated for several hours with trivalent phosphorus esters (phosphites, phosphonites, or phosphinites) at 170–180 °C. The reaction affords bis(phosphonylmethyl)-, bis(phosphinylmethyl)-, and bis(oxophosphinomethyl)phosphinates *(4)* in very good yields.



(3) *(4)*

	R	B.p. (°C/torr)	n_D^{20}	Yield (%)	^{31}P–NMR (ppm) [a]	^1H–NMR (δ) [b] $ClCH_2$	$POCH_2$
(3a)	CH_3	74–78/0.05	1.4878 [d]	79.5		3.75 (8.6)	3.87 (10.7) [c]
(3b)	C_2H_5	104–106/1.0	1.4809 [e]	86.0	−39.7	3.72 (8.6)	4.23 (8.3)
(3c)	n-C_4H_9	85–93/0.05	1.4758	93.0	−37.8	3.74 (8.6)	4.16 (7.3)

[a] With 85% H_3PO_4 as external standard. — [b] With tetramethylsilane as internal standard in $CDCl_3$. The coupling constants J_{PH} (Hz) are given in parentheses. — [c] $POCH_3$ group. — [d] Lit. [4] b.p. 79–80 °C/0.03 torr, $n_D^{20} = 1.4885$. — [e] Lit. [2,5]: b.p. 104–106 °C/1.5 torr, $n_D^{25} = 1.4780$.

	R	R^1	R^2	B.p. (°C/torr)	n_D^{20}	Yield (%)	^{31}P–NMR (ppm) [a] P_α	P_β	α:β
(4a)	C_2H_5	C_2H_5O	C_2H_5O	146–153/10^{-3}	1.4610	72.5	−37.3	−20.0	1:2
(4b)	C_4H_9	C_2H_5O	C_2H_5O	oil [b]	1.4580	93.0	−37.4	−20.4	1:2
(4c)	C_4H_9	iso-C_3H_7O	iso-C_3H_7O	oil [b]	1.4475	75.5	−37.3	−18.5	1:2
(4d)	C_4H_9	C_4H_9O	C_4H_9O	oil [b]	1.4558	98.8	−37.4	−20.7	1:2
(4e)	C_2H_5	C_4H_9O	C_6H_5	oil [b]	1.5318	86.0	−38.8	−33.6	1:2
(4f)	H	C_6H_5	C_6H_5	m.p. 246–250 °C		83.0			

[a] With 85% H_3PO_4 as external standard. — [b] Decomposes on distillation.

Compound *(4f)* is formed by loss of ethylene at the reaction temperature of 170 °C. The same cleavage has been observed with other phosphinates[6].

The structures of compounds *(4a)*–*(4f)* were proved by ^{31}P- and ^1H–NMR spectroscopy. The ^1H–NMR spectrum of *(4a)* contains signals for CH_3 at δ = 1.30 (triplet, J_{HH} = 7 Hz, 15 H), PCH_2P at δ = 2.80 (quartet, $J_{P_\alpha H}$ = 18.5 Hz, $J_{P_\beta H}$ = 20.3 Hz, 3.94 H), $P_\alpha OCH_2$ at δ = 4.18, $P_\beta OCH_2$ at δ = 4.21 (J_{HH} = 7 Hz, J_{PH} = 7.8 Hz in both cases, total number of protons 10.13 H).

Hydrolysis of *(4a)* by refluxing with conc. HCl gives the free acid $HO(O)P_\alpha[CH_2P_\beta(O)(OH)_2]_2 \cdot 2\ H_2O$ as a viscous oil which does not crystallize but which gives a crystalline cyclohexylamine salt, m.p. 205.2 °C. On titration this acid behaves as a tetrabasic acid with breaks at pH = 5.2 (three equivalents) and at pH = 8.8 (one equivalent). The fifth proton can be titrated only after addition of NaCl. The ^{31}P–NMR spectrum of the acid shows signals at −37.3 ppm (P_α) and −17.5 ppm (P_β) in an intensity ratio of 1:2; its ^1H–NMR shows signals for PCH_2P at δ = 3.15 (quartet, $J_{P_\alpha H}$ = 18.2 Hz, $J_{P_\beta H}$ = 20.3 Hz, 4 H) and for OH + H_2O at δ =

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5.68 (singlet, 8.75 H). The acid is an excellent chelating agent for metal ions.

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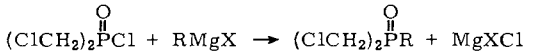
Preparation and Properties of Bis(phosphonylmethyl)alkylphosphine Oxides and the Corresponding Acids[1]

By *Ludwig Maier*[*]

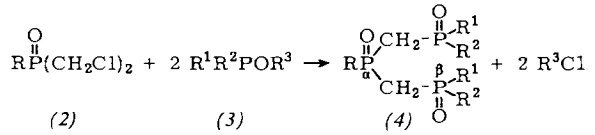
Bis(chloromethyl)phosphinyl chloride *(1)*, which is now readily accessible[1], reacts with Grignard compounds to give bis(chloromethyl)phosphine oxides *(2)* in moderate yields. Like the corresponding phosphinates[1], these compounds undergo a Michaelis-Arbusov reaction when heated for several hours with trivalent phosphorus esters *(3)* (phosphites, phosphonites, or phosphinites) at 170–180 °C to afford bis(phosphonylmethyl)-, bis(phosphinylmethyl)-, and bis(oxophosphinomethyl)alkylphosphine oxides *(4)* in good yields.



(1) *(2)*

	R	M.p. (°C)	Yield (%)	^{1}H–NMR (δ) [a] $ClCH_2$ group
(2a)	CH_3	45–47 [b]	68.5	3.75 (7.0)
(2b)	C_2H_5	42–44	35.5	3.77 (6.8)
(2c)	n-C_8H_{17}	56–59	60.0	3.74 (7.0) [d]
(2d)	n-$C_{12}H_{25}$	57–59 [c]	58.7	3.74 (7.0)
(2e)	C_6H_5	141–143	36.2	3.97 (6.8)

[a] With tetramethylsilane as internal standard in $CDCl_3$. The coupling constants J_{PH} (Hz) are given in parentheses. – [b] Literature [2]: m.p. 49–50 °C. [c] Literature [3]: m.p. 141–142 °C. – [d] ^{31}P–NMR: –45.4 ppm.



(2) *(3)* *(4)*

	R	R^1	R^2	M.p. (°C)	Yield (%)	^{1}H–NMR [a] δ PCH_2P	^{1}H–NMR [a] $J_{P\alpha H}$ (Hz)	^{1}H–NMR [a] $J_{P\beta H}$ (Hz)
(4a)	CH_3	C_2H_5O	C_2H_5O	107	38.3	2.71; 2.76 [b]	15.6	20.5
(4b)	C_2H_5	C_2H_5O	C_2H_5O	45–52	54.0	2.73; 2.77	15.0	20.5
(4c)	$C_{12}H_{25}$	C_2H_5O	C_2H_5O	48–54	85.0	2.73; 2.78	15.0	20.5
(4d)	$C_{12}H_{25}$	C_4H_9O	C_6H_5	oil	49.5	2.93 (broad, not resolved)	–	–
(4e)	$C_{12}H_{25}$	C_6H_5	C_6H_5	63–69	92.5	3.29; 3.53 (broad)	13.0	13.0

[a] With tetramethylsilane as internal standard in $CDCl_3$. – [b] Two quartets are to be seen in each case, indicating the presence of rotational isomers.

The structure of compounds *(4)* was proved by ^{31}P- and ^{1}H–NMR spectroscopy. The ^{31}P–NMR spectrum of compound *(4a)* contains signals for P_α at –34.5 ppm and P_β at –21.3 ppm in an intensity ratio of 1:2. The ^{1}H–NMR spectrum also confirms the given structure: CH_3CH_2 at δ = 1.35 (J_{HH} = 7 Hz, 12 H), PCH_2P at δ = 2.71 and 2.76 ($J_{P\alpha H}$ = 15.6 Hz, $J_{P\beta H}$ = 20.5 Hz, 4.4 H), CH_2OP at δ = 4.15 and 4.18 (J_{HH} = 7 Hz, J_{PH} = 8.5 Hz, 8.05 H), and PCH_3 at δ = 1.81 (J_{PH} = 13.7 Hz, 3.3 H).

Hydrolysis of *(4c)* by refluxing with conc. HCl yields bis(dihydroxyphosphonylmethyl)dodecylphosphine oxide, $C_{12}H_{25}(O)P(CH_2PO_3H_2)_2$, which behaves as a tetrabasic acid on titration, with breaks at pH = 4 (two equivalents), pH = 6.9 (one equivalent), and pH = 9.6 (one equivalent). The acid, the disodium salt (m.p. 405–410 °C), and the tetrasodium salt (m.p. > 460 °C) are highly surface active and are excellent chelating agents.

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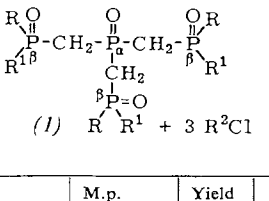
Preparation and Properties of Tris(phosphonylmethyl)phosphine Oxides and the Corresponding Acid[1]

By *Ludwig Maier*[*]

Tris(chloromethyl)phosphine oxide was first prepared by oxidation of tris(chloromethyl)phosphine with nitric acid[2] and it was later obtained in about 30% yield by chlorination of tris(hydroxymethyl)phosphine oxide with PCl_5[3]. We have found that the yield of $(ClCH_2)_3P{=}O$ can be increased to 60% if pure $(HOCH_2)_3P{=}O$ is used as starting material. A yield of 60% of $(ClCH_2)_3P{=}O$ is also obtained when $(ClCH_2)_3P$ is oxidized with bromine, whereas oxidation with H_2O_2 affords a mixture of $(ClCH_2)_3P{=}O$ and $CH_3(ClCH_2)_2PO$, the latter apparently being formed *via* a pseudoallyl rearrangement[4]. When recrystallized from water, tris(chloromethyl)-phosphine oxide forms lustrous crystals having m.p. 100 to 101.5 °C, ^{31}P–NMR (in $CHCl_3$) –39.2 ppm, ^{1}H–NMR (in $CDCl_3$) δ = 3.92 (J_{PH} = 6.5 Hz).

Like the bis(chloromethyl)phosphine oxides[1], tris(chloromethyl)phosphine oxide undergoes a Michaelis-Arbusov reaction when heated for several hours at 170 °C with trivalent phosphorus esters (phosphites, phosphonites, or phosphinites) to give tris(phosphonylmethyl)-, tris(phosphinylmethyl)-, and tris(oxophosphinomethyl)phosphine oxides *(1)* in good yields.



(1)

	R	R^1	M.p. (°C)	Yield (%)	^{31}P–NMR (ppm) [a] P_α	P_β	P_α:P_β
(1a)	CH_3O	CH_3O	169–171	5.7	−31.0	−22.8	1:3
(1b)	C_2H_5O	C_2H_5O	168–170	76.7	−34.0	−21.0	1:3
(1c)	iso-C_3H_7O	iso-C_3H_7O	85–87	85.0	−28.9	−18.6	1:3
(1d)	*n*-C_4H_9O	*n*-C_4H_9O	109–111	61.8	−29.7	−19.6	1:3
(1e)	2-Ethyl-hexyl-O-	2-Ethyl-hexyl-O-	oil	82.0	−29.3	−21.0	1:3
(1f)	C_4H_9O	C_6H_5	oil	83.7	−29.0	−34.7	1:3
(1g)	C_6H_5	C_6H_5	223–234	97.5	−31.0	−24.4	1:3

[a] In $CDCl_3$ with 85% H_3PO_4 as external standard.

Compounds *(1a)–(1e)* possess an extraordinarily high adsorption capacity. For example, a warm 2% solution of *(1b)* in benzene solidifies completely on cooling so that no benzene can be poured off.

The structure of compounds *(1a)–(1g)* was proved by ^{31}P- and ^{1}H–NMR spectroscopy. The ^{31}P–NMR spectrum of *(1b)* contains signals for P_α at −34.0 and P_β at −21.0 ppm (intensity ratio 1:3). The ^{1}H–NMR spectrum also agrees with the structure proposed: $\underline{CH_3CH_2}$ at $\delta = 1.30$ (J_{HH} = 7.0 Hz, 18 H), PCH_2P at $\delta = \overline{2.93}$ ($J_{P\alpha H}$ = 15.6 Hz, $J_{P\beta H}$ = 20.0 Hz, 6 H), and $POCH_2$ at $\delta = 4.15$ (J_{HH} = 7 Hz, J_{PH} = 7.9 Hz, 12.1 H).

Hydrolysis of *(1b)* by refluxing with conc. HCl as well as thermal decomposition of *(1c)* at 190 °C give tris(dihydroxyphosphonylmethyl)phosphine oxide $O{=}P_\alpha[CH_2P_\beta O_3H_2]_3$ in quantitative yield. The ^{31}P–NMR spectrum of the acid shows signals for P_α at −37.8 ppm and P_β at −15.3 ppm. On titration, two breaks are recorded at pH = 4.4 (three equivalents) and pH = 10.7 (three equivalents). The acid forms a crystalline cyclohexylamine salt (m.p. 190 °C) as well as trisodium and hexasodium salts. It is an excellent chelating agent.

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ESR Measurements on Nitrogen-Fixing Titanium-Alkali Metal Systems[1]

By *G. Henrici-Olivé* and *S. Olivé*[*]

In recent communications[2,3] we suggested that negatively charged transition metal complexes with alkali metal counterions are formed during the reduction of transition metal salts with alkali naphthalide in tetrahydrofuran. We now present convincing ESR evidence for the existence of such transition metal-alkali metal interaction, in the particular case of dicyclopentadienyltitanium dichloride (Cp_2TiCl_2), after reduction with alkali naphthalide.

Several of the reduced transition metal complexes are able to fix and to reduce nitrogen under mild conditions[4]. A time-dependent nitrogen fixation has also been observed in the case of the titanium compound described here, and particularly after reduction with lithium naphthalide (LiNp), NH_3:Ti in molar ratios of 0.5, 0.7, and 0.96 being obtained after 2, 4, and 16 hours respectively (at $[Cp_2TiCl_2]_0 = 3\times10^{-2}$ mole/l; LiNp: Ti = 6 (mole/mole), and 1 atm of N_2).

If the reduction is carried out under argon, the reaction solution gives the ESR spectrum shown in Fig. 1a. At molar ratios Li:Ti between 3 and 4 this is the only signal observed. Its intensity has a maximum at Li/Ti = 3.5, and is nearly zero at Li/Ti = 4.0. At higher ratios the signal of LiNp appears. The ESR spectrum shown in Fig. 1a disappears if the argon is subsequently replaced by nitrogen. If the reduction is carried out from the very beginning under nitrogen, conditions under which the system fixes N_2, the spectrum does not appear at all.

The predominant hyperfine splitting (HFS) in the spectrum of Fig. 1a has the intensity distribution 1:2:1, indicating the interaction of the unpaired electron(s) of the titanium with two equivalent hydrogen nuclei within the complex. The relatively high coupling constant (see Table 1) points to Ti–H bonds. Each of the three lines is further split into four equidistant lines of equal intensity. In the present system this can be due only to interaction with one Li nucleus (nuclear spin I = 3/2).

Furthermore, a relatively weak interaction with aromatic hydrogen atoms is to be observed which splits each of the twelve lines mentioned into an odd number of very narrow lines, although well resolved only at $T \leqslant 0$ °C. These protons are situated on the Cp-rings, which are not eliminated during the reduction with LiNp. The spectrum also shows pronounced line width effects in the hydrogen as well as in the lithium HFS that are probably due to anisotropy of the g-value and the hyperfine tensors. However, these effects have not yet been quantitatively interpreted.

A very similar spectrum is obtained if the reduction is carried out with NaNp (Fig. 1b; only the high field part of the spectrum is shown). Whereas the 1:2:1 hydrogen splitting is identical for both complexes, the 1:1:1:1 sodium splitting (I_{Na} = 3/2) is considerably greater than that of the lithium

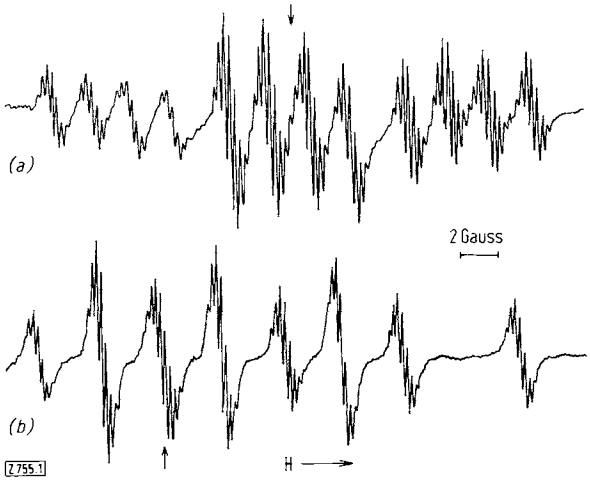


Fig. 1. ESR spectra of the reaction solutions (a) Cp_2TiCl_2 + LiNp and (b) Cp_2TiCl_2 + NaNp at −40 °C in tetrahydrofuran under argon. Arrows indicate center of spectra.

(Table 1); as a consequence, the three quadruplets, which are clearly separated in the upper spectrum, become superimposed in the lower one, the last line of the first and the first line of the last quadruplet coinciding in the center of spectrum 1b.

Table 1. ESR parameters of the complexes formed from Cp_2TiCl_2 and alkali naphthalides.

Alkali naphthalide	g-value	T (°C)	a_H (1:2:1) (gauss)	a_H (aromatic) (gauss)	$a_{alkali\ metal}$ (gauss)
LiNp	1.9938	20	9.5	–	2.5
		0	9.8	0.27	2.4
		−40	9.6	0.27	2.3
		−80	9.5	0.25	2.1
NaNp	1.9938	20	9.5	0.23	6.3
		−40	9.8	0.23	6.7

Second derivative representation of one of the line groups (Fig. 2) shows that the aromatic HFS consists of an odd number of lines. Nine lines can be detected, the intensity distribution of which makes it probable that ten hydrogen atoms, *i.e.* two Cp-rings, are the cause of this HFS. (The extreme lines, the intensities of which are only 0.4/100 of that of the center line, cannot be seen [11]).

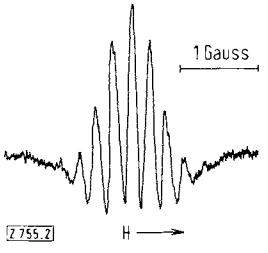
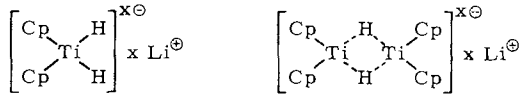


Fig. 2. Second derivative representation of the last high field group of lines of the spectrum of Fig. 1b.

It should be noted that the reaction solution is only weakly paramagnetic at molar ratios $3 < Li:Ti < 4$, and a rough double integration [5] of the ESR spectra intensities accounts only for 10–20 % of the Ti possessing one unpaired electron.

The ESR data suggest either of the two structures:



(1) *(2)*

where x is the number of negative charges, as in the complexes described previously [2, 3]. Presumably several complexes, with varying x, are in equilibrium, but only one is ESR active.

A complex $Cp_2Ti(III)H_2Ti(III)Cp_2$ (*i.e.* a species analogous to *(2)*, but with $x = 0$) has been suggested by *Brintzinger* for the reaction product of Cp_2TiCl_2 and ethylmagnesium chloride in tetrahydrofuran [6]; however, this suggestion was recently rejected in favor of a complex analogous to *(1)* [7]. Also in the present case a dimeric structure containing two Ti(III) species is highly improbable, since no evidence could be detected for the existence of a triplet state (no "half field line" [8], no dipole-dipole interaction in rigid media at low temperatures [9]). The observation, on the other hand, that under nitrogen a molar ratio of NH_3: Ti = 1 (*i.e.* N_2: Ti = 0.5) could not be exceeded, points strongly to a complex containing two Ti atoms. Thus, most probably, structure *(2)* has to be considered, the ESR active species being that with $x = 1$, *i.e.* with only one unpaired electron per complex unit.

The extraordinarily high coupling constants of the alkali metals (Table 1), which indicate about 2.4 % and 2.0 % of unpaired spin density at the Li and Na nucleus respectively, show that these metals must be relatively tightly bound to the Ti, presumably within the inner coordination sphere. This is consistent with the observed low temperature-dependence of the alkali metal splitting, suggesting little or no ionic dissociation.

Concerning the fixation of nitrogen it is assumed at the present stage of the investigation that a similar mechanism is at work as that suggested recently for other reduced metal complexes [4]: the negative charges of the complexes are used up for the reduction of the nitrogen molecule.

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A Productive Method for the Preparation of Geminal Chloronitroso Compounds

By *H. Diekmann* and *W. Lüttke* [*]

Several methods are known for the preparation of geminal chloronitroso compounds $R^1R^2C(NO)Cl$ [1–7], all except one [2] being based on the reaction of oximes with chlorinating agents containing positively polarized chlorine. We have found that treatment of the oximes with alkyl hypochlorites in trichlorofluoromethane represents a method possessing considerable advantages over previous processes: In all cases investigated the yields are almost quantitative; the products are obtained in a high state of purity; and the mild reaction conditions even permit smooth preparation of the very unstable chloronitroso compounds that are derived from aldoximes.

The alkyl hypochlorites used as chlorinating agents are either isolated as such or are prepared in solution [8] by shaking the corresponding alcohol in trichlorofluoromethane with aqueous hypochlorous acid. The solution, whose hypochlorite content can be checked iodometrically, can be used directly for the reaction with the oxime. With most oximes the reaction proceeds smoothly and is complete within a few minutes, even at temperatures as low as −70 °C. It is only in the case of highly substituted reactants, such as *tert*-butyl methyl ketoxime and *tert*-butyl hypochlorite, that the reaction mixture has to stand at room temperature for about half an hour. As a rule, the pre-cooled hypochlorite solution was added dropwise and rapidly to a solution of the oxime kept at −40 °C in a cryostat, the operation being carried out in a darkened room. The reaction mixture was gradually warmed to room temperature while being stirred. If the oxime is insufficiently soluble in trichlorofluoromethane, chloroform is added to the mixture. Product recovery can be executed mildly and simply by virtue of the low boiling point of tri-

chlorofluoromethane (23 °C/760 torr). After the solvent has been evaporated off, if necessary under reduced pressure, the highly volatile, monomeric chloronitroso compounds are fractionally distilled. (Note: to facilitate separation the hypochlorite should be prepared from an alcohol having a sufficiently different boiling point.) The less volatile chloronitroso compounds are either recrystallized from a suitable solvent (*e.g.* methanol) or may be distilled or sublimed under vacuum. Products obtained from aldoximes are precipitated from the reaction solution as colorless nitroso dimers.

No appreciable interference occurs when the reaction is carried out in the presence of compounds having olefinic double bonds. In a competition experiment, a 1:1 mixture of 1-pentene and acetone oxime was treated with 1.05 equivalents of *tert*-butyl hypochlorite; the yield of chloronitroso compound was not affected.

R^1	R^2	$R^1R^2C(NO)Cl$ B.p. (°C/torr)	M.p. (°C)	Yield (%) [b]
H	CH_3		65 (dimer)	> 90
H	C_6H_5		35 (dimer) [a]	> 90
CH_3	CH_3	8/20		> 95
CH_3	$C(CH_3)_3$		122	> 95
CH_3	n-C_4H_9	45/20		> 95
CH_3	$CH_2-C_6H_5$		12	> 95
$-(CH_2)_5-$		52/12		> 95

[a] When heated rapidly the compound melts at about 35 °C with development of a deep blue color, which gives way within a few seconds to the pale yellow color of the rearrangement product α-chlorobenzaldoxime.

[b] The yields were determined spectrophotometrically, measurement being conducted on the n-π* transition of the chloronitroso compound, which lies at about 650 nm. The homogeneity of the product was examined on the basis of this absorption, the NMR spectra, and the melting point or boiling point.

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Asymmetric Synthesis of Geminal Chloronitroso Compounds

By *H. Diekmann* and *W. Lüttke* [*]

Optically active chloronitroso compounds, which are of interest for mechanistic investigations and, on account of the isolated absorption band of their n-π* transition ($\lambda_{max} \approx$ 650 nm), for ORD measurements, were first obtained by *Mitchell et al.* [1–3]. A reaction reported by us [4] opened up the possibility of an asymmetric synthesis of α-chloronitroso compounds by treatment of a suitable oxime with hypochlorites of optically active alcohols. Asymmetric synthesis has advantages over chemical separation for the preparation of rather unstable chloronitroso compounds; moreover, the reaction is less time-consuming but generally it proceeds only stereoselectively. The results obtained on reaction of phenylacetone oxime with a number of different alkyl hypochlorites are given in Table 1. According to the results, the hypochlorite of the readily accessible (−)-isoborneol [5] is, up to the present, the most effective asymmetric reaction partner. The dextrorotatory form of 2-chloro-2-nitroso-1-phenylpropane was obtained only with (−)-neoisopinocampheol; all other alcohols led to the formation of the levorotatory antipodes.

Table 1. Results of the reaction of alkyl hypochlorites of various alcohols with phenylacetone oxime.

Alcohol	$[\alpha]_D^{20}$	React.temp. (°C)	Products $[\alpha]_D^{20}$ [a]
(−)-Isoborneol (1 *R*:2 *R*)	−27.5 ° (c = 0.9; ethanol)	−78	−58 °
(−)-2-Methyl-isoborneol (1 *R*:2 *R*)	−26.2 (c = 2.6; ethanol)	−74	−15.8 °
(−)-Neoiso-pinocampheol (1 *S*:2 *S*:3 *R*)	−35.4 ° (c = 2; benzene)	−76	+18.2 °
(−)-Menthol (1 *R*:3 *R*:4 *S*)	−48 ° (c = 2; ethanol)	−76	−16.4 °
(−)-1-Phenyl-ethanol (*S*)	−47.5 ° (c = 3.6; methanol)	−78	−13.2 °

[a] 2-Chloro-2-nitroso-1-phenylpropane.

Table 2 contains the results obtained on reaction of isobornyl hypochlorite with several different methyl ketoximes.

Table 2.

Oxime	React.temp. (°C)	Product $[\alpha]_D^{20}$
tert-Butyl methyl ketoxime	−70	− 9.8 °
Cyclopropyl methyl ketoxime	−78	−106 °
n-Butyl methyl ketoxime	−78	− 8.4 °
Methyl-i-propyl ketoxime	−78	− 28 °
2,2-Dimethylcyclohexanone oxime	−86	− 8.6 °

The preparations are carried out in the same manner as described in a previous report [4]; however, in order to achieve high stereoselectivity the reactions should be carried out as slowly as possible by reducing the temperature. The reaction products can be worked up by chromatography on silica gel (particle size less than 0.08 mm, deactivated with 10 % water) using petroleum ether (b.p. 35–40 °C) as solvent.

We thank Dr. *F. Woldbye* of the Tekniske Høgskole, Lyngbye (Denmark) for the measurement of an ORD curve of 2-chloro-2-nitroso-1-phenylpropane. It shows the expected Cotton Effect for the absorption maximum of the n-π* transition at 650 nm.

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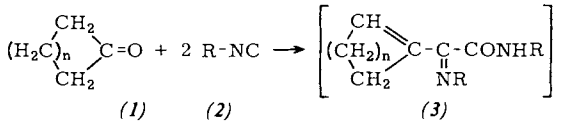
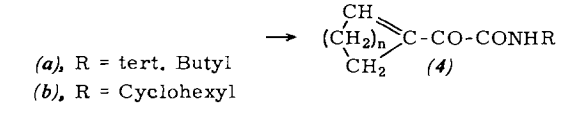
Synthesis of Substituted Oxetane-2,3-diimines from Isocyanides

By *H.-J. Kabbe* [*]

Reaction of alicyclic ketones *(1)* (n = 2–5, 9) with the isocyanides *(2a)* and *(2b)* in the presence of approximately equimolar amounts of boron trifluoride ether affords up to 40 % yields of the unsaturated oxo acid amides *(4)* if the ketimines *(3)* assumed to be formed as intermediates are hydrolyzed by acid at the end of the condensation [1].



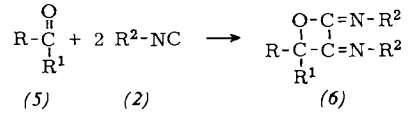
(1) *(2)* *(3)*



(a), R = tert. Butyl
(b), R = Cyclohexyl

(4)

If, however, the reaction is effected in the presence of only catalytic amounts (2–3 mole-%, calculated on the ketone) of boron trifluoride ether and the mixtures are worked up under neutral or weakly basic instead of acid conditions, then the substituted oxetane-2,3-diimines *(6)* are obtained, some of them in very good yield.



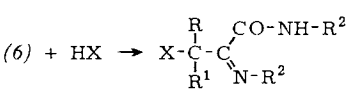
(5) *(2)* *(6)*

R	R^1	R^2	*(6)*, yield (%)	*(6)*, m.p. (°C) [b.p. (°C/torr)]
CH_3	H	*tert*-Butyl	91	[78/12]
CH_3	CH_2Cl	*tert*-Butyl	92	48–50 [65/0.05]
C_6H_5	H	*tert*-Butyl	74	75–76
$-(CH_2)_5-$		*tert*-Butyl	93	55–57
CH_3	CH_3	Cyclohexyl	60	57–59 [120/0.05]
$(CH_3)_2CH$	H	Isobutyl	75	[95/0.01]
CH_3	H	Allyl	53.5	[80/0.06]

Not merely ketones but also aldehydes can be used as the carbonyl components *(5)*; they may contain halogen, ester, ether, nitro, or alkylthio groups.

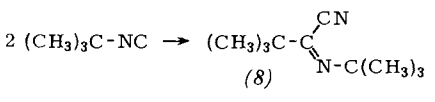
All the oxetanes *(6)* studied so far are characterized by a double band in the IR spectrum between 1720 and 1730 cm^{-1}.

The oxetanes *(6)* may be opened with different reagents H–X (acids, amines, or water) to give amides *(7)*.



(7)

During the course of these investigations it was found that *tert*-butyl isocyanide is dimerized to the nitrile *(8)* in 70 % yield by catalytic amounts of boron trifluoride.



(8)

Synthesis of (6), $R = CH_3$, $R^1 = H$, R^2 = tert-butyl:

Acetaldehyde (88 g, 2 moles), *tert*-butyl isocyanide (460 ml, 4 moles), and light petroleum (400 ml) are stirred together and treated over a period of 15 min with a solution of BF_3-ether (5 ml, 0.04 mole) in ether (200 ml) while being cooled in a CO_2 bath at −15 °C. The temperature of the mixture in a melting ice bath rises from 0 to 20 °C during 20 h. Then the mixture is stirred with saturated sodium hydrogen carbonate solution (400 ml) and extracted with ether. The extract is dried over Na_2SO_4 and distilled, giving *N,N'*-di-*tert*-butyl-4-methyloxetane-2,3-diimine (yield 381 g, 91 %).

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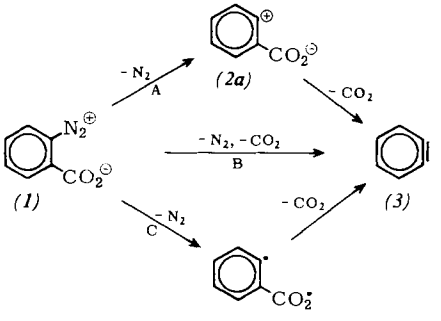
Mechanism of Formation of Dehydrobenzene from Benzenediazonium-2-carboxylate

By *R. Gompper*, *G. Seybold*, and *B. Schmolke* [*]

In recent years benzenediazonium-2-carboxylate *(1)* has been frequently used as starting material for the synthesis of dehydrobenzene *(3)* [1] since it is easy to prepare [2] and reacts at low temperatures to form secondary products of dehydrobenzene in relatively high yields [3].

The decomposition of *(1)* into *(3)* could proceed either synchronously (mechanism B) or asynchronously (mechanisms A and C).

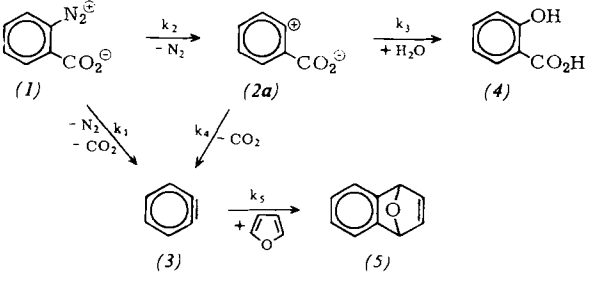


(1) *(2a)* *(3)*

Reaction of *(1)* with water leads to the formation of salicylic acid *(4)* [4] in good yield. This can be assumed to be an S_N1-reaction in which the intermediate *(2a)*, or a similar intermediate is formed (preliminary measurements of the rate of decomposition of *(1)* in acetonitrile/water mixtures support this assumption).

If *(1)* is allowed to decompose in acetonitrile/water/furan mixtures, salicylic acid *(4)* and 1,4-epoxy-1,4-dihydronaphthalene *(5)* can be isolated in overall yields of *ca.* 85 %.

If *(3)* were liberated from *(1)* *via* mechanism B the formation of *(5)* and of *(4)* would be two independent reactions, in which the water concentration does not have any influence on the yield ratio $Q_1 = (5)/(4)$ (which has the constant value $K_B = k_1/k_2$).



(1) *(2a)* *(4)* *(3)* *(5)*

In the case of mechanism A, however, Q_1 does depend on the water concentration. If concentration values are chosen such that $[H_2O] \gg [(1)]$ and it is assumed that $k_5 \gg k_4$[5] then by the method of the quasistationary state

$$Q_1 = k_4/k_3\,[H_2O] \text{ or } Q_1\,[H_2O] = k_4/k_3 = K_A$$

Results obtained in nine experiments are shown in Table 1 [the yields of *(5)* and *(4)* were determined gravimetrically:

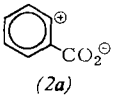
Table 1. Formation of *(4)* and *(5)* from *(1)* [results from nine experiments].

Expt.	[(1)] (mmole/liter)	$[H_2O]$ (mole/liter)	[Furan] (mole/liter)	Total Yield [a] (%)	Q_1 mmole *(5)* / mmole *(4)*	K_A (mole/liter)
a	61.1	1.88	1.48	90.4	2.50	4.70
b	78.0	3.70	1.48	89.7	1.21	4.48
c	69.3	5.56	1.48	86.3	0.71	3.95
d	46.9	1.30	1.13	82.4	2.94	3.93
e	57.6	2.59	1.13	81.8	1.83	4.74
f	43.6	3.86	1.11	94.8	1.28	4.94
g	32.2	2.23	0.56	84.0	1.74	3.88
h	18.7	2.30	0.88	83.4	1.61	3.71
i	21.2	2.24	1.14	84.4	1.97	4.42
					Mean =	4.30

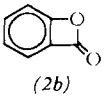
[a] Determined as α-naphthol + dibromosalicylic acid.

(5) as α-naphthol[6], *(4)* as dibromosalicylic acid[7]; the reactions solutions – 150 ml to 250 ml – were homogeneous throughout the duration of the experiment (36 h at 25 °C)]. The ratio Q_1 is inversely proportional to the water concentration; the constancy of K_A appears, in view of the complicated working up, to be quite satisfactory. The experiments (g) to (i) in which the water concentration was kept constant and the furan concentration was varied, show that not only is Q_1 independent of the furan concentration but also indicate that the whole of *(3)* is trapped by furan with formation of *(5)* [phenol, which could be formed from *(3)* and water, could not be detected gas chromatographically].

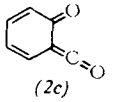
The reactions leading to the formation of *(3)*, *(5)*, and *(4)* from *(1)* are not independent of one another, but involve a common step and thus a common intermediate. Concerning the nature of this common intermediate, one must take into consideration the fact that the valence isomers *(2c)* and



(2a)



(2b)



(2c)

(2b) could in fact exist in a rapidly established thermodynamic equilibrium with the intermediate *(2a)*. One would expect that the intermediate *(2a)* would react with the excess of acetonitrile available (cf. ref.[8]). However, the formation of *N*-acetylanthranilic acid could not be detected. Further, the fact that the formation of *(3)* is possible in such a nucleophilic solvent as dimethyl sulfoxide[9] indicates (cf. also ref. [10]) that *(2a)* plays but a secondary role. The decomposition of *(1)* in acetonitrile/methanol/furan mixtures affords further information about the nature of the intermediate (reaction conditions analogous with those given above). The reaction mixture contains mainly *(5)*, some methyl salicylate, and a little anisole. The yield ratio Q_2 = [*(5)* + anisole]/[methyl salicylate] is inversely proportional to the methanol concentration (Table 2).

Table 2. Formation of *(5)*, anisole, and the methyl ester of *(4)* from *(1)* [results from six experiments].

Expt.	[(1)] (mmole/liter)	$[CH_3OH]$ (mole/liter)	[Furan] (mole/liter)	Q_2 mmole ((5) + anisole) / mmole (4)-methyl ester	$Q_2\,[CH_3OH]$ (mmole/liter)
a	12.7	5.00	1.06	19.25	96.3
b	19.3	6.24	1.18	16.50	102.9
c	18.0	7.50	1.10	14.35	107.6
d	19.4	8.77	1.19	12.15	106.7
e	12.8	10.14	0.99	10.18	103.2
f	16.9	11.32	1.04	9.19	104.0
				Mean =	103.4

The results indicate that *(5)* and methyl salicylate are also formed *via* a common intermediate.

Methyl salicylate can be formed from *(2b)* as well as from *(2c)*. However, the only route to *(3)* *via* elimination of CO_2 is from *(2b)*. If *(2b)* were in equilibrium with *(2c)* the equilibrium would be accessible also from *(2c)* or from suitable precursors; investigation of this is in progress. There are several indications that suggest the occurrence of *(2b)* (cf. ref.[3]); however, no conclusive evidence is as yet available.

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Hydrogen-Deuterium Exchange in Alkoxyalkylcarbene-Transition Metal Complexes

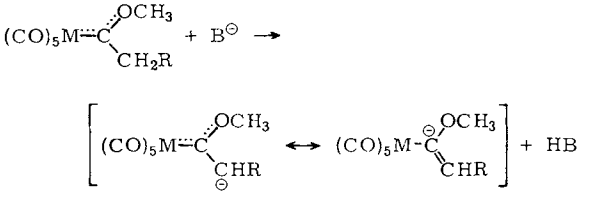
By *C. G. Kreiter*[*]

Replacement of a hydrogen atom in methane by substituents of the type $-NO_2$, $-CHO$, $-COCH_3$, or $-COOR$ leads to enhanced reactivity of the remaining methyl hydrogen atoms. A measure of this reactivity is afforded, for example, by the comparison of coupling reactions of active methylene compounds[1] or by exchange of the protons on the C-atom for deuterium[2]. The bonding of the carbene residue in pentacarbonylphenylmethoxycarbenechromium(0), as determined by X-ray analysis[3], resembles closely that of methyl benzoate. The reactions of various carbene complexes with ammonia or amines also show a certain similarity between the complexes and esters [5]. We have investigated whether the protons of a methyl group attached to the RO–C(M)– residue are as activated as those of a methyl group attached to a RO–C(O)– residue.

$(CO)_5MC(CH_3)OCH_3$ [M = Cr, Mo, W] and π-$CH_3C_5H_4(CO)_2MnC(CH_3)OCH_3$[4] were dissolved in [*O*–D]-methanol at room temperature (99 % D). When catalytic amounts of sodium methoxide[6] are added to the mixture its ^1H–NMR spectrum reveals an immediate exchange of the protons of the $C-CH_3$ group in the carbene residue of the complex. However, the exchange proceeds so rapidly that it cannot be followed ^1H–NMR spectroscopically. Nitromethane is the only substituted methane that exhibits such a rapid H/D exchange under similar conditions.

In the case of acetone and of acetonitrile the rate of exchange of methyl protons for deuterium is orders of magnitude slower[2]. No H/D exchange has been observed in the case of methoxymethylcarbene complexes in [*O*–D]-methanol without sodium methoxide, or in presence of some [D_2]-sulfuric acid.

Ethylmethoxycarbenepentacarbonylchromium(0) possesses activated methylene protons which are similarly replaced very rapidly by deuterium. One can observe the disappearance of the signal of the methylene protons and the collapse of the three components of the triplet of the methyl protons to a somewhat broadened singlet. We assume that the H/D exchange is made possible by virtue of the ready formation of an anion. Stabilization would be possible by the donation of the negative charge in the "vacant" p_z orbital of the carbene C-atom. Methanolic solutions of equivalent amounts of



$(CO_5)MC(CH_2R)OCH_3$ and sodium methoxide become deep red-brown at room temperature and the corresponding hexacarbonylmetals very soon separate out. The compounds deuterated on the $C-CH_2R$ group can be isolated from the solutions in [*O*–D]-methanol with small concentrations of methoxide.

Similarly, the alkoxy group is slowly exchanged in the presence of base catalysts. Ethoxymethylcarbenepentacarbonylchromium(0) reacts with an excess of methanol in the presence of sodium methoxide within a few days at room temperature to give almost quantitative yields of pentacarbonylmethoxymethylcarbenechromium(0).

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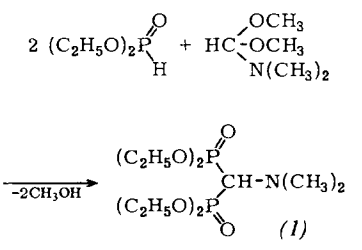
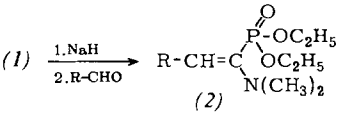
Synthesis of Carboxylic Acids *via* PO-Activated Olefination of Tetraethyl Dimethylaminomethylenediphosphonate

By *H. Gross* and *B. Costisella*[*]

We have succeeded in preparing the hitherto unknown compound tetraethyl dimethylaminomethylenediphosphonate *(1)* (yield 60–62 %, b.p. 114–115 °C/0.03 torr) by warming a mixture of dimethylformamide acetal and 2 moles of diethyl phosphite to 60–80 °C for a short period and then distilling the product under high vacuum. The NMR spectrum of *(1)* (in CCl_4, 60 MHz) contains the following signals: $\tau_{CH_3-CH_2}$ = 8.68 triplet (J = 7 Hz), 5.88 multiplet (J = 4 Hz); $\tau_{N(CH_3)_2}$ = 7.41 triplet (J = 1.5 Hz); $\tau_{=CH-}$ = 6.80 triplet (J = 25 Hz); proton ratio = 12:8:6:1.



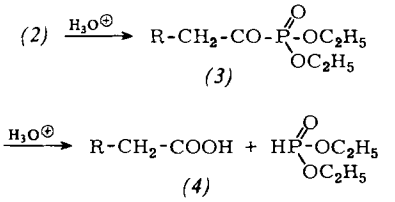
If compound *(1)*, which contains a highly acidic proton, is allowed to react first with sodium hydride and then with aldehydes (equimolar quantities) in dioxane solution according to the Horner olefination method[1], the likewise hitherto unknown compound diethyl 1-dimethylaminoalkenylphosphonate *(2)* is obtained by pouring the reaction mixture into water, extracting into ether, and then distilling the organic phase.



	R	B.p. (°C/torr)	Yield (%)
(2a)	C_6H_5	105–106/0.01	66
(2b)	4-NO_2–C_6H_4		64
(2c)	3,4-(–OCH_2O–)C_6H_3	150–153/0.02	75
(2d)	C_6H_5–CH=CH–	135–139/0.01	60

NMR spectrum of *(2a)*: $\tau_{CH_3-CH_2}$ = 8.67 triplet (J = 7Hz), 5.9 multiplet (J = 8 Hz); $\tau_{N(CH_3)_2}$ = 7.4 doublet (J = 2 Hz); $\tau_{=CH-}$ = 3.36 doublet (J = 15 Hz); $\tau_{C_6H_5}$ = 2.48 to 2.82 multiplet; proton ratio = 6:6:4:1:5.

If the phosphonates *(2)* are dissolved in 2 N hydrochloric acid, the acylphosphonates *(3)* are precipitated as oils that can be purified by distillation.



NMR spectrum of *(3)* [R = C_6H_5, b.p. 100 °C/0.04 torr, yield 66 %]: $\tau_{CH_3-CH_2}$ = 8.72 triplet (J = 7 Hz), 5.96 multiplet (J = 4 Hz); τ_{CH_2} = 6.5 singlet; $\tau_{C_6H_5}$ = 2.81.

	R	M.p. (°C)	Yield (%) [a]
(4a)	C_6H_5	72–74	75 (44)
(4b)	4-NO_2–C_6H_5	143–145	80 (46)
(4c)	3,4-(–OCH_2O–)C_6H_3	126–128	90 (68)

[a] The yields are calculated with respect to pure or crude *(2)*; those in parentheses are calculated on the amount of aldehyde.

Acylphosphonates of type *(3)* are hydrolyzed smoothly in strongly acid media to carboxylic acids *(4)* and dialkyl phosphites[2]. It is not necessary to isolate *(3)* in order to prepare the carboxylic acids *(4)*; if the crude product *(2)* is dissolved in concentrated hydrochloric acid, rapidly heated to boiling, and then cooled the required carboxylic acid is precipitated in some cases in pure form (according to its melting point).

This process permits the ready synthesis of carboxylic acids from the aldehydes containing one less carbon atom. Ketones do not react under the conditions described.

Diethyl 1-dimethylaminostyrylphosphonate (2a)

A solution of *(1)* (3.31 g, 0.01 mole) in dry dioxane (5 ml) is added dropwise at room temperature to a suspension of NaH (0.24 g, 0.01 mole) in dry dioxane (5 ml) (liberation of H_2, temperature of reactants increases to 38 °C). When the reaction has subsided, benzaldehyde (1.06 g, 0.01 mole) is added and the reaction mixture is heated to 60 °C for 1 h. The mixture is finally poured into water, extracted three times with ether, and dried over Na_2SO_4. 1.70 g (66.5 %) of *(2a)* is obtained on distillation.

Phenylacetic acid (4a)

A sample of *(2a)* (2.83 g) is boiled briefly with conc. HCl (5 ml), the mixture is allowed to cool and diluted with water; the acid that is precipitated is filtered off under suction. 1.0 g (74 %) of *(4a)* is obtained after drying over P_4O_{10}.

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High-temperature Synthesis of Amino Acids in the System Acetylene/Ammonia/Carbon Dioxide

By *K. Samochocka, A. L. Kawczynski*, and *M. Taube* [*]

The abiogenetic synthesis of amino acids under conditions such as those prevailing in a primeval atmosphere[1] is usually assumed[2] to proceed according to the scheme of the Strecker reaction:

$$\text{Substrate} \xrightarrow{\text{Pyrolysis}} \text{Radicals} + H_2$$

$$\text{Radicals} + {}^*CO_2 \rightarrow {}^*R\text{–}C(=O)H$$

$${}^*CO_2 + H_2 \rightarrow {}^*CO + H_2O$$

$${}^*CO + NH_3 \rightarrow H{}^*CN + H_2O$$

$$C_2H_2 + NH_3 \xrightarrow{\text{Pyrolysis}} \text{HCN} + \text{other products}$$

$${}^*R\text{–}C(=O)H + HCN \rightarrow {}^*R\text{–}HC(OH)\text{–}CN$$

$${}^*R\text{–}HC(OH)\text{–}CN + NH_3 \rightarrow {}^*R\text{–}HC(NH_2)\text{–}CN$$

$${}^*R\text{–}HC(NH_2)\text{–}CN \xrightarrow{\text{Hydrolysis}} {}^*R\text{–}CH(NH_2)\text{–}CO_2H$$

If $^{14}CO_2$ is used in the synthesis, and if the reaction does in fact proceed according to the Strecker reaction scheme, the amino acids which are formed ought to be labeled in the side chain and in the carboxyl groups.

We used the following gas mixtures:

(i) $C_2H_2 + NH_3$ (1:1 mole/mole)

(ii) $C_2H_2 + NH_3 + {}^{14}CO_2$ (1:1:1)

The gas mixtures were fed through a quartz tube heated at 600 °C (diameter of tube 0.8 cm; rate of flow of gas 500 to 520 cm^3/min) and then collected in water. The resulting solution was heated at 70 °C for 35 hours and then evaporated under vacuum. The residue thus obtained was taken up in 5 N HCl and heated at 70 °C for 5 hours. Subsequent evaporation in vacuum afforded the amino acids, which were analyzed by high-voltage paper electrophoresis (50 V/cm). The results of analysis are given in the Table. In both systems the total yield of amino acids amounted to about 1 % (referred to the amount of ammonia used).

$C_2H_2 + NH_3$		$C_2H_2 + NH_3 + {}^{14}CO_2$	
Gly	β-Ala	Gly	β-Ala
Ala	β-Phe	Ala	β-Phe
Phe	Try	Phe	Leu
Ser	Asp	Ser	Val
Thr		Thr	Lys
			Arg

Remarkably, not one of the amino acids obtained proved to be radioactively labeled. Further, we did not obtain any radioactively labeled carboxylic acids[3], and in the system $C_2H_2 + NH_3 + CO_2$ no carbohydrates. It follows then that the CO_2 does not take part in the reaction; nor does the reaction proceed according to the Strecker reaction scheme. The latter statement is further supported by the fact that we obtained β-amino acids that cannot occur in a Strecker type synthesis.

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Macromolecular Colloquium

The Macromolecular Colloquium was held in Freiburg/Br. from February 29 to March 2, 1968.

From the lectures:

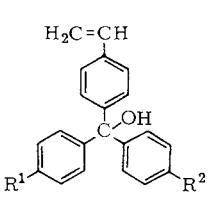
Recent Studies on the Preparation of Stable Polyradicals

By *D. Braun, R. J. Faust,* and *B. Meier*[*]

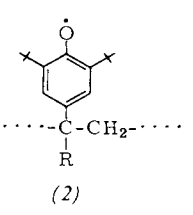
Whereas neutral macromolecular substances and polyions have been extensively studied, very little is known about macromolecules having stable free-radical monomer units. Polymers having an unpaired electron in many or, in the ideal case, in all of their monomer units are known as polyradicals[1].

Polymeric triarylhydrazyls and polyradical-ions have already been described[2]. Polycarbon radicals and polyoxygen radicals have now been synthesized.

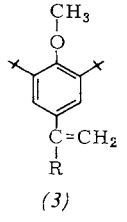
Polymers or copolymers of 4-vinyltriarylmethanols *(1)* can be converted into polymeric triarylmethyl chlorides, which react with zinc or alkali metals in the complete absence of water and oxygen to form polymeric triarylmethyl radicals. The polyradicals react with an excess of alkali metal to form polyanions; reaction with oxygen leads first to polymeric peroxy radicals, which then crosslink with formation of peroxides. The poly-4-vinyltriarylmethyl radicals disproportionate slowly in light to give diamagnetic products containing triarylmethane and quinodimethane groups.



(1a), $R^1 = R^2 = H$
(1b), $R^1 = H$; $R^2 = C_6H_5$
(1c), $R^1 = R^2 = C_6H_5$



(2)



(3)

R = H, CH_3
—+ = $C(CH_3)_3$

Polyphenoxyls of the type *(2)* can be prepared by dehydrogenation of sterically hindered polyphenols with lead dioxide in an inert atmosphere. The starting materials are obtained *e.g.* by cationic homopolymerization or copolymerization of 4-vinyl- or 4-isopropenyl-2,6-di-*tert*-butylphenol, or by polymerization of *(3)* followed by cleavage of the ether linkages with alkali metal. When R = CH_3, a polyradical analogous to 2,4,6-tri-*tert*-butylphenoxyl is obtained; this polyradical is very stable in an inert atmosphere. The polyphenoxyls obtained with R = H are much more stable than the low molecular weight model.

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Nuclear Magnetic Resonance Spectroscopy of Tactic Copolymers

By *E. Klesper, H.-J. Cantow,* and *W. Gronski*[*]

If we consider the formation of binary copolymers from two monosubstituted α-olefins, there are many possible arrangements since each of the monomer units being built into the chain has a pseudoasymmetric carbon atom. Thus, for example, the position of the ^1H–NMR signals of the α-methyl groups in copolymers of methyl methacrylate and methacrylic acid is influenced by the nature and the d or l position of the substituents on the monomer units in the immediate vicinity. There are 20 possible magnetically distinct triads of monomer sequences, six being isotactic, six syndyotactic, and eight heterotactic. In view of the relatively broad line width resulting from the limited mobility of polymer chains, the separation of 20 signals hardly seems possible.

We therefore used Ziegler-Natta catalysts to prepare highly syndyotactic poly(methyl methacrylate), from which cosyndyotactic methyl methacrylate (a) – methacrylic acid (b) copolymer was prepared by partial hydrolysis.

The number of triads then decreased to six; these are the two "chemically pure" (aaa and bbb) and the four composite triads, *i.e.* two resulting from "chemical nodes" between two blocks (aab and abb) and two being due to chemically alternating groups (aba and bab).

The corresponding resonance positions were found by measurements in pyridine at 100 MHz. The signals were assigned on the basis of model substances, chemical shift, results of changing solvents, and statistical considerations. Comparison of the experimentally determined population of the various triads with the calculated values indicates that the hydrolyzing agent attacks randomly along the syndyotactic polymer chain.

On partial hydrolysis of highly isotactic poly(methyl methacrylate), only four strong resonances were found, and these have been tentatively assigned. Improved resolution of proton magnetic resonance signals became possible when we carried out our measurements with the Varian super-conducting nuclear magnetic resonance spectrometer at 220 MHz.

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Incompatibility of Polymer Mixtures

By *R. Kuhn, H.-J. Cantow,* and *W. Burchard*[*]

Light-scattering measurements on a polystyrene (PS) having $\bar{M}_w \approx 10^5$ in the isorefractive polymer/solvent system polymethyl methacrylate (PMMA)/benzene[1] showed that the second osmotic virial coefficient A_2 of PS is strongly dependent on the average viscometric molecular weight M_v and on the concentration of the PMMA, whereas between 20 and 60 °C it is practically independent of the temperature. If c_Θ is the PMMA concentration at the Θ point, at which A_2 of the PS is zero, and if the measured PMMA concentration c is normalized to c/c_Θ, one obtains an unambiguous relationship between A_2 and c/c_Θ, which is independent of the molecular weight and the molecular weight distribution of the PMMA used.

The influence of the monomer, dimer, and trimer and of the hydrogenated monomer of methyl methacrylate on A_2 of the PS is also discussed as a function of the volume ratio of benzene to oligomer. The PS studied forms a Θ system in PMMA at a degree of polymerization of $\bar{P}_w \approx 17$ without the addition of benzene.

The dependence of the phase separation in PMMA/PS/benzene on the variables of the system is assessed from the first cloud point. Predictions concerning compatibility limits have been satisfactorily confirmed with solvent-free films of PMMA/PS [1].

Measurement of the angular dependence of the scattered light for a PS having $\bar{M}_w \approx 10^6$ showed that the c_Θ concentrations are practically independent of the molecular weight of the PS, and that the radii of inertia r of the PS decrease only very slightly with increasing PMMA concentration, and are about 50 % higher at the Θ point than the r_Θ values found in binary solutions. The measured radii of inertia are practically independent of temperature so long as there is no visible clouding. The radii of inertia increase very rapidly at the visual cloud point.

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Polymerization of Unsaturated Highly Strained Ring Systems with Ziegler-Natta Catalysts and with Group VIII Metal Halides

By *G. Dall'Asta* [*]

Monomers such as cyclobutene, 1-methylcyclobutene, 3-methylcyclobutene, bicyclo[4.2.0]oct-7-ene, and bicyclo-[3.2.0]hepta-2,6-diene owe their remarkable ease of polymerization to the highly strained cyclobutene ring. These monomers can therefore be polymerized both with Ziegler-Natta catalysts and with the less active halides of metals of the group VIII triad in polar solvents. The polymerization proceeds either with opening of the double bond or with ring opening. When the monomer contains more than one ring, polymerization always proceeds *via* the more energetic four-membered ring.

The chemical structure of the polymer is determined mainly by the transition element in the catalyst system, though the metal of the organometallic compound also influences the polymerization with respect to both the reaction rate and the structure of the polymer. Conclusions can be drawn from this behavior regarding the nature and mode of action of Ziegler-Natta catalysts.

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Effect of Structure on the Incompatibility of Polymer Mixtures in Solution

By *O. Fuchs* [*]

According to the literature, polyvinyl acetate and polymethyl acrylate are incompatible in the solid state. Though a clear film is obtained on evaporation of a solution of the two polymers, *e.g.* in ethyl acetate, the inhomogeneity of the film becomes evident when it is held for a short time in the vapor of a liquid that solvates only one of the polymers well. As expected, the polymers are also incompatible in solution, and two separate layers are formed. When equal weights of the two polymers are used, IR examination shows that one layer contains twice as much of one polymer as of the other, and *vice versa.*

To determine the effects of small differences in constitution on the incompatibility of polymer mixtures in solution, 15 polyacrylates and polymethacrylates were examined. The polymers differ in the length and branching of the alkyl groups and in their molecular weights. The polymers were examined in pairs in benzene as the common solvent at 20 °C (a total of 98 pairs). The limiting concentration c_g at which the two polymers of a pair just become compatible on dilution of the mixture was taken as the degree of incompatibility. Thus a high c_g value indicates good compatibility. The results show that even slight differences in the constitution of the polymers lead to incompatibility. The variation of the c_g values on variation of the size of the alkyl groups in the polymers can be qualitatively understood from the point of view of molecular physics. The c_g value decreases with increasing molecular weight of one of the two components.

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Diffusion Anomalies and Relaxation in High Molecular Weight Systems with Miscibility Gaps

By *J. Fuhrmann* and *G. Rehage* [*]

The diffusion coefficient and its concentration-dependence can be calculated by the Boltzmann-Matano method if the concentration profile is known. The concentration profiles found by us in interferometric measurements on vitreously solidifying systems with miscibility gaps exhibit a characteristic course, the evaluation of which yields diffusion coefficients that depend in a complicated manner on time. The time-dependence in these systems is due to a second irreversible process induced by diffusion. The superposition of the two processes leads to the anomalous diffusion.

The diffusion anomalies measured by interferometry can be used for the analysis of the second process. The diffusion anomalies occurring in the mixed phase between vitreous polystyrene and pure cyclohexane are discussed with the aid of the measured concentration profile. In the case of this diffusion anomaly, the analysis of the diffusion-induced relaxation from the vitreous state into the state of internal thermodynamic equilibrium can be used to characterize the inhibited non-equilibrium state of the vitreous polymer. Biaxially drawn polystyrene samples with different molecular orientations were used for the experiments.

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Synthesis of Organic Polymer Gels with Very Uniform Mesh Sizes

By *G. Greber* and *P. Haussmann* [*]

In connection with the fractionation of polymers by gel chromatography, we were interested in hitherto unknown organic polymer gels having very uniform but widely variable mesh sizes. One conceivable route to gel systems of this type starts with "living" polystyrene (PST) or poly-α-methylstyrene (PMST) molecules having very narrow molecular weight distributions. These molecules can be crosslinked at their chain ends by direct termination with reactive halogen compounds having three or more active functional groups (*e.g.* $SiCl_4$). This one-step process can also be carried out in

two stages. The first stage is the synthesis of macromolecules having two bifunctional or polyfunctional end groups from "living" polymers; these macromolecules are then crosslinked in the second stage. In both cases the mesh size of the resulting gels is determined by the molecular weight of the "living" polymer molecules used.

Direct termination of "living" PST and PMST with equimolar quantities of $SiCl_4$ at −60 °C, surprisingly, does not result in appreciable crosslinking, but results only in a linear growth reaction. The incorporated Cl−Si−Cl groups are then so strongly sterically hindered by the adjacent macromolecule residues that they cannot react with further organosodium end groups. It is only when the reaction temperature is raised to +20 °C that about 50 % crosslinking of "living" PST takes place. No corresponding reaction occurs with "living" PMST, owing to the low ceiling temperature of this system. On the other hand, this low ceiling temperature is the reason that PMST molecules having a very narrow molecular weight distribution can be prepared much more readily than corresponding PST molecules.

In an attempt to find crosslinking reactions that take place even at low temperatures with PMST molecules, we treated "living" PMST with an excess of *p*-vinylphenyldimethylchlorosilane. When naphthalenesodium is added to a solution of the resulting PMST molecules with two $p\text{-}CH_2{=}CH{-}C_6H_4{-}Si(CH_3)_2{-}$ end groups in tetrahydrofuran at −70 °C, practically quantitative crosslinking takes place *via* the *p*-vinylphenylsilicon end groups. This two-step crosslinking process can be carried out more simply by a one-step procedure. "Living" PMST is terminated with a small deficit of *p*-vinylphenyldimethylchlorosilane, and crosslinked gels are formed directly.

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Separation Efficiency in Gel Chromatography

By *W. Heitz* [*]

The separation efficiency describes the spreading of a chromatographic zone during migration through the column. To investigate the effects of experimental factors on the separation efficiency, polystyrene gels and polyvinyl acetate gels with crosslinking agent concentrations of between 1 and 30 mole-% were prepared by bead polymerization. Sharp bead-size fractions having average particle diameters of 0.015–1 mm were used for the experiments. Methyl-substituted *p*-oligophenylenes were used as the test substances.

With the aid of reduced quantities (reduced plate height $h = H/d_p$, reduced velocity $\nu = vd_p/D$; H = height of the theoretical plate, d_p = particle diameter of the gel, v = linear elution rate of the mobile phase, D = diffusion coefficient of the solute), the separation efficiency found by experiment can be represented, according to *Giddings*, by

$$h = b/\nu + c_s\nu + \sum_i \frac{1}{1/a_i + 1/c_{mi}\nu}$$

The b term is due to the spreading of the zone by diffusion; its effect decreases with increasing flow rate. This term is negligible in the usual gel-chromatographic separations.

The c_s term is due to the nonequilibrium in the stationary phase. The transport of matter in the stationary phase is controlled by the permeation coefficient. c_s is therefore a substance-dependent quantity when the diffusion coefficient in the mobile phase and the permeation coefficient in the gel differ appreciably. In agreement with this, the reduced separation efficiency in gels having low crosslink densities and in macroporous gels can be described by a single curve for the compounds investigated (c_s = 0.1). This curve is independent of the particle size of the gel. In gels whose pore size is determined by the content of crosslinking agent, the substance-dependence increases with increasing crosslink density. These substance-dependent curves are also independent of the particle size of the gel. For substances that cannot penetrate into the gel, c_s is found to be zero, *i.e.* h is independent of ν.

The summation term describes the regularity of the packing (a_i) and the nonequilibrium states in the mobile phase (c_{mi}). Any irregularity in the packing leads to nonequilibrium. Owing to the coupling of the two quantities, the summation term disappears for low reduced velocities, and has a constant value a for higher velocities. This is confirmed by experiment. The magnitude of the summation term is strongly influenced by the nature of the packing.

At extremely high flow rates, the elution volume is not constant, but decreases with increasing flow rate until it is ultimately equal to the external volume v_0. In this case the exchange process is kinetically controlled, and the curves are highly asymmetric.

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Formation of Ordered Structures from Polysaccharide Solutions

By *H. Bittiger, E. Husemann,* and *B. Pfannemüller* [*]

To obtain a better understanding of the formation of ordered structures in plant and animal organisms, the effects of conditions during the crystallization of macromolecules from dilute solution on the nature of the molecular and supermolecular structures were studied.

It is shown that for cellulose and amylose derivatives, the folded individual molecules can change into extended fibrils on alteration of the concentration, and that depending on the solvent, globular particles, folded individual molecules, or single crystals can be formed. The effects of complexing agents are demonstrated for amylose solutions. Single crystals of varying morphology are formed with alcohols, whereas iodine leads to the formation of fibrils, the length of which increases in proportion to the degree of polymerization, while the diameter remains constant. The structure of these amylose-iodine fibrils is discussed in relation to that of natural cellulose fibrils.

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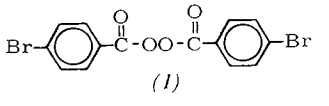
Preparation and Use of Derivatives of Azoisobutyrodinitrile that can be Determined Colorimetrically

By *H. Kämmerer* and *G. Sextro* [*]

The analysis of the end groups of macromolecular substances is of great importance in the determination of the formation or of the structure of macromolecular products. Thus with bis(*p*-bromobenzoyl) peroxide *(1)*, the covalent incorporation



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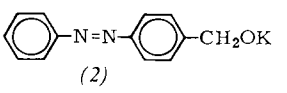

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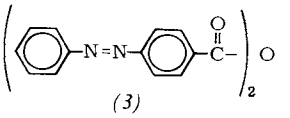
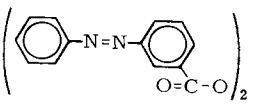


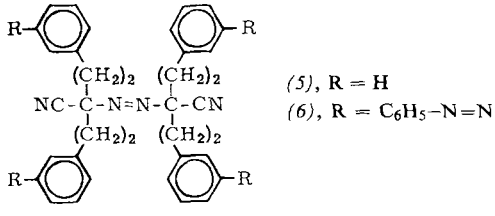
(3)



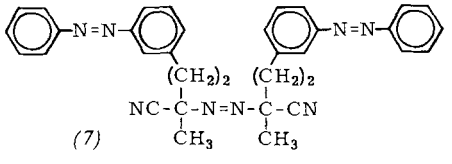
(4)

of initiator fragments in the macromolecules in free-radical chain polymerization was determined by elemental analysis [1]. A transfer reaction with traces of water has been quantitatively determined in the anionic polymerization of ethylene oxide with potassium 4-benzeneazobenzyloxide *(2)* by subsequent reaction of the polyethylene oxides with the anhydride of 4-benzeneazobenzoic acid *(3)* [2]. When styrene is polymerized with bis(3-benzeneazobenzoyl) peroxide *(4)* or with the 4-isomer of *(4)*, the polymer contains end groups that can be determined colorimetrically. This permits the determination of the number average molecular weight or of the degree of branching resulting from a graft reaction [3]. The peroxide *(4)* has the disadvantage that it forms carbon radicals as well as oxygen radicals on decomposition.

To contribute to the discussion of whether monomers can be polymerized by initiators containing azobenzene groups without the occurrence of interfering side reactions [4], the initiators *(5)–(7)* were prepared. These are derivatives of α,α'-azoisobutyrodinitrile. They are expected to decompose by a first-order process, the decomposition not being induced and being practically independent of the solvent.



(5), R = H
(6), R = C_6H_5–N=N–



(7)

Methyl methacrylate was polymerized in bulk at 50 °C with *(5)* and *(7)*, and styrene at 70 °C with *(6)* and *(7)*. It can be shown that initiator fragments are covalently bound in the polymers. The quantitative evaluation is not yet complete.

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[1] *H. Kämmerer*, Dissertation, Universität Freiburg/Br., 1941; *W. Kern* and *H. Kämmerer*, J. prakt. Chem. *161*, 81 (1942); *C. C. Price, R. W. Kell*, and *E. Krebs*, J. Amer. chem. Soc. *64*, 1103 (1942);

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[3] *H. Kämmerer, L. Schmieder*, and *K.-G. Steinfort*, Makromolekulare Chem. *72*, 86 (1964); *H. Kämmerer* and *F. Rocaboy*, C. R. hebd. Séances Acad. Sci. *256*, 4440 (1963).

[4] *O. F. Olaj, J.W. Breitenbach*, and *J. Hofreiter*, Makromolekulare Chem. *91*, 264 (1966).

Submicroscopic Crystal Nuclei in the Solution Crystallization of Polyethylene

By *D. J. Blundell* and *A. Keller* [*]

It was shown in an earlier investigation on single crystals of polyethylene [1] that submicroscopic units can be obtained above the clearing point of suspensions of single crystals (determined from optical clearing and measured dilatometrically). Though these units represent only an extremely small fraction of the original crystals, they act as nuclei for new crystals on cooling, and so have a considerable influence on the course of crystallization. The factors that influence these nuclei and the structure of the nuclei were studied in the present work.

The number of nuclei, which could be estimated from the number of uniform crystals formed from them, depends on the following variables: the highest temperature to which the suspension was heated (T_s), the heating rate, the morphology of the original suspension, and the molecular weight distribution. The number of nuclei per unit mass of polymer was not affected by the time for which the suspension was kept at T_s or by the concentration of the original suspension, and was only slightly influenced by the subsequent crystallization conditions.

The nuclei, which could be identified by electron microscopy from the slight thickening in the center of the crystals which they induced, were also detected by light scattering in solutions that had been kept above the clearing temperature of the original suspensions. These investigations led to the conclusion that the nuclei are formed from a high molecular weight fraction of the polymer (molecular weight $\approx 10^7$), which changes its conformation during the heating process in such a way that it is stable at T_s.

Correlation of the dimensions and number of nuclei with the molecular weight distribution of the starting material indicates that each nucleus is formed from a single molecule. Moreover, the temperature-dependence of the scattering power between T_s and the clearing point indicates that such a monomolecular nucleus is in equilibrium with its own amorphous environment. On the other hand, difficulties arise in the interpretation of the angular dependence of the scattering. It is most readily explained by a nucleus structure having several parts, which also explains the novel twinning observed in the crystals formed from the nuclei.

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[1] *D. J. Blundell, A. Keller*, and *A. J. Kovacs*, J. Polymer Sci. B 4, *481* (1966).

Structure of the Photosynthetic Apparatus

By *W. Kreutz* [*]

The primary photosynthetic processes take place in the green plant cells on a sterically definite structure, the lamellar system of the chloroplasts. The lamellae of this system have a special sublayer and plane structure. The lamellae are also combined in pairs to form morphological and functional units, the thylacoids.

The layer structure of the lamellae was determined by X-ray measurements from the electron density distribution along the axis of the lamella (normal to the plane). Each lamella is found to consist of three sublayers a, b, and c. In the thylacoids two lamellae are combined in such a way as to give a layer sequence abccba (a is a protein layer (36–38 Å), b a layer of porphyrin rings (11–13 Å), and c a lipid layer (21–23 Å)). The two c layers are separated by a water layer 10–20 Å thick. The thylacoids are stacked in a periodic manner. The period is about 250 Å in the living cell, while in the dry state the thylacoids are in contact. Their period is then reduced to 160–170 Å.

The plane structure is determined mainly by the structure of the protein layer. It is possible to distinguish essentially two types of protein in the protein layer, *i.e.* structural protein and enzyme proteins. The structural protein (41.4 Å×41.4 Å) forms two-dimensional microcrystals of only 16 lattice cells in a square arrangement, both *in vivo* and *in vitro*. These microcrystals (size 165.6 Å×165.6 Å) in turn form two-dimensional aggregates to give the basic skeleton of the protein layer. Experimental results indicate that the enzymatic proteins of the primary processes are built into this superstructure in a definite manner.

On the basis of the layer and plane structure, it can be shown, with the aid of the spectroscopic data for chlorophyll

in vivo and the exciton theory, that the porphyrin rings of chlorophyll in layer b must be inclined at an angle of 55° to the plane. It is also possible to provide an explanation of the absorption maxima and a scheme for the two-dimensional distribution of the porphyrin rings.

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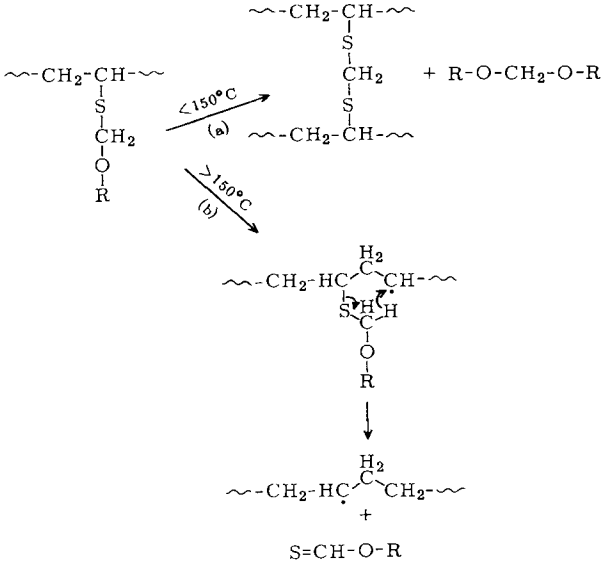
Synthesis and Depolymerization of Poly-*S*-vinyl Monothioacetals

By *K. D. Gollmer, R. Kroker, H. Ringsdorf,* and *U. Zahorsky*[*]

S-Vinyl monothioacetals ($CH_2=CH-S-CH_2-O-R$) were prepared from β-hydroxyethyl compounds by dehydration and the free-radical and cationic polymerization behavior of the monomers was studied. The overall polymerization rates, which are strongly dependent on the substituent (R), are correlated with structure parameters found by spectroscopy (UV, IR, NMR). The influence of the substituent on the polymerization behavior of the vinyl monothioacetals can be traced to inductive and steric effects, and can be correlated with the Taft parameters.

The degradation reactions of the poly-*S*-vinyl monothioacetals and their monomers were investigated by mass spectrometry. Up to 150 °C, practically the only reaction is transacetalization of the polymer (path (a)), while above 150 °C, thioesters and hydrocarbon fragments are formed *via* free radicals (path (b)).



The conclusions concerning the degradation were confirmed with the aid of deuterated model compounds.

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The Chemical Heterogeneity of Copolymers — Experimental Studies on Compatibility

By *F. Kollinsky* and *G. Markert*[*]

Two chemically homogeneous methyl methacrylate/butyl acrylate copolymers form optically homogeneous (*i.e.* clear) mixtures in bulk only if the difference in their methyl methacrylate contents does not exceed 10–20 mole-%.

As torsional vibration experiments show, the mechanical homogeneity limit occurs at the same difference in the methyl methacrylate contents. In inhomogeneous systems, the positions of the damping maxima correspond to the compositions of the two components.

Electron micrographs show the presence of structures of the order of magnitude of 30 Å even in some optically or mechanically homogeneous systems. The phase size increases suddenly near the turbidity limit. In mixtures of three components, the intermediate composition does not aid compatibility.

In copolymers with broad continuous chemical distributions, microphases are formed from mutually compatible macromolecules. Optical and mechanical homogeneity or inhomogeneity is then a question of the size of the individual microphases. Suppression of transfer reactions in the polymer leads to an increase in the size of the microphases, while the size decreases when these reactions are encouraged. In agreement with this, graft copolymerization has a homogenizing effect.

Preliminary experiments on copolymers of other monomers indicate that these observations are generally valid.

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Kinetics of the Free-Radical Polymerization of Styrene and *o*-Halogenostyrenes at Low Initiator Concentrations

By *O. F. Olaj*[*]

The kinetics of the free-radical polymerization of styrene and of some halogenostyrenes at low initiator concentrations have been studied with particular reference to the question of whether the rates of initiation due to spontaneous thermal radical formation in the monomer and due to the decomposition of the added initiator are additive. The analysis of both polymerization rates and degrees of polymerization shows that deviations from additivity occur with all the monomers studied, and particularly with *o*-bromo- and *o*-chlorostyrene. These deviations result in suppression of the contribution due to spontaneous initiation at higher polymerization rates, and frequently in a maximum degree of polymerization at finite initiator concentrations.

These effects generally become more pronounced with decreasing polymerization temperature. The results can be explained on the basis of a chain transfer reaction to the intermediate that leads to spontaneous radical formation; moreover, the termination of the radical chains by the primary radicals formed in the spontaneous initiation process probably also has to be taken into account (particularly in the cases of *o*-bromostyrene and 2,5-dichlorostyrene).

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The Structure of Chromosomes

By *C. Pelling*[*]

In spite of the importance of chromosomes as carriers of genetic information for the cell, their molecular structure is practically unknown. The morphologically relatively simple filament structures have been extensively studied under the microscope, but our chemical knowledge is limited to a simple assignment of the chromosomal components to the three classes of substances deoxyribonucleic acid (DNA), ribonucleic acid (RNA), and proteins. Since RNA is not always present, and since the role of the proteins is unknown, discussions at present are confined to the molecular arrange-

ment of the DNA in the chromosome: Has the chromosomal filament a continuous polynucleotide chain, or does it consist of DNA fragments having different molecular weights, and possibly different functions? The following facts are known so far.

1. The DNA filaments do not occur in bundles in the chromosome, *i.e.* there is only one (double) DNA filament per chromosome element (chromatid). This is shown by the semi-conservatively named replication behavior of the chromosomes of plant and animal cells (*Taylor*).

2. Autoradiographic experiments show that at least in the DNA replication phase, one chromatid breaks down into many independently replicating DNA segments (replicons) arranged in succession (*Lima de Faria, Keyl* and *Pelling, Plaut*). However, it cannot be concluded from this that the DNA is permanently in the fragmented state.

3. If DNA is extracted under particularly mild conditions from isolated cell nuclei, filaments of different lengths are found on examination with the electron microscope. In one case analyzed so far, the length distribution found agrees with that expected on cytological grounds for the DNA growth units (replicons).

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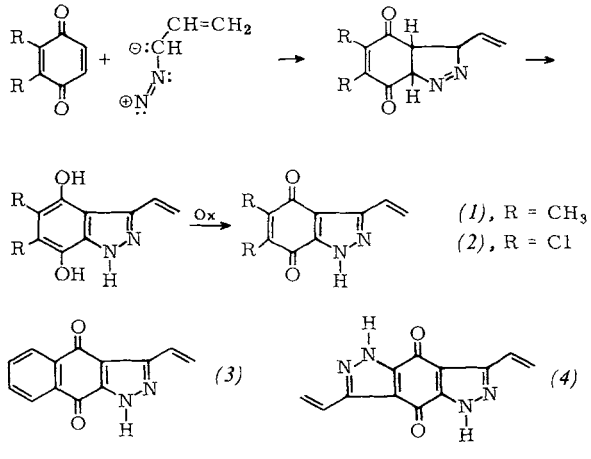
Vinylpyrazoloquinones

By *G. Manecke, G. Ramlow, W. Storck,* and *W. Hübner*[*]

Quinone-based redox polymers have until now been prepared only from carbocyclic quinones. In the present work, several (heterocyclic) vinylpyrazoloquinones were prepared and examined.

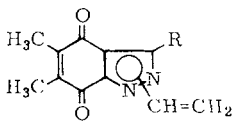
The 3-vinylpyrazoloquinones *(1)–(4)* are formed on addition of vinyldiazomethane to quinones.

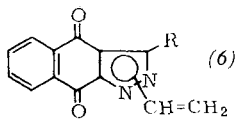


The chemically very stable pyrazoloquinones [with the exception of *(2)*] can undergo free-radical polymerization. Attempts to polymerize the hydroquinone diacetate of *(2)* were also successful. *(4)* acts as a crosslinking agent.

Sulfalkylation on the secondary N atom yielded satisfactorily crystallizing, water-soluble monomers. When the reaction was carried out on crosslinked copolymers, *e.g.* of *(3)* and *(4)*, redox resins that swell in water were formed.

Vinylation with vinyl acetate in the presence of mercury acetate gave *N*-vinylpyrazoloquinones. Both possible isomers, *e.g. (5c)* and *(5d)* from *(1)*, were formed in every case. The *N*-vinyl groups of the anthraquinone-like compounds *(6)* were polymerizable, whereas the naphthoquinone analogs *(5)* did not polymerize.





(a), 1-Vinyl, R = H
(b), 2-Vinyl, R = H
(c), 1-Vinyl, R = Vinyl
(d), 2-Vinyl, R = Vinyl

Readily polymerizable derivatives *(7)* of the pyrazolobenzoquinones could be prepared by epoxidation in the 5,6-position. The epoxide groups could be removed from the polymers by reduction.

Vinylpyrazoloquinones such as *(5c)* or *(6d)* with two vinyl groups gave crosslinked redox copolymers consisting exclusively of quinones. The redox copolymers had a high redox capacity and a high resistance to undesirable degradation reactions.

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Effect of the Solvent on Anionic Polymerizations

By *D. J. Worsfold, E. Franta,* and *P. Rempp*[*]

In the polymerization of styrene and of dienes or other monomers with an organometallic initiator in aprotic solvents the active chain ends are always ion pairs, which can associate or dissociate, depending on the solvent.

In polymerizations in hydrocarbons, the ion pairs can associate to form aggregates if the cation is Li^+ or Na^+. With Rb^+ and Cs^+ ions, this association is suppressed because of the primary charge distribution, and the ion pairs remain independent. This can be seen from the change in the growth rate constants, the order of the reaction increasing from $1/n$ to 1 along the series of alkali metals.

Solvents such as ether, dioxane, or THF solvate the organometallic end groups better, and the ion pairs are stable. In solvents containing ether, the growth reaction always retains its first order kinetics if the dielectric constant is small enough. However, when the dielectric constant of the solvent is increased, the ion pairs can exhibit electrolytic dissociation. Since the free anions take part in the polymerization with much higher rate constants, the order of the growth reaction with respect to the concentration of active end groups is again lower than 1.

However, the reactivity of the ion pair depends on the polarity of the solvent. The polymerization rate can be considerably increased by addition of a polar solvent. This can only be partly explained by the increasing degree of dissociation; it must be assumed that the ion pairs are selectively solvated, so that their reactivity increases. It cannot be decided whether this is due to changes in the solvation of the transition state or to an ion pair separated by the solvent. The addition of highly polar solvents such as hexamethylphosphoramide, even in small quantities, leads to large changes in the kinetics. The effect of the cations in this case can be attributed to differences in solvation.

In some cases the reactivity of the free ions is completely independent of the solvent, *e.g.* in mixtures of benzene and THF or of dioxane and THF.

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Grafting of Polymers on Active Fillers; Polymerization of Styrene in the Presence of Carbon Black

By *J. B. Donnet, L. Geldreich, G. Peter,* and *G. Riess*[*]

The possibilities of grafting polymers on surface active fillers such as carbon black were studied in an effort to increase the compatibility and the adhesion at the polymer-filler interface. Thermal polymerization of styrene in the presence of various carbon blacks results first in retardation, followed by an accelerated reaction, which is usually accompanied by grafting. The retardation could be attributed to quinoid groups on the surface of the carbon black ,which also play an important part in the grafting. The acceleration of the polymerization is due to the growing polystyrene chains, which are adsorbed or grafted onto the surface. This observation could be interpreted by means of the Langmuir-Hinshelwood theory.

The results obtained also show that the degree of grafting depends on the type of carbon black.

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Importance of the Merrifield Synthesis in Macromolecular Chemistry

By *M. Rothe, W. Dunkel, K.-D. Steffen,* and *Hj. Schneider*[*]

The stepwise amide linkage of ε-aminocaproates on the Merrifield insoluble polymeric support was investigated with the object of obtaining rigorously molecularly uniform macromolecules. By the use of dimeric and tetrameric units for the chain growth and by linkage with the aid of diester chlorides of phosphorous acid instead of the carbodiimide used in the original process, it was possible to obtain low polymers $H[NH(CH_2)_5CO]_nOH$ containing up to 25 monomer units (molecular weight 2847) that were uniform on thin layer electrophoresis.

Sequence oligomers of the structure H(prolyl-glycyl-glycyl)$_n$OH and oligopeptides of L-proline containing up to seven monomer units were also synthesized in view of their possible suitability as collagen models. Spectroscopic and optical rotation measurements indicate the existence of stable conformations of the polyproline helix type, even at these low degrees of polymerization. For example, mutarotation occurs between a strongly and a weakly levorotatory form (rotation difference of $\approx 300°$ in the case of hepta-L-proline), which can be distinguished by IR spectroscopy, and which are thought to exist in a left-handed helix with *trans*-amide linkages and a right-handed helix with *cis*-amide linkages.

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Diffusion-Controlled Reaction Steps in Free-radical Polymerization

By *J. P. Fischer, G. Mücke,* and *G. V. Schulz*[*]

Stationary measurements and measurements with intermittent chain initiation (sector method) were used to determine the absolute rates of all the reaction steps of the polymerization of polymethyl methacrylate initiated by the photochemical decomposition of azobis(cyclohexanonitrile): decomposition (quantum yield), chain initiation (efficiency), propagation, transfer, and termination. The viscosity of the solvent, including monomer, was varied by a factor of 170; the termination rate constant decreases to the same degree, showing that this reaction step is entirely diffusion-controlled. The efficiency decreases by a factor of 5, which leads to certain conclusions regarding the cage effect. The propagation rate is independent of the viscosity.

A model proposed for the diffusion-controlled chain termination provides an explanation both for the fact that the termination constant is independent of the molecular weight and for the increase in the termination constant during the early stages of the polymerization.

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A Polymerization Reaction of Trimethylaluminum

By *H. Sinn, F. Bandermann,* and *H. Hinck*[*]

The band at 460 nm in the spectrum of the reaction product of bis(cyclopentadienyl)titanium(IV) compounds with $Al(CH_3)_3$ corresponds to the formation of $\geq Ti-CH_2-Al\leq$ groupings by the reaction

$$\geq Ti\text{-}CH_3 + CH_3\text{-}Al\leq \longrightarrow CH_4 + \geq Ti\text{-}CH_2\text{-}Al\leq$$

The $-CH_2-Al\leq$ residue on the titanium can be exchanged in the same way as a normal alkyl group:

$$\geq Ti\text{-}CH_2\text{-}Al\begin{matrix}CH_3\\CH_3\end{matrix} + Al(CH_3)_3 \longrightarrow$$

$$\geq Ti\text{-}CH_3 + (CH_3)_2Al\text{-}CH_2\text{-}Al(CH_3)_2 \quad (1)$$

The organoaluminum products *(1)* react further, with elimination of methane:

$$\geq Ti\text{-}CH_3 + \underset{(1)}{(CH_3)_2Al\text{-}CH_2\text{-}Al\begin{matrix}CH_3\\CH_3\end{matrix}} \xrightarrow{-CH_4}$$

$$\geq Ti\text{-}CH_2\text{-}\underset{CH_3}{Al}\text{-}CH_2\text{-}\underset{CH_3}{Al}\text{-}CH_3$$

The reaction sequence continues indefinitely, and leads to polymers of the type *(2)*.

$$CH_3\text{-}\underset{CH_3}{Al}\text{-}CH_2(Al(CH_3)\text{-}CH_2)_n\text{-}\underset{CH_3}{Al}\text{-}CH_3 \quad (2)$$

These polymers are practically insoluble in aliphatic hydrocarbons, are swollen by aromatic compounds, and dissolve in tetrahydrofuran. They react *e.g.* with titanium tetrachloride to form products having an atomic ratio Ti:Al ≤ 1. These reaction products polymerize olefins and diolefins, sometimes stereospecifically.

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Investigations on the Agglomeration of Polymer Latices

By *H.-G. Keppler, H. Wesslau,* and *J. Stabenow*[*]

Polymer dispersions are not always compatible with one another, even when prepared with the same emulsifier. If the polymer of one dispersion contains hydrophilic groups, *e.g.* as a result of the use of small quantities of water-solubel

monomers in the emulsion polymerization (type A), while the other contains no hydrophilic groups (type S), a mixture of the two dispersions often coagulates within a few seconds after preparation. However, addition of a small percentage of type A can lead to agglomeration of the particles of an S-type dispersion. For example, when a polybutyl acrylate dispersion having an average particle size of 800 Å is mixed with 1 wt-% of a dispersion of a copolymer of 95 % of ethyl acrylate and 5 % of acrylic acid, followed by adjustment of the pH to 8–9, a latex having $\overline{D}_n$ = 6300 Å and $\overline{D}_w$ = 7300 Å is obtained. The particles continue to grow on further addition of any S-type dispersion.

Schemes for the agglomeration were developed on the basis of particle size distribution functions and with the aid of latices labeled with polymerizable dyes, as well as by the use of electron micrographs with special preparation techniques. The emulsifier sheath is thought to afford the latex particles only limited protection against association (coagulation). When latex particles of type S meet only other particles of the same type, the electrical double layer formed by the emulsifier provides adequate protection against coagulation. When type-S particles collide with type-A particles, on the other hand, irreversible association takes place. Any S particle coming into contact with the surface of an A particle is held fast and fused with other particles to form a secondary particle, with the hydrophilic A particle "floating" on its surface. The A particle remains active practically indefinitely, and takes up further S-type particles that may be added.

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New Gels from Cellulose and their Uses in Chromatography

By *H. Determann* and *Th. Wieland*[*]

Spherical cellulose particles are prepared by emulsification of aqueous solutions of cellulose (in tetramminecopper(II) hydroxide or solutions of complex Cd^{2+} or Fe^{2+} salts) or of sodium cellulose xanthate in benzene followed by regeneration with organic acids. The density of the network can be varied by variation of the cellulose concentration in the complex salt solutions. The beads obtained are substantially amorphous, whereas those formed on slower precipitation from xanthate solution contain large crystalline regions. The efficiency of the new cellulose gels in chromatographic separations could be seen in the perfect separation of *E. coli* bacteria, dextran blue, and benzyl alcohol. The elution position of the polydisperse high molecular weight dextran dye depends on the crosslink density.

The new gels can also be used for the separation of macromolecular substances up to the range of microscopically visible particles (mitochondria, microsomes). [VB 118 IE]

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Ternary Compounds as Semiconductors

By *H.-U. Schuster*[*]

Not only binary compounds with the crystal structure of zinc blende and of wurtzite but also a large number of ternary compounds with tetrahedral structures (*e.g.*, chalcopyrite type) are now known to be semiconductors.

Semiconductor properties are, however, not confined to compounds with tetrahedral structures. The semiconductors Mg_2Si, Mg_2Ge, and Mg_2Sn crystallize in the antifluorite-type lattice. In these compounds only the Mg atoms are in tetrahedral environments, and the Si, Ge, and Sn have coordination number 8. Finally a filled antifluorite-type lattice can be ascribed to the semiconductor Li_3Bi[1], the cubic face-centered bismuth lattice having Li atoms occupying not only the tetrahedral vacancies but also the octahedral vacancies that are still free in Mg_2Si. Ternary compounds with a modified Li_3Bi structure are the Li_2MgSn prepared by *Laves*[2], which according to *Mooser* and *Pearson*[1] has semiconductor properties, and a series of compounds prepared during the present investigations:

$LiCu_2Si$ pale violet		
$LiCu_2Ge$ pale violet	Li_2CuGe medium brown	$Li_2Zn\,Ge$ gray
	Li_2CuSn dark violet	Li_2CdGe gray
$LiAg_2Sn$ pale blue	Li_2AgSn deep violet	Li_2HgGe gray
	Li_2AuSn orange	

These compounds are sensitive to hydrolysis, are prepared by reaction of the elements in tantalum crucibles under argon, have a metallic sheen, and, when they contain elements of the copper group, are colored. Their structure is composed of a cubic face-centered unit cell of atoms X (X = Si, Ge, or Sn), whose octahedral vacancies are all occupied by Li and whose tetrahedral vacancies of the composition LiM_2X are occupied only by IB atoms, and of the composition Li_2MX are occupied statistically by IB or II B atoms (M) and Li.

On measurement of the electrical resistance in relation to temperature for polycrystalline samples, the weakly diamagnetic compounds of IB elements show metallic behavior and compounds of the II B elements show semiconductor properties. Excitation energies were calculated from the absorption spectra of the germanides of the zinc group (maxima between 1080 and 1300 nm): ΔE = 1.10 (Li_2ZnGe), 0.99 (Li_2CdGe), 0.93 (Li_2HgGe) eV.

Lecture at Kiel (Germany) on October 26, 1967 [VB 111 IE]
German version: Angew. Chem. *80*, 369 (1968)

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[1] *E. Mooser* and *W. B. Pearson*, J. chem. Physics *26*, 893 (1957).
[2] *F. Laves*, personal communication referred to in [1].

d-Orbital Effects in PN and SiC π-Electron Systems

By *H. Bock*[*]

Phosphorus-azo compounds $X_2OP{-}N{=}N{-}POX_2$ are violet; the n → π* excitation energy of the four-center chromophore P–N=N–P is unexpectedly low. Investigations by electron spectroscopy as well as MO calculations on numerous carbon-azo compounds have led to the assumption that the long wavelength shift in the absorption maximum is, in the main, caused by additional d–π* interaction between unoccupied phosphorus 3d orbitals and the N=N π* state[1].

To obtain information on d-orbital effects of this type, by means of which many differences in properties between compounds of elements with principal quantum numbers n = 2 and those with $n \geqslant 3$ are explained under the general heading of "$p_\pi d_\pi$-contributions", we have used R_3Si- and R_3C-substituted compounds as simple models. More than two hundred derivatives of linear and cyclic, alternant and

nonalternant, isoconjugated and heteroatomic π-electron systems (polyenes, polyines, aromatic compounds, aryl ethers, ketones, ketimines) have been synthesized and the relative energy differences between them have been measured[2]: ground-state changes by means of vertical ionization potentials as well as charge-transfer transitions in suitable donor-acceptor complexes, and variations in antibonding orbitals by means of half-wave reduction potentials as well as ESR coupling constants of radical anions. The total differences are obtained from the electronic spectra.

The experimental results can be interpreted by different inductive polarization $+ I_{SiR_3} > + I_{CR_3}$ and an additional electron back-donation $Si_{(d)} \leftarrow C_\pi$, which also explain other characteristic properties of the molecules, such as stretching and deformation vibrational frequencies, ^1H-NMR signals, and dipole moments. Calculations by HMO and PPP procedures permit correlation and numerical reproduction of the experimental values. Whether the acceptor function of the R_3Si groups simulated in the Si parameters used are to be ascribed solely to silicon 3d-orbitals and what degree of importance attaches to the σ-states that have so far been neglected, will be subject of further investigations on this central problem of inorganic non-metal chemistry.

Lecture at Braunschweig (Germany) on January 29, 1968 [VB 138 IE]
German version: Angew. Chem. *80*, 368 (1968)

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[1] *H. Bock, G. Rudolf, E. Baltin*, and *J. Kroner*, Angew. Chem. *77*, 469 (1965); Angew. Chem. internat. Edit. *4*, 457 (1965).

[2] Cf. preliminary communications: *H. Bock et al.*, Angew. Chem. *79*, 932, 933, 934, 1106; Angew. Chem. internat. Edit. *6*, 941, 941, 943, 1085 (1967); Chem. Commun. *1967*, 1299.

Optical Excitation and Ionization of Adsorbed Molecules

By *H. Moesta*[*]

The lack of spectroscopic information is felt in our still unsatisfactory ideas about the nature of the bonding in adsorption. New methods have now been developed for UV-spectroscopic investigation of chemisorptive bonding. Technical requirements are the use of ultrahigh vacuum processes (UHV) and of an extremely powerful light source that operates also in the short-wave ultraviolet region (~800 Å) under UHV conditions. Further, methods of detecting changes in the bonding state are needed that permit measurement with very small samples (some 10^{10} molecules). We have studied:

1. Adsorbed alkali atoms on W and Pt as models for the investigation of the principal processes.

2. Polyatomic gases such as CO, N_2, H_2, NH_3, HCN, *etc.*, on metals such as Fe, Pt, and Ni.

3. NaCl molecules on NaCl cleavage planes as model for non-metallic systems.

Experiments in project (1) were carried out with a UHV mass spectrometer and a surface-ionization ion source. Differences in ionization were observed on irradiation with visible or near-ultraviolet radiation; this dependence on wave length can be correlated with adsorption in shifted or broadened atomic terms of the adsorbate.

Experiments for project (2) have only just begun. An exploding-wire light source has been developed that delivers monochromatic light with 10^{16} quanta per flash behind a monochromator at 1500 Å. Changes in the contact potential were measured for detecting photoreactions of adsorbed molecules.

Experiments for project (3) concern the rate of evaporation of NaCl crystals, which was measured in a UHV microbalance, (i) with illumination and (ii) without illumination. The evaporation corresponds to desorption of NaCl molecules. The enthalpy of evaporation decreases on irradiation by light in the region of the ground lattice absorption.

Findings in the three lines of research were discussed in relation to catalysis and to modern problems of extra-terrestrial chemistry.

Lecture at Köln (Germany) on January 26, 1968 [VB 137 IE]
German version: Angew. Chem. *80*, 368 (1968)

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Properties of the Allosteric Forms of Yeast Glyceraldehyde-3-phosphate-dehydrogenase

By *K. Kirschner*[*]

At pH 8.5 and 40 °C nicotinamide-adenine dinucleotide (NAD) is bound to glyceraldehyde-3-phosphate-dehydrogenase (GAPDH) from bakers' yeast by a cooperative process; the saturation curve of the tetrameric enzyme has a sigmoid shape. Temperature-jump relaxation measurements have shown that this behavior can be described by *Monod*'s allosteric mechanism[1]. The isomerization of one allosteric form of the enzyme into the other is so slow ($t_{1/2}$ = 0.1–5 sec) that various properties of the less affine T form can be studied with the aid of the "stopped-flow" method. After rapid mixing of apo-GAPDH with NAD the kinetics of the formation of the enzyme-coenzyme complex can be followed by its absorption spectrum. The time course is clearly biphasic. The first, very rapid phase can be interpreted as the binding of coenzyme to the preferred form of the pre-equilibrium ($4\ NAD + T_0 \rightarrow T_4$). In the second, slow phase the transient species T_4 changes into the stable form R_4.

The number of binding sites ($n' = 4$) and the dissociation constant K' of the T form can both be determined by rapid titration with NAD; the results agree satisfactorily with those obtained from relaxation measurements. Further, the difference spectrum of the two forms T_4 and R_4 was measured by the same procedure: T_4 has a weaker absorption band at 360 nm. The spectrophotometric titration curve was calculated by means of the extinction coefficients of T_4 and R_4 obtained in this way; agreement with experiment was good.

Similar experiments show that, even when all the substrates are bound (3-phosphoglyceraldehyde, NAD, and arsenate), the T form is enzymatically inactive. The kinetic results are supported by the results of rapid spectrophotometric titration of the SH groups of the enzyme with *Ellman*'s reagent [5,5'-dithiobis(nitrobenzoic acid), DTNB] in the presence and then in the absence of NAD. The two allosteric forms T and R behave differently: the four identical SH groups of the enzymatically inactive T form react with DTNB eighty times faster than those of the R form. To a first approximation the rate constants do not depend on the presence or absence of NAD. Quantitative evaluation of the SH titration permits an independent determination of the characteristic equilibrium constants L_0 and L_4 and calculation of the theoretical $\bar{R}$ function[2]; agreement between experiment and theory is satisfactory.

Lecture at Göttingen (Germany) on December 14, 1967 [VB 140 IE]
German version: Angew. Chem. *80*, 369 (1968)

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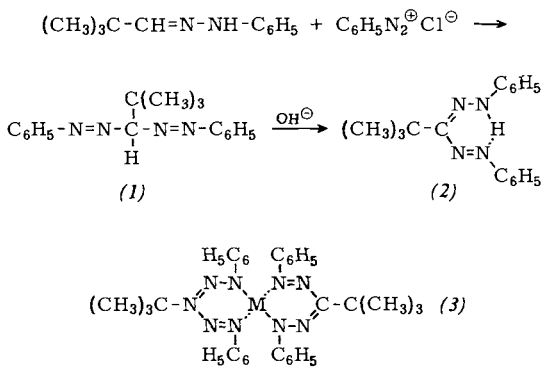
[1] *K. Kirschner, M. Eigen, R. Bittman*, and *B. Voigt*, Proc. nat. Acad. Sci. U.S.A. *56*, 1661 (1966).

[2] *J. Monod, J. Wyman, and J.-P. Changeux*, J. molecular Biol. *12*, 88 (1965).

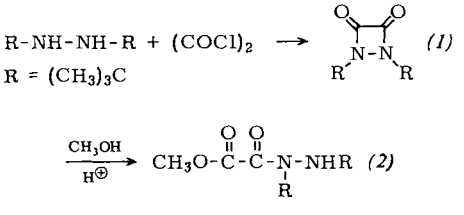
1,1-Bis(benzeneazo)-2,2-dimethylpropane *(1)* is formed on coupling of benzenediazonium chloride with dimethylpropionaldehyde phenylhydrazone in pyridine/DMF. During an attempt to prepare 3-*tert*-butyl-1,5-diphenylformazane *(2)* *F. A. Neugebauer* and *H. Trischmann* obtained *(1)* instead of the expected product.



Whereas the known bis(arylazo)methanes immediately rearrange above pH = 8 to give formazanes, and are unstable in bulk, *(1)* can be stored for months in the dark and can be recrystallized from pyridine/water. This compound is converted into the formazane *(2)*, *via* the anion, only by strong bases (NaOH, NaOR) in aprotic solvents. *(1)* and *(2)* give the metal complex *(3)* with nickel or cobalt acetate in methanol. / Liebigs Ann. Chem. *706*, 107 (1967) / –DK.

[Rd 794 IE]

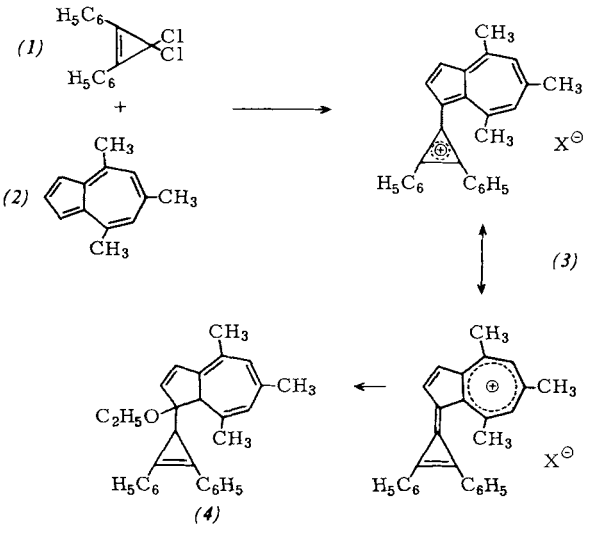
1,2-Diazetidinedione has been prepared for the first time in the form of its di-*tert*-butyl derivative *(1)* by *J. C. Stowell*. The reaction of *N,N'*-di-*tert*-butylhydrazine with oxalyl chloride gave *(1)* as yellow crystals, m.p. 56–57 °C, b.p. 64 °C/0.2 torr. *(1)* can be stored indefinitely at room temperature under nitrogen, but is rapidly decomposed by air. The IR absorption of *(1)* occurs at about 1813 cm^{-1} (amide carbonyl).



On addition of a trace of HCl to a methanolic solution of *(1)*, methyl oxalate *N,N'*-di-*tert*-butylhydrazide *(2)* is rapidly formed. *N,N'*-Di-*tert*-butylhydrazine was prepared by hydrogenation (Pd/C) of 2,2'-azoisobutane, which was obtained by the reaction of *N,N'*-di-*tert*-butylsulfamide with aqueous alkaline hypochlorite solution. / J. org. Chemistry *32*, 2360 (1967) / –DK.

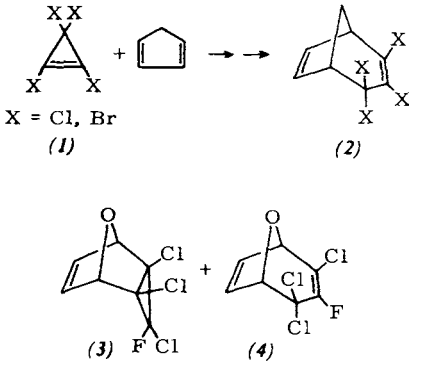
[Rd 799 IE]

The synthesis of a cyclopropenylideneazulenium salt *(3)* has been described by *B. Föhlisch* and *P. Bürgle*. 4,6,8-Trimethylazulene *(2)* reacts with an equimolar quantity of 3,3-dichloro-1,2-diphenylcyclopropene *(1)* (which can be readily prepared from diphenylcyclopropenone and phosgene) when heated in benzene, to give the red-brown chloride *(3)*. This can be readily converted into the more stable perchlorate (X = ClO_4; yield 67%. dec. p. 199–200 °C). Nucleophilic addition of ethanol to *(3)* leads to the blue-violet azulene derivative *(4)* (yield 81%, dec. p. 160 °C). No formation of calicene derivatives has been observed in the nucleophilic reaction. /



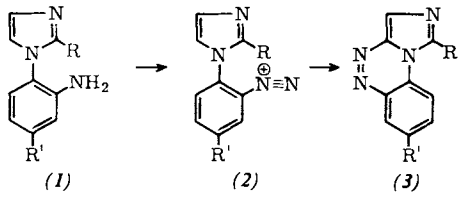
Liebigs Ann. Chem. *705*, 164 (1967) / –DK. [Rd 796 IE]

The reaction of halogenated cyclopropenes with 1,3-dienes has been studied by *S. W. Tobey* and *D. C. F. Law*. Tetrachloro- and tetrabromocyclopropene *(1)* react with an excess of cyclopentadiene at room temperature, probably *via* a tricyclic intermediate, to give very good yields of *(2)*. Furan reacts similarly. 1,2,3-Trichloro-3-fluorocyclopropene gives two products with furan, *i.e.* the tricyclic compound *(3)* (Diels-Alder adduct) and the rearranged bicyclic compound *(4)*.



Stable Diels-Alder adducts are also formed from 1,3-butadiene and tetrahalogenocyclopropenone at 100 °C. The reactivity of *(1)* decreases in the order Br > Cl > F. / Chem. Engng. News *45*, No. 42, p. 45 (1967) / –Ma. [Rd 814 IE]

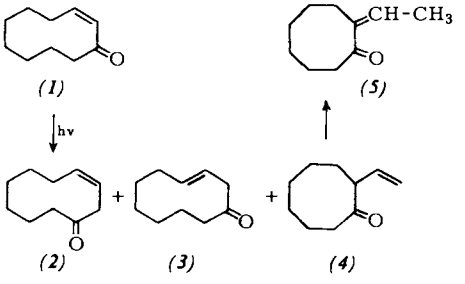
An unusual azo coupling reaction in the imidazole series has been described by *A. M. Simonov, L. M. Sitkina*, and *A. F. Pozharskii*. Salts of the *o*-(imidazol-1-yl)phenyldiazonium ion *(2)*, which are prepared by diazotization of *N*-(*o*-aminophenyl)imidazoles *(1)*, undergo intramolecular coupling in position 5 of the imidazole ring to form the new aromatic imidazo[5,1-*c*][1,2,4]benzotriazine system *(3)*. When position 5 is already occupied, the coupling takes place in position 2, though less readily. The reaction probably involves the unprotonated imidazole ring.



(1) *(2)* *(3)*

(3): R = R′ = H, m.p. 210–211 °C; R = CH_3, R′ = H, m.p. 229–230 °C; R = H, R′ = OCH_3, m.p. 251–252 °C; R = H, R′ = Br, m.p. 242–243 °C; R = H, R′ = NO_2, m.p. 194 to 195 °C. / Chem. and Ind. *1967*, 1454 / –Ma. [Rd 817 IE]

The photochemical rearrangement of *cis*-2-cyclodecenone *(1)* has been studied by *R. G. Carlson* and *J. H. Bateman*. Irradiation of a 1% solution of *(1)* in benzene or *tert*-butanol led to rapid isomerization into *cis*- and *trans*-3-cyclodecenones [*(2)* and *(3)*] and this was followed by the slower formation of 2-vinylcyclooctanone *(4)* (approx. 35%). Compound *(4)*



(1) *(5)* *(2)* *(3)* *(4)*

isomerizes readily into 2-ethylidenecyclooctanone *(5)*. The photolytic ring contraction to give *(4)* is reversible. / Tetrahedron Letters *1967*, 4151 / –Ma. [Rd 818 IE]

A new synthesis of triazane derivatives has been described by *D. J. Blackstock* and *D. A. R. Happer*. Acetone 2-phenylsemicarbazone *(1)* reacts quantitatively with 1 mole of I_2 to form the isocyanate *(2)*, which results from a Hofmann rearrangement:

$$(CH_3)_2C{=}N{-}N(C_6H_5){-}CO{-}NH_2 \xrightarrow{I_2} (CH_3)_2C{=}N{-}N(C_6H_5){-}N{=}C{=}O + HI$$

(1) *(2)*

(2) (b.p. 91–93 °C/0.5 torr) reacts with amines and alcohols to give ureas and urethanes *(3)*:

$$(CH_3)_2C{=}N{-}N(C_6H_5){-}N{=}C{=}O \xrightarrow{H-R} (CH_3)_2C{=}N{-}N(C_6H_5){-}NH{-}CO{-}R$$

(2) *(3)*

R = OCH_3, OC_2H_5, $OC(CH_3)_3$, NH_2, NC_5H_{10}

The triazaneurethanes *(3)* can also be obtained directly from the semicarbazone *(1)* with 1 mole of I_2 and 3 mole of sodium alkoxide, and the urea derivatives with 1 mole of I_2, 2 mole of sodium alkoxide, and 1 mole of NH_3 or amine. Acetone 2-phenylthiosemicarbazone gave a 65% yield of an isothiocyanate, which afforded analogous triazane derivatives. / Chem. Commun. *1968*, 63 / –Ma. [Rd 820 IE]

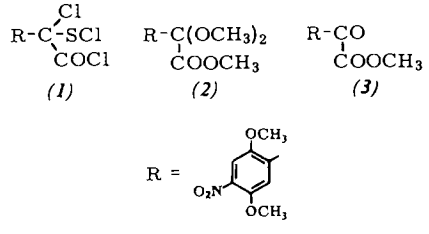
Di-*tert*-butyloxadiaziridine *(1)*, the first known compound with an azoxy group in the cyclic form, has been synthesized by *S. S. Hecht* and *F. D. Greene* by irradiation of the open-chain compound *(2)* in pentane at 10 °C with a quartz lamp. Chromatography of the product gave an oil that does not exhibit the UV absorption shown by *(2)*, and which evidently

$$(CH_3)_3C{-}\overset{\ominus}{O}{-}\overset{\oplus}{N}{=}N{-}C(CH_3)_3 \longrightarrow (CH_3)_3C{-}\underset{O}{N}{-}N{-}C(CH_3)_3$$

(2) *(1)*

has the constitution *(1)*. The compound is thermally unstable and changes quantitatively back into *(2)* ($t_{1/2}$ at 20 °C approx. 8 h in CCl_4, 3 h in CH_3NO_2). *(1)* does not react with water and is moderately stable in acidic media. / J. Amer. chem. Soc. *89*, 6761 (1967) / –Ma. [Rd 821 IE]

A new reaction of thionyl chloride with a carboxylic acid in the presence of a tertiary amine has been described by *M. S. Simon*, *J. B. Rogers*, *W. Saenger*, and *J. Z. Gougoutas*. 2,5-Bis(methoxy)-4-nitrophenylacetic acid gave about 80% of a compound containing sulfur, which was identified by X-ray analysis as α-chloro-α-chlorosulfenyl-2,5-bis(methoxy)-4-nitrophenylacetyl chloride *(1)*. Phenylacetic acid gave a similar compound, so that the reaction is probably generally applicable. Compound *(1)* is converted back into the substituted



(1) *(2)* *(3)*

phenylacetic acid on reaction with water. Reaction with boiling CH_3OH yields the ketal ester *(2)*, while boiling water/CH_3OH gives both *(2)* and the keto ester *(3)*. *(1)* reacts vigorously with DMSO at 100 °C to form 2,5-bis(methoxy)-4-nitrobenzoic acid. / J. Amer. chem. Soc. *89*, 5838 (1967) / –Ma. [Rd 822 IE]

BOOK REVIEWS

Einführung in die Stereochemie (Introduction to Stereochemistry). By *K. Mislow*. Translation of the American Original by *H. Grünewald*. Verlag Chemie GmbH., Weinheim1967. 1st Edit.,vii,172 pp., 84 figures, paper, DM 19.-.

After the absence of a German textbook on stereochemistry for some decades, a translation of 'Eliel' and now of the 'Introduction to Stereochemistry' by *Mislow* have become available. The 'Introduction' treads new paths both in classification of the material and in terminology. It contains three chapters: Structure and Symmetry, Stereoisomerism, and Separation and Configuration of Stereoisomers.

Chapter 1 begins by explaining, with the aid of numerous diagrams, the relationship between the bond geometry of carbon compounds and the coordination number and then extends the results to hybridized states. Symmetry elements are utilized from the start and point groups are soon introduced, particular emphasis being placed on mirror-image symmetry. A section on molecular distortion and strain

energy follows, which treats the relationships between the change in molecular geometry and the energy content. The chapter closes with a critical discussion of conventional molecular models.

Chapter 2, Stereoisomerism, opens with the sentence that is fundamental to further understanding of the book: "Isomers or structural isomers are defined as chemical species which have the same molecular formula but differ in structure and are separated by energy barriers". Constitutional isomers and stereoisomers are next distinguished ("Stereoisomerism arises because molecules which have the same constitution may still differ in the spatial arrangements of their atoms") and this is followed by the important definition: "Stereoisomers which are related as object and nonsuperimposable mirror image are called enantiomers or antipodes, whereas those which are not so related are called diastereomers". If this widely based definition is accepted, the *cis-trans* olefins designated as geometrical isomers in the past must now be regarded as diastereomers. The chapter goes on to discuss optical activity, including optical rotatory dispersion and circular dichroism. A section that deserves special mention is that describing rotational isomerism of single bonds (conformational isomerism) in which two very useful terms are coined. The terms enantiomeric and diastereomeric are replaced in those cases where they refer to the stereochemistry of the surroundings of an atom or group by enantiotopic and diastereotopic. After a useful introduction to the stereochemistry of macromolecules, the chapter concludes with a discussion of topological isomerism (*e.g.* catenanes).

In Chapter 3 the main emphasis is placed on the development and interpretation of the fundamentals of kinetic resolution of racemates and asymmetric synthesis, and on the determination of absolute configurations by both chemical and physical methods.

A set of exercises is given at the end of each chapter, answers following at the end of the book.

In its few pages the book provides an outline of modern stereochemistry, and as a result the high information density does not make for easy reading. True understanding and appreciation of the material is possible only if the reader works his way through the exercises, which are described by the author as an integral part of the book, since they are designed to advance the student, through the inclusion of new subject matter, beyond the descriptive material.

The broad definitions of stereoisomerism and diastereomerism are very useful for the advanced reader, but are difficult to understand for the beginner because the subordinate terms geometrical isomerism, conformational isomerism, and "conventional" diastereomerism are used without sufficient discrimination.

Viewed as a whole, *Mislow*'s "Introduction" is too difficult for the true beginner. For students preparing for their first degree, however, the book is not only a valuable supplement but a good textbook which offers fundamentals and results of stereochemical research in concentrated and modern form. In this sense the book can be recommended to all advanced students and postgraduates. *H. J. Bestmann* [NB 689 IE]

Kristallchemie (Crystal chemistry). By *J. Zemann*, Sammlung Göschen, Vol. 1200/1220a, Walter de Gruyter & Co., Berlin 1966, 144 pp., 90 figures, paper covers, DM 5.80.

To fit a rapidly growing field of research such as crystal chemistry into the framework of the Sammlung Göschen necessitates the practice of the art of omission. The author has deleted material in those realms in which even long monographs and collective works prove unsatisfactory, owing to the obvious impossibility of comprehensive treatment, *e.g.* in the compiling of special structural data. This small book is intended mainly for chemists, for whom it represents a well conceived introduction by virtue of its lucid general chapters on structural units and their bonding, and the fundamental treatment and description of chemical structures in the crystalline state. A desirable feature in future editions would be the provision of space for discussing additional material, *e.g.* the structure of molecules and complexes or possibly crystallographic and chemical comparisons of transition metal compounds, for the benefit of chemists taking an increasing interest in these problems.

H. G. v. Schnering [NB 693 IE]

Die Anwendung der paramagnetischen Elektronenresonanz in der Chemie (The Use of Paramagnetic Electron Resonance in Chemistry). By *L. A. Bljumenfeld, V. V. Vojevodski* and *A. G. Semjonow*. Translated from the Russian by *K. Heuer* and *Hannelore Heuer*. Akademische Verlagsgesellschaft, Frankfurt/Main 1966, 308 pages, 120 figures, and 20 tables, DM 55.–.

This book is addressed to the reader who wishes to use electron resonance to solve his chemical problems. The monograph, completed in 1961–1962 (with a few more recent additions by the translators) consists of a predominantly theoretical part (experimental technique, theory, evaluation of results) and of a part dealing with the application of the method.

A relatively large amount of space is devoted to a description of the design principles of the spectrometer. The chemist will generally skip this chapter because a commercial instrument is normally available. The theory of spectra (fine structure, *g*-factor and its anisotropy) in crystals is discussed in detail, whereas the anisotropic hyperfine structure and also the isotropic hyperfine structure are dealt with rather briefly. The treatment of the evaluation of the spectra is biased toward the study of crystalline samples.

Few publications, and these mostly the authors' own, are discussed to illustrate applications (chemical reactions, delocalization phenomena, radiolysis of solids, kinetics, *etc.*). This method prevents the inquiring chemist from becoming confused by a mass of individual results and directs him to fundamentals, but it does mean that he can seek solutions to his own particular problems only in the literature, especially in view of the year of publication of the original edition. The reproduction of the spectra leaves something to be desired, and the collection of the literature references at the end of the book makes reading more difficult. In view of the quantity of theoretical and experimental work published in the field during recent years the book only partially satisfies the needs of research workers in this field. For the chemist who wishes merely to familiarize himself with the method and its possibilities, the book will prove to be a useful acquisition.

K. Scheffler [NB 692 IE]

Dynamische Biochemie, Teil II. (Dynamic Biochemistry, Part II). By *E. Hofmann*. Wissenschaftliche Taschenbücher, Vol. 37. Akademie-Verlag, Berlin 1966. 1st Edit. 270 pages, 38 figures, 9 tables, paper covers, DM 12.50.

Among the pocket books published in recent years those of the Akademie-Verlag, Berlin, are distinguished by thorough, didactic editing and scientific accuracy. The volume "Dynamic Biochemistry, Part II" describes the fundamentals of protein and nucleic acid metabolism and the modern discoveries about cell make-up, regulation mechanisms, and molecular biology in a concise, pregnant, and scientifically impeccable manner. This well written book contains an amazing wealth of detail and interesting biochemical comparison material for such a small volume. Complicated relationships are illustrated by means of clear, if necessarily somewhat abridged diagrams. Even where the scope permits only indications, they are never given merely as keywords. Objections to modern interpretations are also discussed, though it has of course not been possible to take into account the results of the last two years, which have destroyed many

hypotheses. The one real feature whose absence will be felt is a reference to the chemo-osmotic theory of oxidative phosphorylations. Actual mistakes are neither frequent nor significant. Particular mention is due to the exceptionally neat and faultless presentation, combined with the very acceptable price. Every student interested in this (alas all too often neglected) subject will be able to afford the sound information contained in this excellent volume.

L. Jaenicke [NB 720 IE]

Mass Spectrometric Analysis of Solids. Edited by *J. Ahearn*. Elsevier Publishing Company, Amsterdam-London-New York 1966. 1st Edit., viii, 175 pp., 46 figures, 13 tables, Dfl. 30.–.

As a result of its high sensitivity, the simplicity of handling samples, and the relative ease of interpreting spectra, mass spectrometric analysis of solids is finding ever-increasing fields of application. The present book, which comprises five chapters written by experts, provides a review of the present state of this field.

Chapter 1, by *A. J. Ahearn*, gives a general introduction to the subject. In Chapter 2, *R. E. Honig* treats the methods of ion production used in analysis of solids. Methods of evaluation and analytical errors are also dealt with insofar as they are affected by the type of ion source. The use of photographic plates in quantitative mass spectroscopic analysis is decribed by *E. B. Owens* in Chapter 3, in which the blackening process, properties of photoemulsions for ion detection, density measurements, and methods for quantitative evaluation of spectra receive a critical treatment. Chapter 4, by *J. W. Guthrie*, deals with special analytical processes and mentions investigations of liquids, organic substances, metals of low melting point, as well as insulators and powders of varying conductivity. Further, the application of standards and measurements on very small samples are treated thoroughly. In the last Chapter, *W. M. Hickam* and *G. G. Sweeney* describe the application of the mass spectrograph as a microprobe. In such work the surface of the sample is examined by means of a tungsten tip, which serves as a spark electrode. There is also a short section dealing with the use of negative ions for analysis – a subject that is all too often neglected.

The text is written clearly and concisely, and apart from providing a general introduction it contains a wealth of data, in the form of tables and diagrams, that will also be of value to the expert. The bibliography at the end of each section is also useful. The book can be recommended to all who are concerned with analysis of solids, and particularly with trace analysis, as well as to all libraries frequented by chemists and physicists.

H. Hintenberger [NB 696 IE]

Spectrometric Identification of Organic Compounds. By *R. M. Silverstein* and *G. C. Bassler*, John Wiley and Sons, New York-London-Sydney 1967, 2nd Edit., ix, 256 pages, numerous illustrations, 75 s.

The publication of the 2nd edition of Silverstein-Bassler in 1967 follows four years after that of the 1st[1]. The aim and presentation remain unaltered, but the text has been completely rewritten, the exercises revised and supplemented, and numerous new figures, tables, and literature references inserted. Thus, practically all the shortcomings of the 1st edition have been eliminated. It is only difficult to understand why the UV bands are still denoted by the out-of-date system of *Burawoy* and why in the compilation of the notations for the aromatic bands it is precisely those of *Clar* and *Platt* that are missing.

In view of the increasing importance attached to physical methods in organic chemistry today, the trouble taken by the authors in preparing the 2nd edition is extremely welcome. Chapter 2 (Mass Spectroscopy) has been considerably expanded. All mass spectra are now shown graphically (instead of in tabular form as previously), so that typical spectra are much easier to recognize. Chapter 3 (IR Spectroscopy) clarifies the discussion of characteristic group frequencies of individual classes of compounds by reproducing more than 40 typical spectra. Chapter 4 (NMR spectroscopy) contains new sections dealing with protons on heteroatoms, coupling of protons with other nuclei, more complex spin-spin coupling, chemically but not magnetically equivalent protons, effects of an asymmetric center, virtual coupling, vicinal and geminal coupling in rigid systems, long-range coupling, and spin-spin decoupling.

In all chapters the data has been expanded and supplemented to such an extent that this excellent guide to identification of spectra will serve not merely as a text-book and exercise book but also as a quick reference source for the organic chemist in his laboratory. The book can be recommended without reservation to all who wish to learn about the application of spectroscopic methods to structural problems in organic chemistry, and to those who use spectroscopic methods in their research.

M. Klessinger [NB 713 IE]

Organic Chemistry of Synthetic High Polymers. By *R. W. Lenz*. Interscience Publishers, a Division of John Wiley & Sons, New York-London-Sydney, 1967. 1st Edit., xvi, 837 pages, 120 s.

This book attempts for the first time to present the entire field, including up-to-date results, in very concise and clear form. In principle the attempt has succeeded. Having regard to the vast amount of material covering such a wide range of topics, it would have succeeded even better if more than three of the chapters had been written by specialists. Some of the chapters are very short and assume considerable knowledge. To compensate, the most important literature references have been included – though only a few Russian ones – enabling the original works to be studied.

A number of detailed objections may be raised, of which the most important are the following: The gain recorded by the new systematic classification of polyreactions (1.1–1.3) over older concepts is outweighed by the future confusion that will arise, particularly for the non-specialist. The chapter dealing with inorganic polymers (6.6) leads to a wrong emphasis by omitting the most important classes. The degradation of a cationic chain end with an anion (9–15, p. 245) is much more like the degradation of an anionic chain end with an electrophilic group than a radical recombination (9–13, p. 245).

A β-elimination (9–16, p. 245) does not represent a disproportionation. By contrast to anionic end groups, the degradation reaction on free radical end groups is governed by the probability of the collision of two chain ends, *i.e.* purely thermodynamically; the comparison between "living polymers" and relatively stable radicals (cf. p. 247) is therefore not justified.

A great advantage of the book is the strict classification of the material and the generally concise and clear style. The references to model reactions involving species of low molecular weight that are given for many polyreactions are extremely useful and the frequent numerical examples given with the formulas contribute much to the clarity of the book. This welcome new publication undoubtedly enriches the literature in this field and will find a wide readership.

G. Greber [NB 711 IE]

Kinetics of Inorganic Reactions. By *A. G. Sykes*, Pergamon Press. Oxford 1966, 1st Edit., viii, 310 pages, 35 figures, 42 tables, paper covers, 30 s.

The fields of chemistry which have recently emerged out of the shadows into the limelight of general interest undoubtedly include that of inorganic reaction mechanisms. The retail book trade provides as good a confirmation as any of

this statement: within 12 months the new edition of the standard work by *Basolo-Pearson*, and the admirable monograph by *Langford-Gray* on ligand exchange reactions, are now being followed by the present book by *A. G. Sykes* which would be better entitled "Kinetics and Mechanisms of Inorganic Reactions".

The detailed classification seems a little confusing at first sight, but becomes sensible after a more detailed study of the material. The introduction is followed by a discussion of the experimental methods underlying kinetic investigations; one notes with satisfaction that the very topical technique of the study of fast chemical reactions has not been neglected. This chapter is likely to be very instructive, especially to the uninitiated. By contrast, the subsequent guide to the evaluation of experimental results is very brief indeed. The main part of the book (Chapters 4–15) is divided into two large sections: Gas-phase reactions and reactions in solution. The latter include isotope exchange reactions, redox reactions, acid-base reactions, substitution reactions of octahedral, square-planar, and tetrahedral complexes, and reactions of the hydrated electron. Unfortunately, no mention is made of catalytically controlled reactions in solution.

The book must be regarded as an introduction – and no more – into the field of kinetics and mechanisms of inorganic reactions. As revealed in the preface, it is intended primarily for senior undergraduate students, to whom it can be thoroughly recommended. The reasonable price offers no obstacle in this respect. *H. Werner* [NB 704 IE]

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Luciferins, Bioluminescent Substances

BY T. GOTO AND Y. KISHI[*]

The bioluminescence of the American firefly Photinus is due to the reaction of 2-(6-hydroxybenzothiazol-2-yl)-Δ^2-1,3-thiazoline-4-carboxylic acid ("firefly luciferin") with the enzyme luciferase in the presence of ATP and magnesium ion. In the crustacean Cypridina, on the other hand, the bioluminescence is due to the reaction of a luciferase with 8-(3-guanidinopropyl)-6-indol-3-yl-2-(1-methylpropyl)-3,7-dihydroimidazo[1,2-a]-pyrazin-3-one ("Cypridina luciferin"). The luciferin in Latia is 1,3,3-trimethyl-2-(4-formyloxy-3-methyl-3-butenyl)-1-cyclohexene and that in Renilla is a tryptamine derivative that has not yet been accurately identified; the luciferins of other luminescent organisms are not yet known. A review is given of the investigations which have been carried out on the above luciferins and the course of the luciferin-luciferase reaction is examined. Numerous spectral data obtained during the examination of these compounds are included in the text.

1. The Luciferin-Luciferase Reaction[1]

Some eighty years ago, *Dubois* found that the bioluminescence of the luminescent beetle *Pyrophorus* is due to the luciferin-luciferase reaction. Bioluminescence was observed when a hot aqueous extract ("luciferin") of the insect was mixed with a cold aqueous extract ("luciferase") after the initial luminescence had disappeared. This observation led to numerous studies on the luciferin-luciferase reaction in many bioluminescent organisms (see Table 1). It is now known that hot water extracts luciferin and destroys luciferase; the cold-water extract contains luciferase, and also luciferin at first, but the latter changes into an inactive oxidation product on standing in air.

The luciferin-luciferase reaction is the emission of light as a result of the enzyme (a luciferase)-catalyzed oxidation (generally with oxygen) of a substrate (a luciferin). Thus "luciferin" is the name given to a substance having special properties, and is not the name of one compound or of a class of compounds. For example, luciferin from the American firefly *Photinus*

Table 1. Dates of discovery and names of discoverers of the luciferin-luciferase reaction in various luminous organisms.

Pyrophorus (elaterid beetle)	1885	*Dubois*
Pholas dactylus (clam)	1887	*Dubois*
Photinus (American firefly)	1916	*Harvey*
Luciola (Japanese firefly)	1917	*Harvey*
Cypridina (ostracod crustacea)	1917	*Harvey*
Pyrocypris (ostracod crustacea)	1921	*Harvey*
Odontosyllis (marine fireworm)	1931	*Harvey*
Systellaspis (shrimp)	1931	*Harvey*
Latia (fresh-water snail)	1950	*Bowden*
Achromobacter (luminous bacteria) *Photobacterium* (luminous bacteria)	1953	*Strehler* *McElroy*
Heterocarpus (shrimp)	1955	*Haneda*
Gonyaulax (dinoflagellate)	1957	*Hastings* and *Sweeney*
Apogon and *Parapriacanthus* (fish)	1958	*Haneda* and *Johnson*
Renilla (sea pansy)	1959	*Cormier*
Collybia, *Armillaria*, and *Omphalia* (fungi)	1959	*Airth* and *McElroy*
Balanoglossus (marine euteropneust)	1963	*Dure* and *Cormier* [2]
Octochaetus multiporus (earthworm)	1966	*Johnson*, *Shimomura*, and *Haneda* [3]
Hoplophorus (shrimp)	1966	*Johnson*, *Stachel*, *Shimomura*, and *Haneda* [4]

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[1] *F. H. Johnson* and *E. H.-C. Sie* in *W. D. McElroy* and *B. Glass*: A symposium on light and life. Johns Hopkins Press, Baltimore 1961, p. 206.

[2] *L. S. Dure* and *M. J. Cormier*, J. biol. Chemistry *238*, 790 (1963).

[3] *F. H. Johnson*, *O. Shimomura*, and *Y. Haneda* in *F. H. Johnson* and *Y. Haneda*: Bioluminescence in progress. Princeton Univ. Press, New Jersey 1966, p. 385.

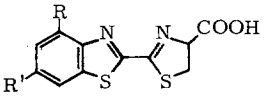
[4] *F. H. Johnson*, *H.-D. Stachel*, *O. Shimomura*, and *Y. Haneda* in [3], p. 523.

is completely different from luciferin from the marine crustacean *Cypridina*. The luciferases of these organisms are also different.

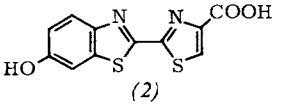
2. Isolation and Structure of Firefly Luciferin

The luciferin-luciferase reaction in firefly was discovered by *Harvey* [5] in 1916. This author first prepared "luciferin" and "luciferase" solutions from the lanterns of luminous insects as well as from non-luminous insects. Luciferin and luciferase from luminous insects emitted light when mixed, as did luciferin from non-luminous insects and luciferase from luminous insects. Luciferin and luciferase from non-luminous insects or luciferin from luminous insects and luciferase from non-luminous insects did not exhibit luminescence when mixed. The emission of light thus evidently depended on the source of the luciferase.

In 1947, *McElroy* showed that the "luciferin" obtained by *Harvey* was in fact adenosine triphosphate (ATP) [5]. The firefly luciferin was first isolated in 1957 from *Photinus pyralis* [6]. This substance is stable in oxygen-free alkaline media, but is readily oxidized by oxygen to dehydroluciferin, a compound that can also be isolated from the firefly. The UV spectrum of the luciferin indicates a benzothiazole chromophore, and acid hydrolysis affords 6-hydroxybenzothiazole and cysteine. Consideration of these facts led to the assignment of structure *(1)* to the luciferin [7] and of structure *(2)* to the dehydroluciferin.



(1) R = H, R' = OH
(3) R = H, R' = NH_2
(4) R = R' = OH



(2)

The structures of the compounds were also verified by total synthesis from ethyl *N*-(*p*-methoxyphenyl)oxamate. Only D-(−)-luciferin produced light, and was therefore identical with the natural compound; L-(+)-luciferin was inactive. The UV, fluorescence, and emission spectra of firefly luciferin *(1)* and dehydroluciferin *(2)* are shown in Figures 1 and 2 [8].

Of several analogs of luciferin [9] that have been synthesized and tested for bioluminescence, only "aminoluciferin" *(3)* and "4-hydroxyluciferin" *(4)* gave a positive reaction, aminoluciferin giving red luminescence.

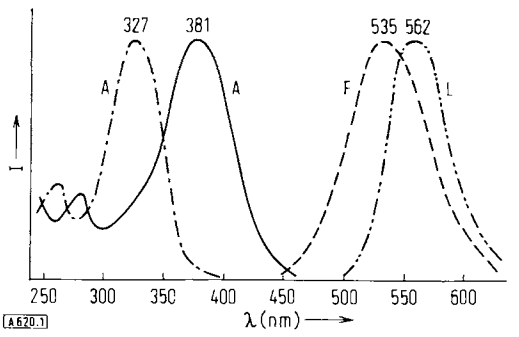


Fig. 1. Spectrum of the luciferin *(1)* of the American firefly *Photinus*. (—·—·) acid, (—) base, (— — —) base. A, absorption; F, fluorescence; L, luminescence.

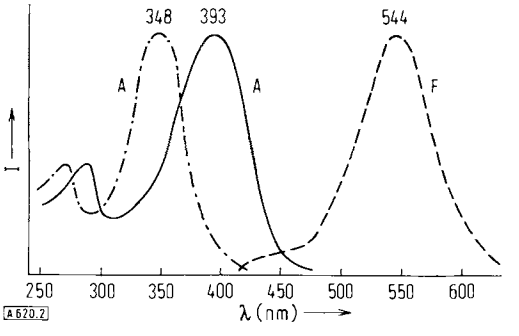


Fig. 2. Spectrum of dehydroluciferin *(2)* of the American firefly *Photinus*. (—·—·) acid, (—) base, (— — —) base. A, absorption; F, fluorescence.

Though the various species of fireflies differ in the color of the light emitted (from green to yellow), all the species examined, including *Photinus*, *Photuris*, *Pyrophorus*, *Diphotus*, and *Lecontea*, contain the luciferin *(1)* [10]. The luciferin of *Luciola cruciata* was also identical with that of *Photinus* [11].

3. The Luminescence of the Firefly [12]

The luminescence of the firefly requires the presence of luciferin (LH_2), luciferase (E), magnesium ions, ATP, and oxygen. The first step is a dark reaction leading to the formation of enzyme-bound luciferyl adenylate (LH_2–AMP) [13].

$$LH_2 + ATP + E \underset{}{\overset{Mg^{2+}}{\rightleftharpoons}} E\text{-}(LH_2\text{–}AMP) + P\text{–}P$$

As can be seen from Figure 3a, this reaction depends on the concentrations of luciferin and of ATP. In the next step the enzyme complex E–(LH_2–AMP) reacts with oxygen and light is emitted; the reaction product remains bound to the enzyme. Because of this product inhibition, the reaction leading to the emission of light also depends on the quantity of luciferase (cf. Fig. 3b).

[5] *E. N. Harvey*: Bioluminescence. Academic Press, New York 1952.

[6] *B. Bitler* and *M. D. McElroy*, Arch. Biochem. Biophysics *72*, 358 (1957).

[7] *E. H. White*, *F. McCapra*, and *G. F. Field*, J. Amer. chem. Soc. *83*, 2402 (1961); *85*, 337 (1963).

[8] *M. D. McElroy* and *H. H. Seliger*, Advances in Enzymology *25*, 119 (1963).

[9] *E. H. White*, *H. Wörther*, *G. F. Field*, and *W. D. McElroy*, J. org. Chemistry *30*, 2344 (1965); *E. H. White* and *H. Wörther*, *ibid. 31*, 1484 (1966); *E. H. White*, *H. Wörther*, *H. H. Seliger*, and *W. D. McElroy*, J. Amer. chem. Soc. *88*, 2015 (1966).

[10] *H. H. Seliger* and *W. D. McElroy*, Proc. nat. Acad. Sci. USA *52*, 75 (1964).

[11] *Y. Kishi*, *T. Goto*, *S. Inoue*, *O. Shimomura*, and *Y. Hirara*, paper read at the XI. Pacific Science Congress, Tokyo 1966.

[12] *W. D. McElroy* and *H. H. Seliger* in [3], p. 427.

[13] *W. D. McElroy* and *A. Green*, Arch. Biochem. Biophysics *64*, 257 (1956); *W.E. Rhodes* and *W.D. McElroy*, Science (Washington) *128*, 253 (1958); J. biol. Chemistry *233*, 1528 (1958).

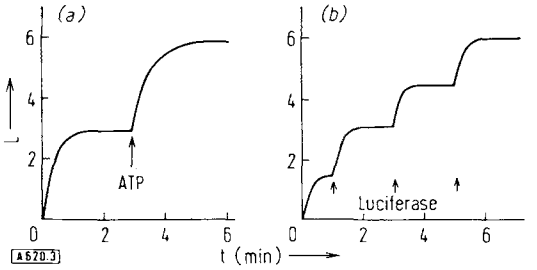


Fig. 3. Luminescence of the American firefly *Photinus*.
(a) on introduction of ATP and (b) on successive introduction of luciferase. L = integrated light units (arbitrary units).

Dehydroluciferin (L) was formerly regarded as a direct product of the reaction leading to light emission. However, more recent results indicate that dehydroluciferin does not correspond to the ground state of the excited intermediate, but is instead an alternative oxidation product, which is not involved in the emission of light, and cannot be regarded as a product formed from the excited intermediate.

Since one mole of luciferin consumes one mole of oxygen [8], equation (a) cannot be correct. The alternative equation (b) is also wrong, since it would not provide the required energy of more than 60 kcal/mole, and

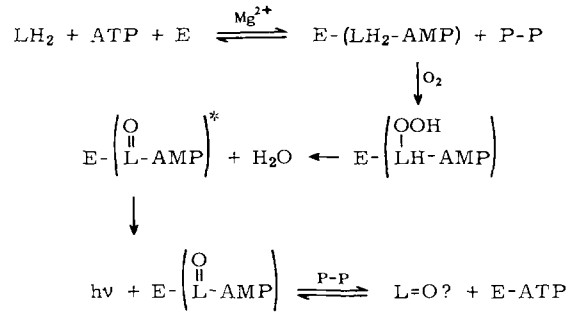
$$E\text{–}(LH_2\text{–}AMP) + {}^1/_2\,O_2 \rightarrow E\text{–}(L\text{–}AMP) + H_2O + h\nu \quad (a)$$

$$E\text{–}(LH_2\text{–}AMP) + O_2 \rightarrow E\text{–}(L\text{–}AMP) + H_2O_2 + h\nu \quad (b)$$

no H_2O_2 has been detected in the reaction mixture. Moreover, the fluorescence spectra of dehydroluciferin and its derivatives do not agree with the bioluminescence spectra. UV spectroscopic studies point to a possible intermediate having an absorption maximum at 400–410 nm [14]. Since the bioluminescence quantum yield is close to one [15], the fluorescence yield of the intermediate must be almost 100 %.

Synthetic L-luciferin does not exhibit bioluminescence and does not consume oxygen, but like D-luciferin, it reacts with ATP to liberate pyrophosphate (P–P) when treated with ATP, luciferase, and magnesium ions [12]. On the basis of all the known results, it is possible to formulate Scheme 1.

The reaction would provide more than 100 kcal/mole; the product L=O has not yet been detected. L and possibly L=O inhibit the production of light, and can be removed from the enzyme by the addition of pyrophosphate or of coenzyme A.

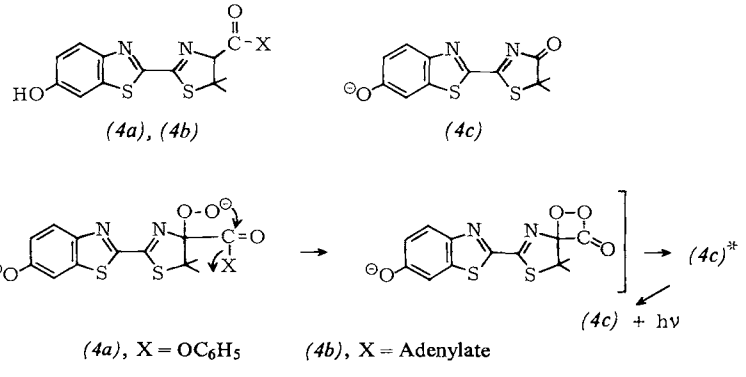


Scheme 1. Suggested scheme for the luciferin (LH_2)-luciferase(E) reaction.

The active center of firefly (Photinus) luciferase was thought to consist of two thiol groups. However, contrary to the belief that the energy source for the bioluminescence would be the energy-rich phosphate bond, there is no indication of any rupture of the anhydride bond in luciferyl adenylate and formation of an LH_2–S–E bond during bioluminescence [12].

Synthetic firefly luciferyl adenylate exhibits chemiluminescence in the absence of the enzyme when treated with KOH or potassium *tert*-butoxide in dimethyl sulfoxide [16].

Recently, *McCapra et al.* [16a] and *Seliger et al.* [16b] reported the chemiluminescence of 5,5-dimethylluciferin derivatives, *i.e.* the phenyl ester *(4a)* and the adenylate *(4b)*, respectively, and identified the ketone *(4c)* as the reaction product. The fluorescence spectrum of *(4c)* is superimposable on the chemiluminescence spectrum. The proposed mechanism involves a peroxide intermediate having a four-membered ring; similar intermediates occur in the chemiluminescence of lophine derivatives and of derivatives of acridinecarboxylic acids.



The chemiluminescence of luciferyl adenylate in DMSO and the fluorescence of the spent chemiluminescence reaction mixtures are identical with the fluorescence of the anion *(4c)*. The product of this chemiluminescence, however, proved to be too unstable to be isolated. *In-vitro* bioluminescence of luciferin at pH 7.5 is yellow-green (565 nm), but in acidic media (pH 6.0) it becomes red (620 nm). The chemiluminescence of luciferyl adenylate (red emission) corresponds

[14] *H. H. Seliger* and *W. D. McElroy* in [3], p. 405.

[15] *H. H. Seliger* and *W. D. McElroy*, Arch. Biochem. Biophysics *88*, 136 (1960).

[16] *H. H. Seliger* and *W. D. McElroy*, Science (Washington) *138*, 683 (1962).

[16a] *F. McCapra*, *Y. C. Chang*, and *V. P. Francois*, Chem. Commun. *1968*, 22.

[16b] *T. A. Hopkins*, *H. H. Seliger*, *E. H. White*, and *M. W. Cass*, J. Amer. chem. Soc. *89*, 7148 (1967).

to the bioluminescence, and little information is available concerning the yellow-green emitting species in bioluminescence. *Seliger et al.* suggested the possibility of the dianion of *(4c)* acting as the emitter.

4. Isolation and Structure of Cypridina Luciferin

The crustacean *Cypridina hilgendorfii* is abundant along the coast of Japan. The organism is about 3 mm long, and emits a strongly luminescent secretion into sea water. The luciferin-luciferase reaction of *Cypridina* was discovered by *Harvey* in 1917 [5]. The luminescent activity is preserved almost indefinitely in completely dry *Cypridina*, and the luminescence is restored by moisture. Attempts to isolate the luciferin from dry *Cypridina* led at first to a "purified", but not to a crystalline luciferin [17].

The reason for the difficulty encountered in the extraction and purification of the luciferin is that the substance is present in dry *Cypridina* only in very small quantities, and is extremely unstable to oxygen and water. The most successful of the methods developed was the benzoylation method described by *Anderson* [18], in which the luciferin is benzoylated in butanol extract with a large excess of benzoyl chloride and without a basic catalyst.

Crystalline luciferin was obtained in 1957 [19] from *Anderson*'s benzoyl luciferin, which was first purified by chromatography on cellulose powder. The luciferin crystallized out from an aqueous-methanolic solution as the hydrochloride on acidification with concentrated hydrochloric acid.

Since 1917, several workers have proposed partial structures for luciferin on the basis of the "purified" product. For example, the luciferin is claimed to be a peptone, a phospholipid, a polyhydroxybenzene derivative, a hydroquinone-like compound having a ketohydroxy side chain, a flavoprotein, a pyridine nucleotide, and a chromopolypeptide [20].

Though the UV spectra indicate that "purified" luciferin is practically identical with the crystalline product, acid hydrolysis of the "purified" luciferin gives about 20 amino acids [20], whereas that of crystalline luciferin gives only a few [19]. Catalytic hydrogenation gives a compound (hydroluciferin) whose UV spectrum is typical of an indole [19]. It has been difficult to carry out a structural analysis of the luciferin because of the small quantity of material available, and a structure that seemed plausible at first [21] was later found to be wrong. Quantitative determination of the amino acid compositions of luciferin and of hydroluciferin with the aid of the amino acid analyzer [22, 24] gave the results shown in Table 2.

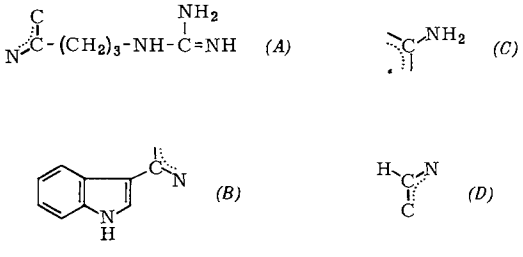
Table 2. Amino acids obtained from Cypridina luciferin and hydroluciferin by acid hydrolysis *in vacuo* or under oxygen.

	From luciferin *(11)*		From hydroluciferin	
	Vacuum	O_2	Vacuum	O_2
Glycine	0.96	0.93	0.03	0.12
Arginine [a]	0.62	0.38	0.03	0.41
Isoleucine [b]	0.16	0.16	0.98	0.96
Ammonia	0.27	0.33	0.40	0.41

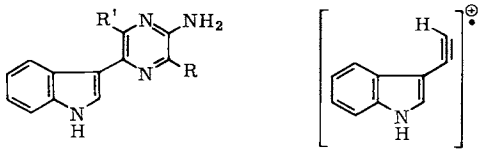
[a] Combined amounts of arginine, γ-guanidinobutyric acid, and proline.
[b] Combined amounts of isoleucine and alloisoleucine; both acids being produced in nearly the same amounts.

In 1961, *Johnson et al.* extracted luciferin directly from living *Cypridina* [23]. Apart from saving a great deal of time, this permits an increase in the yield by a factor of more than ten (about 20 mg of crystalline luciferin per kg of moist *Cypridina*).

The complete structure of *Cypridina* luciferin *(11)* was determined chemically in 1966 [24]. Enzymatic (luminescence) or non-enzymatic air oxidation of *(11)* yields two fluorescent substances, *i.e.* oxyluciferin *(9)* and etioluciferin *(5a)*; *(9)* can be converted into *(5a)* by acid hydrolysis. The structure of etioluciferin *(5a)* was established as follows: On hydrolysis with $Ba(OH)_2$ in the absence of oxygen it gave etioluciferamine, the composition of which was found by high-resolution mass spectrometry to be $C_{15}H_{17}N_5$. The etioluciferin itself has a guanidino group in place of an amino group, and has the composition $C_{16}H_{19}N_7$. On catalytic hydrogenation it gave a compound (hydroetioluciferin) having a UV spectrum typical of the indole nucleus; the pH-dependence of the UV spectrum pointed to a β-aminomethylindole structure (*B*). The NMR spectrum of *(5a)* in conjunction with the amino acid composition led to the partial structures (*A*) and (*D*). The partial structure (*C*) was deduced from the p*K* values and the diazo coupling reaction of *(5a)*.



There are only two possible complete structures *(5a)* and *(5b)* that can be formed from these four partial structures. *(5b)* is ruled out by the mass spectrum of etioluciferamine, since the peak at $m/e = 141$ must be assigned to the radical ion *(6)*.



(5a) R = $(CH_2)_3$-NH-C(=NH)-NH$_2$, R' = H

(5b) R = H, R' = $(CH_2)_3$-NH-C(=NH)-NH$_2$

(6) m/e = 141

[17] *F. I. Tsuji, A. M. Chase,* and *E. N. Harvey* in *F. H. Johnson*: The Luminescence of Biological Systems. Amer. Assoc. for the Advancement of Sci., Washington 1955, p. 127.

[18] *R. S. Anderson*, J. gen. Physiol. *19*, 301 (1935).

[19] *O. Shimomura, T. Goto,* and *Y. Hirata*, Bull. chem. Soc. Japan *30* 929 (1957).

[20] Cf. p. 130 in [17].

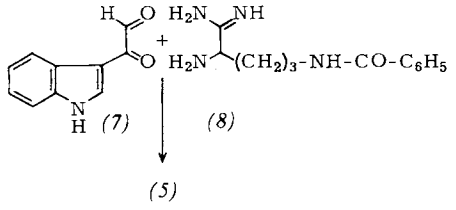
[21] *Y. Hirata, O. Shimomura,* and *S. Eguchi*, Tetrahedron No. 5, p. 4 (1959); *O. Shimomura*, J. chem. Soc. Japan *81*, 179 (1960).

[22] *S. Eguchi*, J. chem. Soc. Japan *84*, 86 (1963).

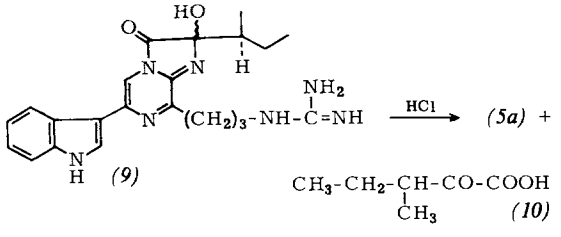
[23] *Y. Haneda, F. H. Johnson, Y. Masuda, Y. Saiga, O. Shimomura, H.-C. Sie, N. Sugiyama,* and *I. Takatsuki*, J. cellular comparat. Physiol. *57*, 55 (1961).

[24] *Y. Kishi, T. Goto, Y. Hirata, O. Shimomura,* and *F. H. Johnson*, Tetrahedron Letters *1966*, 3427; in [3], p. 89.

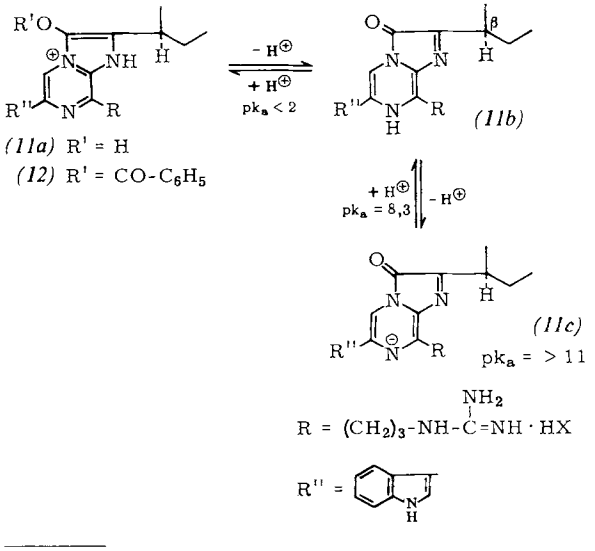
The structure *(5a)* was finally confirmed by total synthesis from *(7)* and *(8)* [25], which were treated successively with sodium hydroxide solution, methanolic KOH, and $H_2N-C(=NH)-SCH_3$. The assumptions concerning the relative positions of the amino and indole groups on the pyrazine nucleus were confirmed by the UV and NMR spectra [26].



On treatment with hydrochloric acid, oxyluciferin *(9)* gives α-oxo-β-methylvaleric acid *(10)* as well as *(5a)*. The NMR spectrum of *(9)* contains a sharp OH singlet signal. It can be seen from Table 2 that the nitrogen atom that appears as isoleucine does not also form arginine or glycine. Since the keto acid *(10)* must be derived from the isoleucine part, C-2 of *(10)* must have been attached to the primary amino group of *(5a)*. This leads to the structure *(9)* for the oxyluciferin.



The NMR spectrum of Cypridina luciferin contains no OH signal. The orange-red solution of luciferin hydrobromide in methanol is decolorized by anhydrous HBr, and the UV spectrum of the solution is then very similar to that of *(5a)*. Luciferin has three pK_a values, *i.e.* <2, 8.3, and >11; it is yellow in basic media. The three forms of the luciferin are best formulated as *(11a)*, *(11b)*, and *(11c)*.



The UV, fluorescence, and emission spectra of Cypridina luciferin and oxyluciferin are shown in Figures 4 and 5.

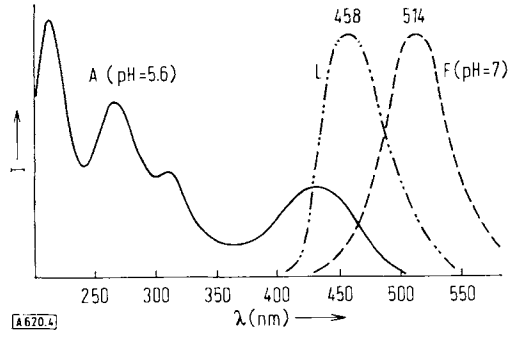


Fig. 4. Spectrum of Cypridina luciferin *(11)*. (—) acid, (— — —) base. A, absorption; F, fluorescence; L, luminescence.

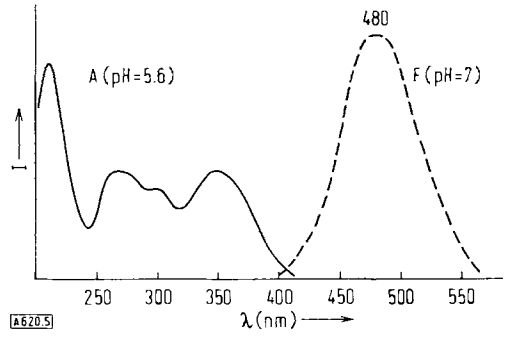


Fig. 5. Spectrum of Cypridina oxyluciferin *(9)*. (—) acid, (— — —) base. A, absorption; F fluorescence.

The benzoylated Cypridina luciferin obtained by *Anderson*'s method has a UV spectrum similar to that of *(5a)* or *(11a)*, and probably has the structure *(12)*.

The absolute configuration at the β carbon atom of the isoleucine portion was determined enzymatically as follows: Hydrolysis of hydroluciferin gave a mixture of isoleucine and alloisoleucine; this mixture was treated with L- and D-amino-acid oxidases and the products were examined with an amino acid analyzer. It was found that Cypridina luciferin is built up from tryptamine, arginine, and L-isoleucine portions. This structure explains the unusual result of the amino acid analysis (Table 2) [27].

Cypridina luciferin has been obtained by total synthesis from *(10)* and *(5a)* (reaction with Pt/H_2 or Al/Hg followed by reaction with dicyclohexylcarbodiimide).

The luciferins of the luminous fish *Apogon* and *Parapriacanthus* are identical with Cypridina luciferin [28].

5. The Luminescence of *Cypridina*

As early as 1919, *Harvey* observed that the *in-vitro* luminescence of *Cypridina* is a first-order reaction (Fig. 6) [5]. Further kinetic studies by *Chase* and *Lorenz* showed that two first-order reactions take place, one of which produces light while the other is a dark re-

[25] *Y. Kishi, T. Goto, S. Inoue, S. Sugiura*, and *H. Kishimoto*, Tetrahedron Letters *1966*, 3445.

[26] *T. Goto* and *S. Inoue*, unpublished.

[27] *Y. Kishi, T. Goto, S. Eguchi, Y. Hirata, E. Watanabe*, and *T. Aoyama*, Tetrahedron Letters *1966*, 3437.

[28] *F. H. Johnson, N. Sugiyama, O. Shimomura, Y. Saiga*, and *Y. Haneda*, Proc. nat. Acad. Sci. USA *47*, 486 (1961); *Y. Haneda, F. H. Johnson*, and *O. Shimomura* in [3], p. 533.

action [29]. According to *Johnson et al.* [30], one molecule of luciferin consumes one atom of oxygen during luminescence; the quantum yield is at least 0.28. Since the light-producing reaction and the dark reaction gave the same products, *i.e.* oxyluciferin *(9)* and etioluciferin *(5a)*, the luminescence reaction can be represented by

$$LH_2 + {}^1/_2\,O_2 \xrightarrow{\text{Enzyme}} (9) + (5a) + h\nu$$

In air, an orange-red aqueous luciferin solution turns red, and then colorless, owing to autoxidation (Fig. 7) [19].

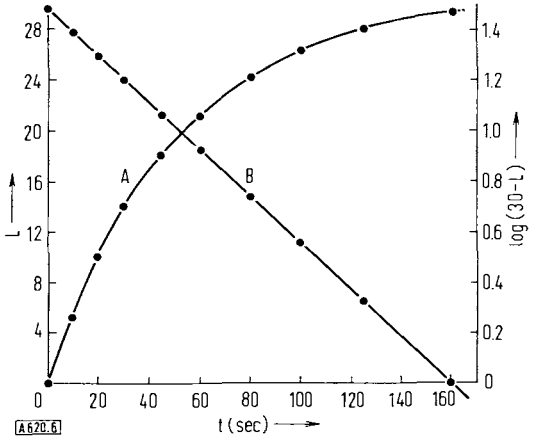


Fig. 6. Bioluminescence in the system Cypridina luciferin/luciferase. The left-hand ordinate refers to curve A (L = integrated light units) and the right-hand ordinate to curve B.

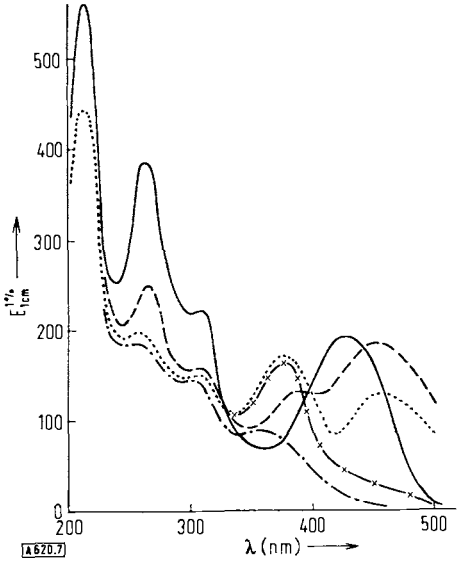
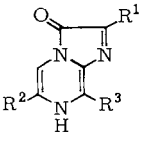


Fig. 7. Non-enzymatic oxidation of Cypridina luciferin with air in phosphate-buffered aqueous solution at pH = 5.6.
(—) freshly prepared solution, (— — —) after 1 day, (. . . .) after 3 days, (—×—) after 7 days, (—·—·) after 52 days.

A similar change is observed in the spectrum of the bioluminescence in the presence of the enzyme [31], but the enzyme-catalyzed reaction is extremely fast. The initial red shift points to the formation of a red substance, which can be isolated from the reaction mixture. This red substance emits very little light in the presence of the enzyme, but the luminous activity can be restored by chemical reduction; addition of a reducing agent such as ascorbic acid to the reaction mixture prevents the formation of the red substance [32]. This phenomenon was observed by *Harvey*, *Anderson*, and others, who regarded it as a reversible oxidation of the luciferin [5]. However, the structure of this substance and its role in the reaction leading to the emission of light are not yet known.

Cypridina luciferin exhibits spontaneous chemiluminescence [33] when dissolved in dimethyl sulfoxide, with or without a base, in the presence of oxygen, though the quantum yield of this chemiluminescence is low (*ca.* 0.15% of bioluminescence). When diglyme containing acetate buffer is used as the solvent, the quantum yield of the chemiluminescence of luciferin increases to more than 10% of that of bioluminescence and is then about twice as great as that of luminol chemiluminescence in DMSO with potassium *tert*-butoxide [33a]. The simplest analog *(13)* of luciferin is also chemiluminescent in DMSO with acetate buffer and consumes one mole of oxygen during the reaction [33a]. *McCapra* and *Chang* [33b] studied the chemiluminescence of the 6-phenyl-2,8-dimethyl derivative *(14)* in



(13), $R^1 = R^2 = R^3 = H$
(14), $R^1 = R^3 = CH_3$, $R^2 = C_6H_5$
(15), $R^1 = CH(CH_3)\text{-}CH_2\text{-}CH_3$, $R^2 = C_6H_5$, $R^3 = (CH_2)_3\text{-}NH\text{-}C(=NH)\text{-}NH_2$
(16), $R^1 = CH(CH_3)\text{-}CH_2\text{-}CH_3$, $R^2 =$ Indolyl, $R^3 = CH_2\text{-}CH_2\text{-}NH\text{-}C(=NH)\text{-}NH_2$

DMSO in the presence of potassium *tert*-butoxide. They isolated as the reaction product 2-acetamino-3-methyl-5-phenylpyrazine (shown as the anion *(17)*), whose fluorescence spectrum in the alkaline medium corresponds to the chemiluminescence spectrum, and suggested a mechanism involving a four-membered ring peroxide intermediate (see Section 3). Kinetic investigations indicate a participation of radical intermediates [33a].

Bioluminescence of *Cypridina* is more dependent on the structure of the substrate than the above chemiluminescence. Thus, phenyldesindolylluciferin *(15)* is very weakly bioluminescent, whereas the bioluminescence activity of norluciferin *(16)* is comparable with that of luciferin [33c]. Replacement of the alkyl side

[29] *A. M. Chase* and *P. B. Lorenz*, J. cellular. comparat. Physiol. *25*, 53 (1945).

[30] *F. H. Johnson*, *O. Shimomura*, *Y. Saiga*, *L. C. Gershman*, *G.T. Reynolds*, and *J. R. Waters*, J. cellular. comparat. Physiol. *60*, 85 (1962).

[31] *A. M. Chase* and *E. H. Brigham*, J. biol. Chemistry *190*, 529 (1951).

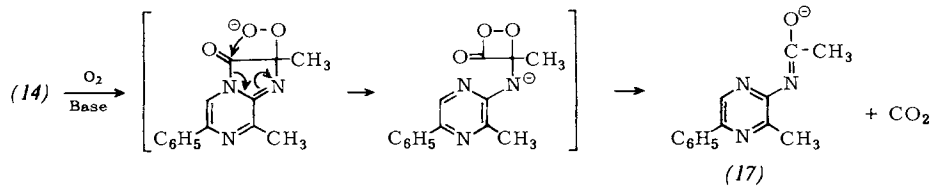
[32] *A. M. Chase*, *J. H. Ball*, *C. E. Cornelius*, and *R. J. Lederman* in [1], p. 258.

[33] *F. H. Johnson*, *H.-D. Stachel*, *E. C.Taylor*, and *O. Shimomura* in [3], p. 67.

[33a] *T. Goto*, *S. Inoue*, and *S. Sugiura*, unpublished.

[33b] *F. McCapra* and *Y.C.Chang*, Chem. Commun. *1967*, 1011.

[33c] *D. A. Coviello*, *S. Inoue*, and *T. Goto*, paper read to the Chemical Society of Japan in Nagoya (Oct. 17, 1967).



(17)

chain (R^1) of luciferin by other alkyl groups diminishes the bioluminescence activity moderately, but hydrolysis of the guanidino group of luciferin to the corresponding amino group lowers the activity [25, 33d] considerably.

6. Bacterial Luciferin

In bacterial luminescence, reduced flavin mononucleotide, an enzyme, oxygen, and a long-chain aliphatic aldehyde are essential factors for the production of light. The quantum yield is very low and the reactions involved are complicated. The aldehyde was initially regarded as the bacterial luciferin [34], but its role in the reaction has not yet been definitely established [8, 35]. Despite extensive efforts to explain the luminescence, it is not certain which substance is to be regarded as the bacterial luciferin.

7. Renilla Luciferin

Renilla luciferin was isolated in a purified form from *Renilla reniformis* by *Cormier et al.* [36]. It is stable in neutral or basic solution, and in acidic solution it is converted into "activated luciferin", which emits light (λ_{max} = 485 nm) in the presence of luciferase or on autoxidation (without enzyme), with formation of an oxidized luciferin. Activated luciferin is also formed on incubation of luciferin with luciferase, calcium ions, and adenosine 3′,5′-diphosphate under anaerobic conditions.

Renilla luciferin is a tryptamine derivative with an anionic group. Alkaline hydrolysis of the dehydroluciferin yields tryptamine. Activation of the luciferin is accompanied by removal of the anionic group, which may be sulfate.

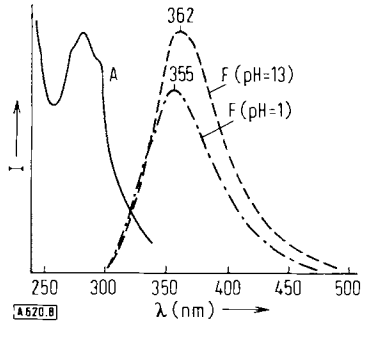


Fig. 8. Spectrum of Renilla luciferin. (—) neutral, (— — —) base, (—·—·) acid. A, absorption; F, fluorescence.

Thus the reaction leading to the emission of light again proceeds in at least two steps. In the first step, which is a dark reaction, sulfate is probably transferred from the luciferin to the adenosine 3′,5′-diphosphate, with formation of active luciferin. This is enzymatically oxidized in the second step, and light is emitted. The absorption and fluorescence spectrum of Renilla luciferin are shown in Figure 8.

8. Odontosyllis Luciferin

The luminescence of *Odontosyllis* involves a luciferin, luciferase, and oxygen. *McElroy* [8] found a fluorescence emission maximum at about 510 nm for partly purified luciferin; this maximum agrees with that observed during luminescence. Autoxidized luciferin can be reduced to the active form.

Shimomura et al. [37] recently obtained a purified luciferin from *Odontosyllis enopla* as a colorless, nonfluorescent substance. After light emission (λ_{max} = 507 nm), a fluorescent product having a fluorescence maximum at 507 nm was obtained. Attempts to convert this product into an active luciferin with reducing agents have been unsuccessful. The absorption and luminescence spectra of Odontosyllis luciferin and of the luminescent product are shown in Figure 9.

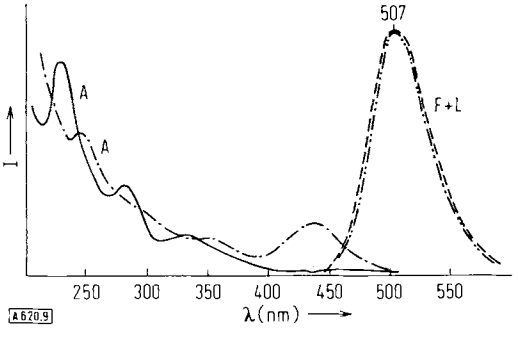


Fig. 9. Spectrum of Odontosyllis luciferin (neutral) (——) and of the luminescent product(s) (neutral) (—·—·), neutral (— — —), (—··—··) neutral. A, absorption; F, fluorescence; L, luminescence.

In the absence of enzyme, Odontosyllis luciferin can be readily oxidized to a pink substance having absorption maxima at 260, 330, and 520 nm. This change can be brought about by the addition of iodine. The pink substance remains unchanged in the presence of oxygen and luciferase.

[33d] *Y. Kishi*, Dissertation, Nagoya University, 1966.

[34] *W. D. McElroy, J. W. Hastings, V. Sonnenfeld*, and *J. Coulombre*, J. Bacteriol. *67*, 402 (1954).

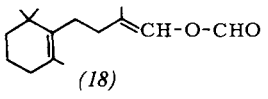
[35] *J. W. Hastings, Q. H. Gibson, J. Friedland*, and *J. Spudich* in [3], p. 151, and further literature cited there.

[36] *K. Hori* and *M. J. Cormier*, Biochim. biophysica Acta *102*, 386 (1965); *M. J. Cormier, K. Hori*, and *P. Kreiss* in [3], p. 349.

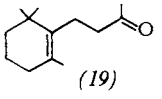
[37] *O. Shimomura, F. H. Johnson*, and *Y. Saiga*, J. cellular. comparat. Physiol. *61*, 275 (1963).

Luciferin has been isolated in an almost pure state from the fresh-water snail *Latia* [38]. The substance gives an absorption maximum at 212 nm and two IR bands at 1745 cm^{-1} (strong) and 1685 cm^{-1} (weak). Latia luciferin is fairly volatile, and has a molecular weight of 236 (determined by mass spectrometry). When the luciferin is mixed with luciferase solution, a luminescence with an emission maximum at 520 nm can be observed.

Recently, *Shimoura* and *Johnson* deduced the structure of Latia luciferin *(18)* and its luminescent product



(18)



(19)

(19) [38a]. The product, dihydro-β-ionone, however, may not be regarded as the emitter of the bioluminescence.

[38] *O. Shimomura, F. H. Johnson,* and *Y. Haneda* in [3], p. 391.
[38a] *O. Shimomura* and *F. H. Johnson,* Biochemistry, in press.
[39] *S. Kuwabara* and *E. C. Wassink* in [3], p. 233.

Kuwabara and *Wassink* [39] isolated fungal luciferin from the luminous fungus *Omphalia flavida.* In the presence of luciferase or NaOH and H_2O_2 it emits light. The absorption, fluorescence, and emission spectrum are shown in Figure 10.

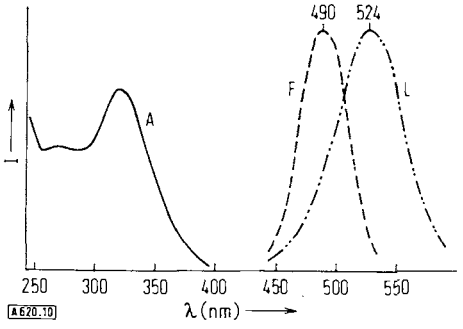


Fig. 10. Spectrum of luciferin from the fungus *Omphalia flavida* at pH = 6.5. A, absorption; F, fluorescence; L, luminescence.

The authors are grateful to Professor Y. Hirata for his interest in this work.

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Soot Formation in Premixed Hydrocarbon Flames

BY K. H. HOMANN [*]

The critical fuel-oxygen ratio for soot formation and its dependence on temperature and pressure are discussed for various hydrocarbons. It is shown in the case of the Bunsen flame that the shape and structure of the flame front also have a decisive effect on soot formation. In the reaction zone of fuel-rich hydrocarbon flames, unsaturated compounds are formed, and the concentration profiles of these products can provide quantitative information about their importance in soot formation. The "mechanism" of soot formation is discussed on the basis of the concentrations of higher hydrocarbons and the variation of the number and size of the soot particles. The effects of electric fields and foreign additives on soot formation have been given consideration.

1. Introduction

The familiar yellow light of a candle flame is due to the continuous thermal radiation of solid particles of soot, whereas the bluish light of an oxygen-rich hydrocarbon flame is mainly due to the emission from molecules. Interest in soot particles as a source of light has been rather pushed into the background by the importance of soot formation in other fields. Large quantities of soot are used as a filler in the rubber industry. Fine carbon blacks with high blackening powers are finding growing use in paints and lacquers. On the other hand, soot formation is very undesirable in many combustion processes, such as in diesel engines or in gas turbines, since soot particles are difficult to burn, and are partly deposited as a hard coating or leave the motor together with the exhaust gases to pollute the atmosphere. In industrial firing systems, soot is desirable in the flame because of the radiation of heat, but not in the cool exhaust gases.

Thermal processes yield various types of carbon-like deposits, ranging from very hard, brittle, and sometimes vitreous substances to the loose, oily gas blacks.

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They differ in their chemical composition, as well as in their color, which can be from brown to deep black. The properties of a carbon black, though well known, give little information about its formation. In order to establish how and through what intermediates solid particles of soot are formed in the gas phase, it is necessary to measure both the concentrations of the gaseous reactants and the course of the growth of the particle in the flame. The chemistry of soot formation depends, not only on the nature of the fuel, but also on the structure of the flame, its temperature distribution, and the pressure at which it burns. In the following we shall deal with premixed flames burning without secondary air and examine the conditions necessary for the generation of solid carbon particles from gaseous reactants.

2. Experimental Facts

2.1. Limits of Soot Formation

The critical fuel/oxygen (air) ratio in the unburnt gas at which soot formation can just be observed will be called the limiting ratio for soot formation, or simply the soot limit.

If thermodynamic equilibrium were completely established between the gaseous components and solid carbon (graphite) in the burnt gas of fuel-rich flames the overall flame reaction would be represented by the equation

$$C_mH_n + y\,O_2 \rightarrow 2\,y\,CO + \frac{n}{2}\,H_2 + (m-2\,y)\,C_{solid.}$$

Solid carbon would separate out when $m \geq 2y$, *i.e.* when the C/O ratio rises above ~ 1. This is valid in good approximation for a temperature range between 1500 and 2500 °K. At higher temperatures the concentrations of acetylenic hydrocarbons and also of atoms (mainly H), carbon species C_n, and hydrocarbon radicals have to be taken into consideration.

The above temperature range includes rich hydrocarbon-air and hydrocarbon-oxygen flames, with the exception of an acetylene-oxygen flame at atmospheric pressure. (The adiabatic temperature for this flame having a C/O ratio ≈ 1 is around 3300 °K, so that the burnt gas contains 17% of H atoms and 2% of unburnt acetylene in equilibrium; the theoretical soot limit in this case lies between C/O ratios of 1.03 and 1.07 [1].)

In practice, not all the reactions are in equilibrium, and the burnt gas of soot forming flames contains considerable quantities of water vapor and carbon dioxide, together with various hydrocarbons [2]. Neither the Boudouard equilibrium nor the equilibrium between hydrocarbons and solid carbon is established.

If an equilibrium is assumed between acetylene and soot in the burnt gas of rich acetylene flames (Fig. 11), the Gibbs free energy of the soot should be more than 10 kcal/mole higher than that of graphite. However, this is not confirmed by measurements of its heat of combustion [3]. Moreover, even a Gibbs free energy of this order would not explain a corresponding soot–CO_2–CO equilibrium.

The soot limit depends not only on the nature of the fuel, but also on flame properties such as the structure of the flame front, the temperature, quenching effects of the burner, and dilution by inert gas. In many investigations the appearance or disappearance of soot when changing the fuel/oxygen ratio was determined by visual observation of the radiation due to the soot. This method is simple and gives, within certain limits, reproducible results. However, the question of whether the emission from a given soot concentration is visible depends on the temperature of the flame and on the optical properties of the soot particles. Thus, the soot limits determined in this way correspond to a very low, but not always equal, concentration of soot. Moreover, the limiting ratio of the starting mixture in most cases is not the same as the true C/O ratio at the point of formation of the soot (cf. Section 2.4). However, this does not detract from the significance of these soot limits for practical purposes.

Street and *Thomas* [4] used the visual method to determine the soot limits of many hydrocarbons and oxygenated organic compounds; all the results differ appreciably from the theoretical limits. The results obtained by these authors are listed in Table 1 as critical C/O atomic ratios and (cf. *Daniels* [5]) as the number of oxygen atoms per molecule of fuel (N_O) at the soot limit.

These soot limits were determined for Bunsen flames, which sometimes exhibited disturbances of the flame front (see

Table 1.

Hydrocarbon	$(C/O)_{crit.}$	Number of oxygen atoms per molecule of hydrocarbon at the soot limit (N_O)	$\frac{\Delta N_O}{\Delta CH_2}$
Ethane	0.475	4.2	2.2
Propane	0.47	6.4	2.3
n-Butane	0.46	8.7	2.2
n-Pentane	0.46	10.9	2.2
n-Hexane	0.46	13.1	2.5
n-Octane	0.45	18.0	2.3
n-Hexadecane	0.44	36.3	
iso-Pentane	0.47	10.7	2.4
iso-Hexane	0.46	13.1	2.1
iso-Octane	0.46	17.3	2.3
iso-Dodecane	0.46	26.3	
Ethylene	0.60	3.3	2.1
Propene	0.56	5.4	2.3
n-Butene	0.48	7.7	2.1
n-Pentene	0.51	9.8	2.35
n-Heptene	0.48	14.5	
Acetylene	0.83	2.42	
Cyclohexane	0.51	11.9	
Benzene	0.57	10.5	3.0
Toluene	0.52	13.5	3.1
Xylene	0.48	16.6	2.6
Cumene	0.48	18.7	

[1] *N. R. Gay, J. T. Agnew, O. W. Witzell,* and *C. E. Karabell,* Combust. and Flame *5*, 257 (1961).

[2] *K. H. Homann, M. Mochizuki,* and *H. Gg. Wagner,* Z. physik. Chem. N.F. *37*, 299 (1963).

[3] *K. H. Homann* and *H. Gg. Wagner,* Ber. Bunsenges. physik. Chem. *69*, 20 (1965).

[4] *J. C. Street* and *A. Thomas,* Fuel *34*, 4 (1955).

[5] *P. H. Daniels,* Combust. and Flame *4*, 45 (1960).

Section 2.4) and did not have the same temperature at the region of soot formation; thus, for reasons mentioned earlier, their absolute values are of no great theoretical significance. The difference in the N_0 value per additional CH_2 unit is strikingly constant[5]. However, these patterns will have to be checked by measurements on flat flames at approximately the same temperature, where the uniform occurrence of soot can be more readily correlated with the initial composition of the mixture.

The dependence of the soot limit on the shape of the flame can be seen from Figure 1; extensive measurements on flat flames of various fuels have not yet been

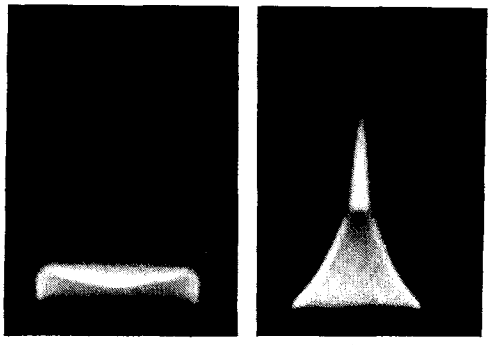


Fig. 1. (a) Approximately flat, non soot forming benzene-air flame on a nozzle burner.
(b) Conical flame of the same composition and with equal throughput; soot formed at tip (type 2).

completed. Despite these reservations, it is safe to say that the critical C/O ratio for the three C_2-hydrocarbons in stationary flames at atmospheric pressure decreases in the order acetylene > ethylene > ethane. Thus acetylene, which forms copious amounts of soot in rich mixtures, requires less oxygen to prevent the appearance of soot than ethylene, which in turn requires less than ethane. This has sometimes led to the erroneous belief that acetylene cannot play a very important part as an intermediate in soot formation. One reason for the higher oxygen consumption of ethane and ethylene is the increased formation of water as compared to the acetylene flame. *Jost*[6] discussed the possibility that OH radicals attack acetylene less at the C–H bond than at the C≡C bond; the result is preferential formation of CO and H_2. This is supported by recent estimations, according to which the C–H bond energy is more than 15 kcal/mole higher in acetylene than in ethane[7]. Another reason for the difference in the soot limits of these three hydrocarbons is the difference in the maximum flame temperatures of the corresponding mixtures. Whereas *Bone et al.*[8] found no soot in explosion flames of mixtures $C_2H_4 + O_2$ and $C_2H_2 + O_2$ (*i.e.* C/O = 1) in closed vessels, soot is formed in stationary burner flames of corresponding fuel-air mixtures.

A more appropriate criterion for the comparison of the soot limits of various fuels is provided by the composition of the burnt gas. *Fenimore et al.*[9] found an empirical relationship between the concentrations of some burnt gas components at the soot limits for flat flames at reduced pressure on cooled burners:

$$\frac{(p_{CH_4} + 2\,p_{C_2H_2})\,(p_{H_2})^{1/2}}{p_{H_2O}} \approx \text{const.}$$

The validity of this relationship is satisfactory for short-chain paraffins (methane to butane, isobutane, neopentane), ethylene, and acetylene with pure oxygen; the maximum temperature of the flames was kept at 1600 °K.

The formula can be interpreted as showing that soot formation is promoted by hydrocarbons and inhibited by hydroxyl radicals, since the OH concentration is proportional to $p_{H_2O}/(p_{H_2})^{1/2}$ when the components H, H_2, OH, and H_2O are in equilibrium. When investigating the soot limits in flat ethylene-air flames, *Millikan*[10] found that soot formation takes place only in a flame zone in which the OH concentration has reached its equilibrium concentration in the burnt gas; the OH concentration may be significantly higher in the main reaction zone than at equilibrium[11–13].

2.2. Dependence of the Soot Limits and Soot Yield on Temperature

Street and *Thomas*[4] studied the dependence of the soot limits of fuel-air mixtures on the maximum flame temperature by preheating of the unburnt gas. *Millikan*[10] as well as *Flossdorf* and *Wagner*[14], varied the temperature of flat ethylene-air flames on cooled burners by variation of the flow velocity. In both methods, higher temperatures allow the burning of richer mixtures without soot formation. Fig. 2 shows how both the absolute soot concentration and the visually determined soot limit vary with the temperature.

The C/O ratios corresponding to the soot limit are given by the intersections of the curves with the broken lines. It can be seen from this diagram that even for the same fuel-air mixture, the soot limits found visually are to some extent arbitrary.

Under certain conditions, however, the quantity of soot in the burnt gas may increase with rising temperature. This is particularly so when the flame burns at a higher pressure and the burnt gas is protected against loss of heat. Most of the soot in this case is produced by pyrolysis of unburnt hydrocarbons in the exhaust gas. Apart from the heating of the gas, this soot formation is unconnected with the processes in and a short way behind the oxidation zone (cf. Section 3.3).

[6] *W. Jost*, Naturwissenschaften *31*, 392 (1943).

[7] *M. Cowperthwaite* and *S. H. Bauer*, J. chem. Physics *36*, 1743 (1962).

[8] *W. A. Bone*, Proc. Roy. Soc. (London), Ser. A *137*, 263 (1932).

[9] *C. P. Fenimore, G. W. Jones*, and *G. E. Moore*: Sixth Internat. Symposium on Combustion. Reinhold, New York 1956, p. 242.

[10] *R. C. Millikan*, J. physic. Chem. *66*, 794 (1962).

[11] *W. Jost*: Explosions- und Verbrennungsvorgänge in Gasen. Springer, Berlin 1939, p. 361.

[12] *U. Bonne* and *H. Gg. Wagner*, Ber. Bunsenges. physik. Chem. *69*, 35 (1965).

[13] *U. Bonne, Th. Grewer*, and *H. Gg. Wagner*, Z. physik. Chem. N.F. *26*, 93 (1960).

[14] *J. Flossdorf* and *H. Gg. Wagner*, Z. physik. Chem. N.F. *54*, 113 (1967).

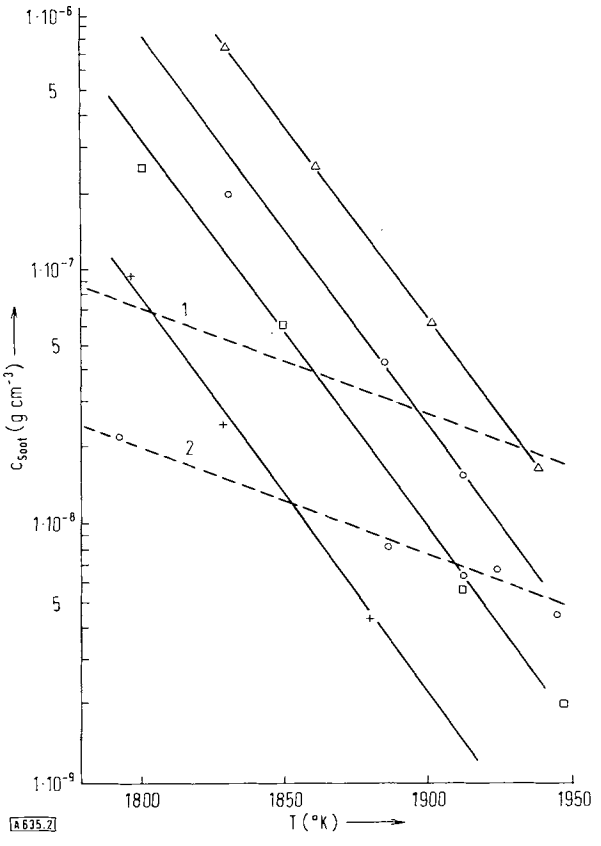


Fig. 2. Soot concentration and soot limits (1 after *Millikan* [10], 2 after *Flossdorf* [14]) in the burnt gas of flat ethylene-air flames as a function of the maximum flame temperature, C/O = 0.620 (+), 0.646 (□), 0.660 (○), and 0.678 (Δ). The soot concentration is normalized to a burnt gas density at 2000 °K and 1 atm.

The temperature-dependence of the yield of soot under these conditions was studied by *Macfarlane et al.* [15] for *n*-hexane flames by diluting their mixtures with inert gases of different molar heat capacities (Fig. 3). At pressures > 1 atm, a rise in temperature still moves the soot limit to higher C/O ratios. On further enrichment with fuel, however, the yield of soot in the hotter flame B increases much more rapidly, and then

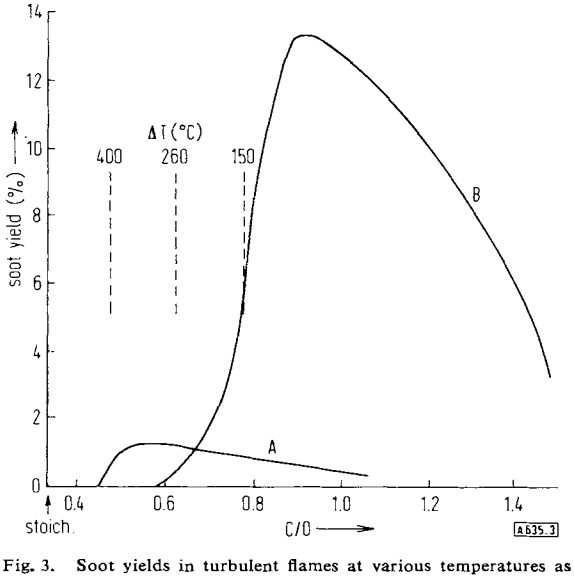


Fig. 3. Soot yields in turbulent flames at various temperatures as a function of the C/O ratio in the unburnt gas. Combustion mixture: *n*-hexane/oxygen + nitrogen (A), + argon (B). $p = 15$ atm [15].

[15] *J. J. Macfarlane, F. H. Holderness,* and *F. S. E. Whitcher,* Combust. and Flame *8*, 215 (1964).

decreases again. The temperature rise in relation to A is not the same for all mixtures. The calculated difference in the maximum temperatures is given for three compositions. The decrease in soot formation in very rich mixtures as a result of the fall in the maximum flame temperature can be observed for most fuels only at increased pressures. At atmospheric pressure mixtures as rich as this in many instances lie outside the ignition limits.

2.3. Dependence of the Soot Limits and Yield of Soot on Pressure

The question of whether the critical C/O ratio for soot formation depends on the total pressure has been studied both for stationary flames between pressures of 10 torr and 20 atm and for explosion flames at pressures up to 100 atm. For acetylene flames on Bunsen burners, *Gaydon et al.* [16] found only a very small change in the soot limit over a pressure range extending from a few torr to atmospheric pressure. *Bonne* and *Wagner* [12] used absorption measurements to determine the quantity of soot formed in flat flames of acetylene-oxygen between 15 and 100 torr; when the flow rate of the unburnt gases was kept constant, the soot limit showed no dependence on pressure. Figure 4 gives the dependence on pressure of some properties of acetylene-oxygen flames at subatmospheric pressure.

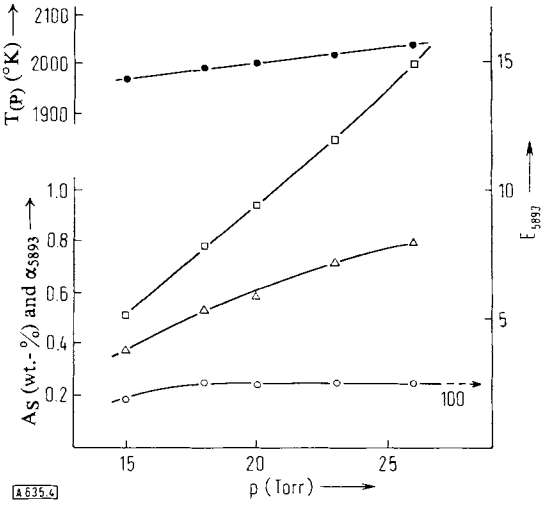


Fig. 4. Continuous emission (E; □) and absorption (α,Δ) at 5893 Å, quantity of soot (A_S; ○), and particle temperature ($T_{(P)}$; ●) at various pressures in the burnt gas of an acetylene-oxygen flame (C/O = 1.3) [12].

Though the soot limits are only slightly influenced by pressure, the yield of soot in rich flames changes considerably at high pressures. This is important to the operation of jet motors. At a working pressure of 10 to 15 atm, combustion is often accompanied by considerable soot formation, as may be observed *e.g.* when a jet aircraft takes off. However, it is again necessary to distinguish between the soot formation that is directly associated with the reactions in the oxidation zone and the formation of soot by pyrolysis

[16] *A. G. Gaydon* and *H. G. Wolfhard*: Flames. Chapman and Hall, London 1960, p. 182.

in the burnt gas. Experiments on low-pressure flames [12] show that the soot formation immediately behind the flame front is practically unaffected by variation of the pressure, whereas pyrolysis in the burnt gas is strongly dependent on pressure.

This is shown by experiments carried out by *Macfarlane et al.* [15] on the combustion of C_3- and C_6-hydrocarbons with air at pressures up to 20 atm. Some of their results are illustrated in Fig. 5. Benzene gives large quantities of soot even in

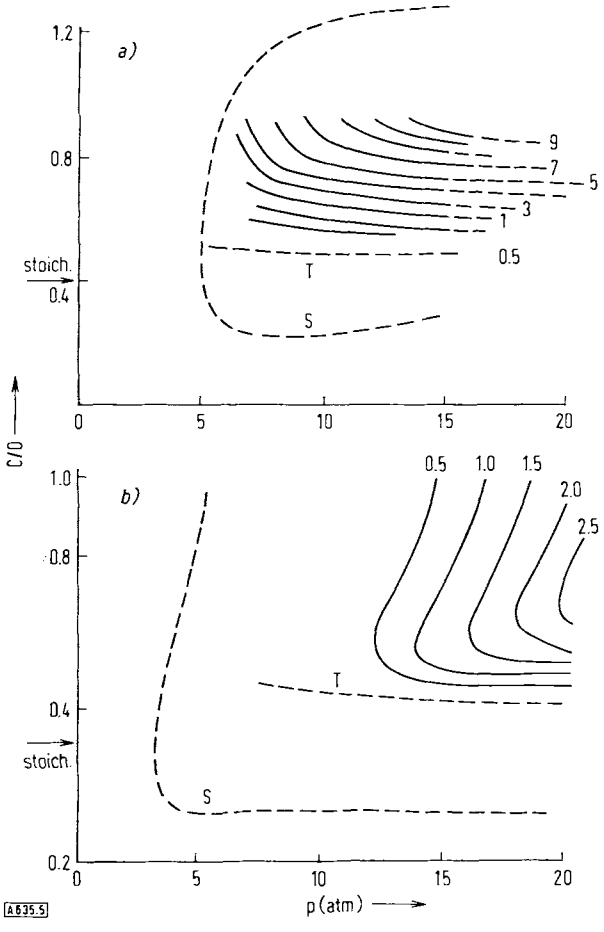


Fig. 5. Soot yield (as parameter in % of C in the fuel) as a function of the pressure and C/O ratio in turbulent flames of (a) benzene, (b) *n*-hexane. T = soot limit, S = stability limit of the flame [15].

relatively lean mixtures; between C/O = 0.5 and 0.8, the yield of soot increases only slightly with pressure, but rapidly with the C/O ratio. The situation is substantially reversed in the case of *n*-hexane; the yield of soot for relatively rich mixtures increases faster with the pressure, whereas at C/O > 0.6 and at constant pressure, it decreases with increasing C/O. These measurements again show the insensitivity of the soot limits to changes in pressure.

Soot formation in explosion flames has been studied at even higher pressures. The only results available are those for methane and ethane obtained in earlier work by *Bone* and *Townend* [17], who found a complicated relationship between soot formation and pressure. For mixtures $2\,CH_4 + O_2$ and $C_2H_6 + O_2$, 20–30% of the hydrocarbon used reacted to form soot between 1 and 10 atm, only 1–3% of soot was obtained at 100 atm. No attempt will be made here to explain these results, since the "temperature history" of the non-isentropically compressed gas before combustion probably influences the soot formation.

[17] *W. A. Bone* and *D. T. A. Townend*: Flame and Combustion in Gases. Longmans, Green and Co., London 1927.

2.4. Appearance of Soot-Forming Burner Flames

The simplest case of a stationary burner flame is a flat "one-dimensional" flame having a planar flame front. Such flames can be approximately realized by the use of flat porous plates as flame holders. If a flame of this type forms soot, the planes of equal soot concentration and of equal soot emission are situated downstream from and parallel to the flame front (Fig. 6). Thus the luminous soot zone is linearly related to the flame front at all points [*]. In practice, there are deviations from this behavior at the burner rim (cf. [12]). The extent to which the soot zone overlaps with the oxidation zone depends *inter alia* on the fuel, the maximum flame temperature, and the combustion pressure [2, 10].

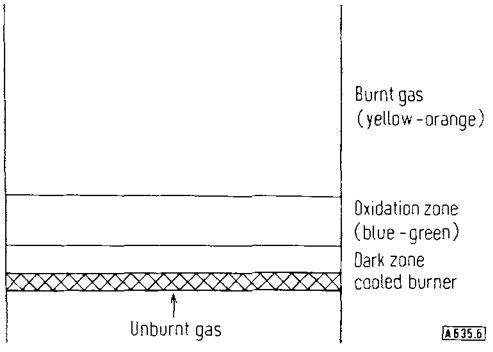


Fig. 6. Oxidation and soot zones in a flat flame (schematic).

The complexity of the mutual effects of chemical reactions, transport processes, and hydrodynamics is externally scarcely visible from a one-dimensional flame; however, they become obvious if the conditions for one-dimensional behavior are no longer satisfied.

An example of this is the formation of soot in an approximately conical flame, which is familiar in the form of the Bunsen flame or the nozzle burner flame. The soot formation in this case depends on the concentration ratios of many substances, the temperature at the site of soot formation, and the thermal history of the mixture present at this point. Thus luminosity due to soot that is nonuniform with respect to the flame front can be a sensitive indication of a nonuniform distribution of concentrations and temperatures along the flame front.

Bunsen flames can be classified into four types, according to the spatial distribution of the luminosity due to soot; many flames encountered in practice are mixtures of two or more of these basic types [4, 14, 18].

Type 1: The yellow luminosity extends with approximately uniform brightness over the entire cone, corresponding roughly to the uniform distribution of soot over a flat flame; *Behrens* [18] calls this the "acetylene type", since it occurs in a particularly pure form with this fuel (Fig. 7).

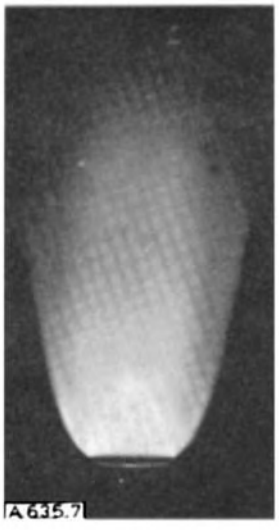
Type 2: The soot is formed only above the tip of the cone, and extends into the burnt gas as a more or less narrow strip [19]. The soot formation begins either closely above the

[*] The same is true of ideally spherical flames, which may also be regarded as one-dimensional in this sense.

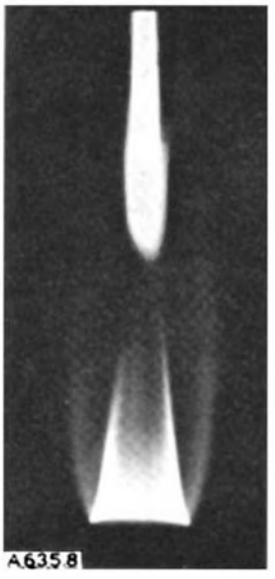
[18] *H. Behrens*, Naturwissenschaften *32*, 299 (1944); Z. physik. Chem. *196*, 78 (1950); *ibid. 199*, 1 (1952).

[19] *W. Jost*, Naturwissenschaften *39*, 418 (1952).

tip (Fig. 1b) or some distance away from it (Fig. 8). This ("benzene type" according to *Behrens*) is how soot formation takes place in flames of benzene and other aromatic compounds, paraffins ($n > 3$), cycloparaffins, and some fuels containing oxygen, such as alcohols (except methanol), ketones, and ethers, *i.e.* generally in fuels having high molecular weights.



flame (type 1 + 3).



air flame; the thread of soot is separated from the cone (type 2).

Type 3: The luminosity due to soot occurs only at the base of the cone, and surrounds the flame like a bowl [18]. This type of soot formation occurs only in flames that are in close contact with the rim of the burner, *i.e.* for mixtures with high burning velocities (Fig. 7).

Type 4: The soot distribution in this type is associated with the occurrence of a disturbance of the flame front. In rich mixtures, many fuels give an undulating flame front, which partially breaks up when the fuel content is further increased. With Bunsen flames this disturbance appears as wave crests and troughs extending from the base of the cone to below the tip [20]; in plan view, flames of this type resemble a polyhedron with spokes (polyhedral flames). When the mixture is sufficiently rich, the soot forms above the wave crests, so that several bands of soot extend from the disturbed cone into the burnt gas (Fig. 9). If the flame front is sufficiently well developed at the apex of the cone, soot formation of type 2 also takes place here. A corresponding disturbance with luminous streaks above the crests in the flame front can also occur in flames that are flat when burning in lean mixtures (Fig. 10) [14].

Fig. 9. Disturbed benzene-air flame with several threads of soot (type 4 + 2).

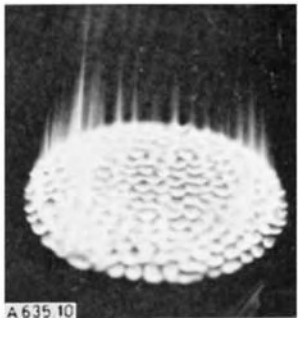


Fig. 10. Cellular benzene-air flame with threads of soot over the crests of the flame front.

What is the explanation for these various appearances of soot? In view of the complexity of the relationships and the lack of adequate quantitative measurements, we must confine this discussion to qualitative considerations. It is useful, not only to compare the properties of the fuels, but also to examine the external factors that particularly favor or suppress a given type, or that cause a transition from one type to another.

The uniform distribution of the luminous soot over the cone (type 1) shows that the surfaces of equal concentration of the substances that are important to soot formation and those of equal temperature, have a form very similar to that of the flame front, at least in the neighborhood of the latter.

Deviations from a uniform distribution in relation to the flame front can be caused by various factors. The most important of these include partial pyrolysis of the fuel before combustion and variation of the concentration ratios along the flame front as a result of selective diffusion of various particles. This occurs when concentration and temperature gradients exist transverse to the local flow direction, as is the case *e.g.* in Bunsen flames, when the flame front is disturbed, and also in turbulent flames [21, 22]. Other factors are temperature changes due both to pyrolysis and to variations in the heat of reaction and thermal conductivity, which depend on the composition of the mixture.

Measurements of the composition of the burnt gas above the apex of the cone in benzene flames (type 2) by *Jost et al.* [23] gave a higher C/O ratio than lower down over the cone. The temperature in the tip of the flame is lower than in the flame front under the tip; this is shown by a darker spot in the flame front at the tip, where soot formation begins when further fuel is supplied to the unburnt gas.

The hydrogen content inside the cone increases with increasing height; for example, in the case of *n*-heptane-air mixtures [24], the mole fraction of hydrogen slightly below the tip of the flame is about three times that of the original fuel mole fraction. The reason for this accumulation is that of all the combustion products hydrogen diffuses back farthest into the fresh gas; as a result of the superimposed flow and the narrowing of the cone, its concentration increases from the base upward. Hydrogen atoms contribute to this diffusion. The diffusion of the hydrogen into the unburnt gas leads to opposing fuel and oxygen concentration gradients. Though diffusion into a multicomponent mixture cannot be quantitatively described without detailed calculations, it may be assumed that

[20] *A. Smithells* and *H. Ingle*, J. chem. Soc. (London), Transactions *61*, 204 (1892).

[21] *G. H. Markstein*: Non-steady Flame Propagation. Pergamon, Oxford 1964, Section D.

[22] *W. Jost* and *B. Krischer*, Z. physik. Chem. N.F. *5*, 398 (1955).

[23] *W. Jost, J. Krug*, and *L. Sieg*: Fourth Internat. Symposium on Combustion. Williams and Wilkins, Baltimore 1953, p. 535.

[24] *J. Flossdorf*, Dissertation, Universität Göttingen, 1968.

the oxygen diffuses more rapidly towards the flame front than the heavier fuel molecules, so that the fuel accumulates along the axis of the cone [22, 23].

We determined fuel build-ups inside the cone by injection of a fuel-air mixture into the apex of the cone of a very slightly sooting benzene-air flame from underneath by means of a quartz capillary. The composition and flow of the mixture were adjusted so that the natural soot formation was not perceptibly disturbed; the injected mixture then just corresponded to the natural mixture in the tip of the flame. The increase in benzene concentration found in this way was about 5%, which agrees with the results obtained for the C/O ratio in the burnt gas above the tip.

However, this fuel build-up only partly explains the soot formation at the tip. This can be seen from the fact that a corresponding addition of fuel to the original unburnt mixture leads to a reinforced soot formation at the top, but there is still no soot formation over large parts of the flame front. The build-up of combustible substances can increase with advancing pyrolysis of the unburnt fuel to form higher hydrocarbons inside the cone; the accumulation of pyrolysis products along the axis of the cone is another reason for the preferential soot formation at the tip of the flame.

Pyrolysis, accumulation of fuel along the axis of the cone, and lowering of the temperature at the apex of the cone (because of the richer mixture at this point) together result in the formation of soot at the tip. Which of these factors has the greatest effect on the soot formation varies from one case to another. The extent to which pyrolysis and selective transport processes take place depends on the time for which the fuel mixture is exposed to these effects. Thus, long cones and low flow rates (corresponding to low burning velocities) favor soot formation at the apex; conversely, flames with flat cones and high flow rates (*i.e.* with relatively high burning velocities) exhibit more uniform soot formation distributed over the entire cone (acetylene, ethylene). Thus, fuels that tend to pyrolyze and those having high molecular weights mainly form soot as in flame type 2, whereas fuels that are thermally relatively stable and have a molecular weight comparable with that of oxygen favor flame type 1.

The effect of the back-diffusion of hydrogen can be substantially eliminated if, instead of nitrogen, sufficient hydrogen is added to a fuel-oxygen mixture to make its mole fraction in the unburnt gas equal to that in the burnt gas, so that there is no diffusion of molecular hydrogen. The soot formation in a flame of this nature corresponds almost perfectly to type 1. However, the preferential soot formation at the apex cannot be entirely avoided, since the pyrolysis of the fuel is not completely prevented by the addition of hydrogen.

Substantially the same observations apply to the formation of soot above the wave crests of disturbed flames (type 4) as for the apex of the cone [14, 22]. However, if the disturbance becomes so strong that the front breaks up over the wave crests, the combustion mixture, which is also enriched in fuel, flows straight into the hot burnt gas of the environment, and the soot formation is even more strongly promoted by pyrolysis than in a closed flame front. The flame disturbance and the resulting irregular soot distribution can also be prevented by the addition of hydrogen to the original mixture.

The soot formation at the bottom edge of the cone (type 3) is only due to the quenching effect of the burner rim; it disappears if the flame can be raised slightly from the rim of the burner by an increase in the flow rate. In addition to the removal of heat by the burner, the elimination of active particles (which promote combustion) by recombination at the surface undoubtedly also plays some part. The nature of this effect is not yet known in detail.

2.5. Formation of Higher Hydrocarbons

The first phase of the formation of soot in flames with a continuous front is strongly influenced by the processes in the oxidation zone. To obtain an understanding of these relationships, therefore, it is necessary to carry out concentration measurements in the flame front itself. Methods for the analysis of more or less stable intermediates in the reaction zone of flames have been greatly refined during the past ten years [2, 25–27]. Since spatial resolution of the principal reaction zone of premixed flames is difficult at atmospheric pressure, most of the concentration profiles were measured at low pressures, at which the reaction zone is correspondingly extended.

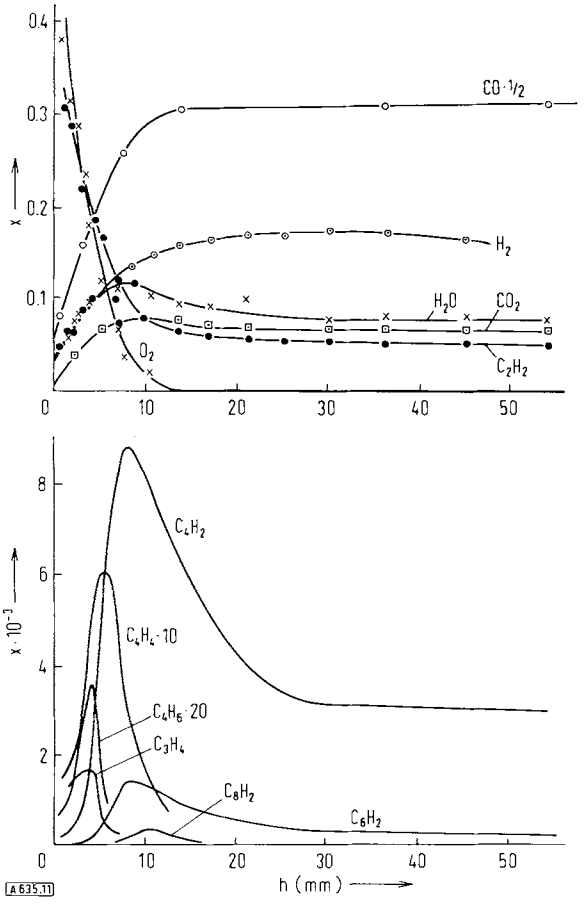


Fig. 11. Concentration profiles (h = height over burner) of a slightly soot forming acetylene-oxygen flame. C/O = 0.95, p = 20 torr.

[25] *R. M. Fristrom* and *A. A. Westenberg*: Flame Structure. McGraw-Hill, New York 1965.

[26] *T. A. Milne* and *F. T. Greene*, J. chem. Physics *44*, 2444 (1966).

[27] *K. H. Homann* in *C. F. H. Tipper*: Oxidation and Combustion Reviews. Elsevier, Amsterdam 1967, Vol. 2, p. 230.

Even in the oxidation zone of oxygen-rich flames, small concentrations of other, generally less saturated hydrocarbons are formed, the number of carbon atoms being either equal to or smaller than the number in the original fuel [28]. The higher the fuel content of the mixture, the greater is the concentration of these intermediates formed, and hydrocarbons containing more carbon atoms than the original fuel are also formed [29]. We have determined concentration profiles in soot forming flat methane, ethylene, acetylene, propane, and benzene flames by mass spectroscopy (the samples passed directly from the flame into the ion source *via* a molecular beam) [2, 3, 30, 31]. It is possible in this way to analyze, not only stable reaction products, but also free-radical intermediates.

Fig. 11 shows concentration profiles of some hydrocarbon intermediates in an acetylene-oxygen flame. The C_3-intermediates such as propylene and methylacetylene (C_3H_4) reach their maximum concentration in the oxidation zone; they disappear again before the oxygen is consumed, and soot is formed. The same is true of butadiene, dimethylacetylene (C_4H_6), and vinylacetylene (C_4H_4), the concentration maxima of which occur before those of diacetylene (C_4H_2) and the higher polyacetylenes. C_5-hydrocarbons can be detected in traces in rich mixtures of the light aliphatic fuels, but no aliphatic hydrocarbons with a higher odd number of C atoms have been found. Benzene is formed in the oxidation zone of acetylene, ethylene, and propane flames in concentrations of the order of 10^{-2} mole-%, and largely disappears before the soot formation [2].

In contrast to these relatively hydrogen-rich intermediates, the polyacetylenes C_4H_2, C_6H_2, *etc.*, which have been found up to $C_{12}H_2$ in rich acetylene flames, reach their maximum concentration only at the end of the oxidation zone; these form the greater part of the unsaturated hydrocarbons. Lower polyacetylenes are formed even in non-sooty acetylene flames, but are completely oxidized again in the case of burning mixtures having a C/O ratio of up to 0.75 [3]. In richer flames their concentration at first decreases behind the oxidation zone, but subsequently shows practically no further change in the burnt gas. At $C/O > 0.9$, the soot formation begins at the zone where the polyacetylene concentration falls off again (see Section 2.6). With richer mixtures, the concentrations of all the polyacetylenes steadily increase, and "equilibria" of the type

$$C_4H_2 + H_2 \rightleftharpoons 2\,C_2H_2$$
$$C_6H_2 + H_2 \rightleftharpoons C_4H_2 + C_2H_2$$
$$C_8H_2 + H_2 \rightleftharpoons C_6H_2 + C_2H_2$$
etc.

exist between acetylene, polyacetylenes, and hydrogen.

Polyacetylenes are not the only higher hydrocarbons in the burnt gas of rich flames. A large number of high molecular weight polycyclic compounds can be detected [32, 33]. It has long been known [34–37] that polycyclic aromatic hydrocarbons can be extracted from many types of soots. Concentration profiles of these

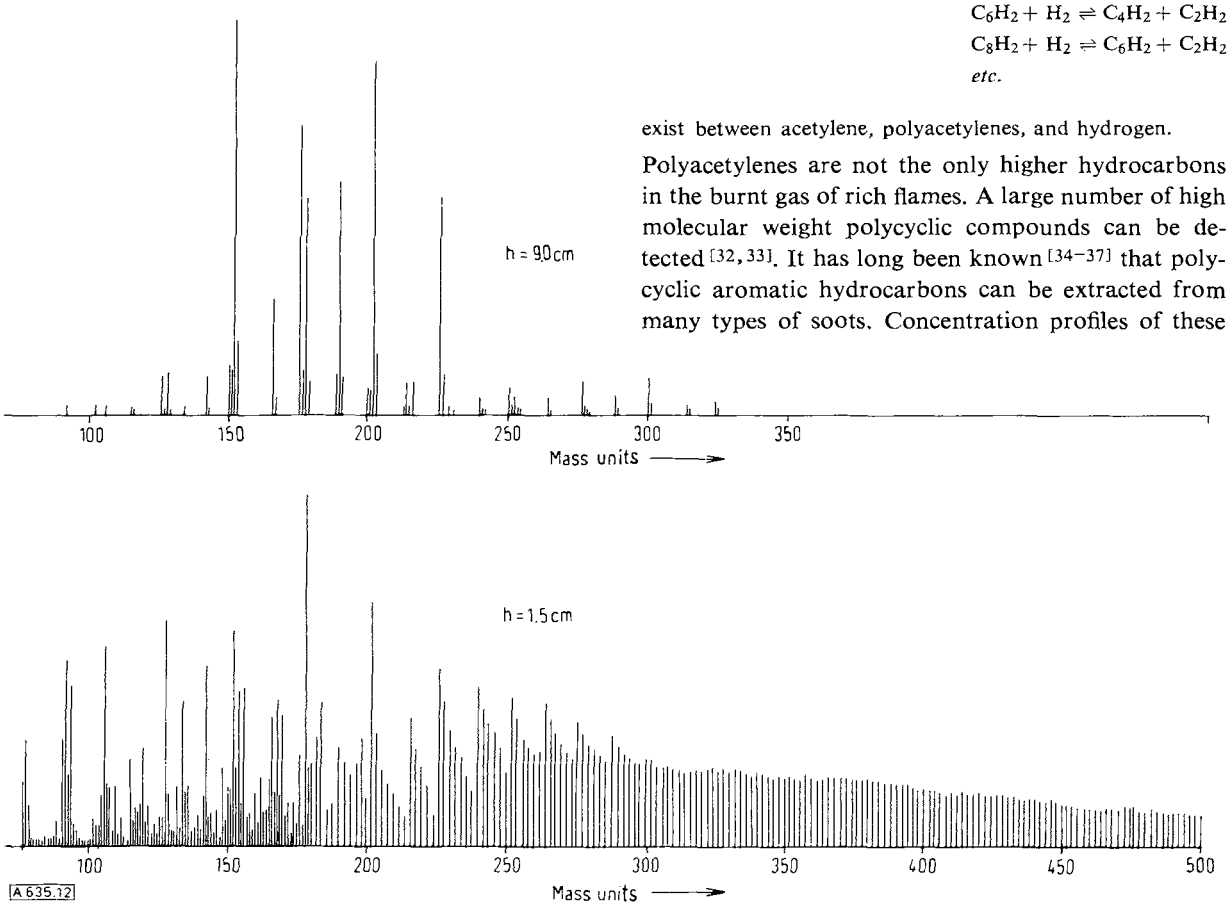


Fig. 12. Mass spectra of the volatile components in soot from various heights (h = height over burner) in a flat acetylene-oxygen flame. C/O = 1.37, p = 20 torr. The odd numbered mass peaks due to the ^{13}C isotopes above 180 mass units are not shown.

[28] *R. M. Fristrom, W. H. Avery*, and *C. Grunfelder*: Seventh Internat. Symposium on Combustion. Butterworths, London 1959, p. 304.

[29] *J. M. Singer* and *J. Grumer*: Seventh Internat. Symposium on Combustion. Butterworths, London 1959, p. 559; Rep. Invest. U.S.-Bureau of Mines No. *6007* (1962).

[30] *K. H. Homann*, Dissertation, Universität Göttingen, 1964.

[31] *U. Bonne, K. H. Homann*, and *H. Gg. Wagner*: Tenth Internat. Symposium on Combustion. The Combustion Institute, Pittsburgh 1965, p. 503.

[32] *U. Bonne* and *K. H. Homann*, Kurznachr. Akad. Wiss. Göttingen, II. math.-physik. Kl. No. *4* (1965).

[33] *K. H. Homann* and *H. Gg. Wagner*: Eleventh Internat. Symposium on Combustion. The Combustion Institute, Pittsburgh 1967, p. 371.

[34] *K. Rummel* and *P. O. Veh*, Arch. Eisenhüttenwes. *14*, 489 (1941).

[35] *N. Thorp, R. Long*, and *H. Garner*, Fuel *34*, Supplement p. 1 (1955).

[36] *S. K. Ray* and *R. Long*, Combust. and Flame *8*, 139 (1964).

[37] *J. R. Arthur, B. T. Commins, J. A. S. Gilbert, A. J. Lindsey*, and *D. H. Napier*, Combust. and Flame *2*, 267 (1958).

components have recently [33] been determined directly in the flame by mass-spectrometric analysis. The nature of the hydrocarbons is strongly dependent on the flame zone from which the soot sample is obtained (Fig. 12). The most abundant at 9 cm above the burner are pyrene (202 mass units), acenaphthylene (152), and anthracene or phenanthrene (178). The electron energy in the ionization was 10 eV, so that there was no fragmentation of the molecule-ions. The concentrations of these aromatic compounds steadily increase with increasing height in the flame.

Very many more compounds are present close behind the oxidation zone 1.5 cm above the burner. The mass gaps between the pure aromatic compounds are filled with substances that contain more hydrogen and have side chains. Their masses extend over a range of from $\approx$ 90 to over 500 mass units; almost every even mass number in this range is occupied by a molecule peak. Most of these substances do not remain unchanged, but are converted into soot. Not only can they be evaporated from quenched soot samples in a high vacuum, but they can also be determined directly in the flame by mass spectrometry [33]. At 20 torr burning pressure, these intermediates reach their maximum concentration 4–5 mm after the end of the oxidation zone (the maximum being earlier for the lighter products and somewhat later for the heavier), and have completely disappeared after a further 15 mm. Their individual mole fractions are of the order of 10^{-7}. The hydrocarbon intermediates in the flames of the other lower aliphatic compounds are qualitatively very similar [2].

The formation of hydrocarbons from aromatic compounds at high temperatures has been studied mainly in thermal decompositions [38–40]. Acetylene and polyacetylenes are also formed in the oxidation zone of benzene flames [2], and partly react further in the burnt gas as in aliphatic fuels. However, whereas aromatic compounds (apart from benzene) are formed only behind the oxidation zone and in relatively low concentrations (mole fraction $\approx 10^{-5}$) in the flames of lower aliphatic fuels, they are formed in relatively large numbers and quantities together with the oxidation products in the principal reaction zone of the benzene flame. The concentrations of *e.g.* phenylacetylene, indene, methylnaphthalene, and biphenyl pass through a maximum at the end of the oxidation zone and fall off again in the burnt gas; the concentrations of other compounds such as naphthalene, acenaphthylene, anthracene, and pyrene continue to increase in the burnt gas. In addition to the pure aromatic compounds a large number of very reactive polycyclic compounds having higher hydrogen contents are also formed as intermediates similar to those from aliphatic fuels, though still inside the oxidation zone [33].

2.6. Growth and Properties of Soot Particles

Two phases can be recognized in the growth of the soot particles in premixed flames. The first phase is strongly coupled with the reactions in the oxidation zone, and finishes relatively quickly. The second phase, which lasts very much longer, is based on a thermal decomposition, and extends for some distance into the burnt gas (depending on the temperature distribution and the hydrocarbon concentrations). These phases are often referred to in the literature as nucleation and growth, but this is not an entirely adequate description (see Section 3).

The characteristic appearance of various types of soot in electron micrographs, which show the formation of bulky aggregates of clusters or chains of more or less spherical particles is due to the second phase (Fig. 13b). During the first phase of growth, the particles grow without forming clusters of distinguishable individuals (Fig. 13a). To gain an insight into the kinetics of the formation and growth of individual particles, it is necessary to follow the variation of the number and size of the particles and the total quantity of soot; a chemical analysis of the growing particles can also provide information about the substances involved in their formation.

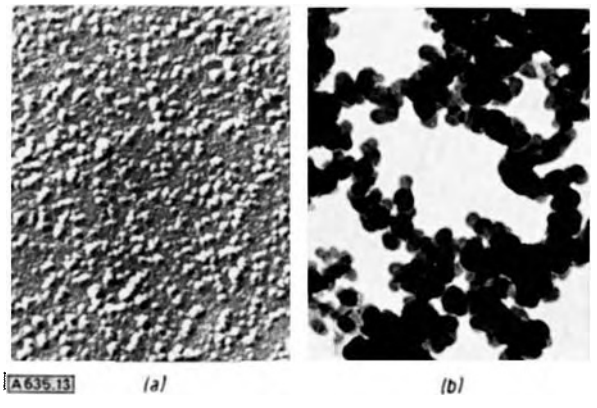


Fig. 13. Electron micrographs of soot from an acetylene-oxygen flame (magnification 51 000 ×).
(a) Close behind the oxidation zone (20 torr; oblique shadowing at 30 °).
(b) In the exhaust gas (1 atm).

The particle size may be determined by optical methods as well as by electron microscopy [41,42]. Electron microscopy has the advantage that the diameters of individual particles down to $\approx$ 40 Å can be measured directly with ordinary instruments, and the size distributions can be determined. In optical measurements, the flame is not affected by sampling, but these methods have the disadvantage that they give only an average particle size. Moreover, the calculation of the particle size involves the optical properties and the shape of the soot particles; these are not very well known, particularly in the case of the very small particles close to the oxidation zone.

Thus the particle size determination described by *Becker* [43], which is based on the dispersion of the absorption coefficients of the particles, cannot be used for the soot near the oxidation zone, since the soot in this region has anomalous optical properties. These are possibly associated with its high initial hydrogen content [12,44,45]. *Bonne* [12,46] found average par-

[38] *F. C. Stehling, J. D. Frazee,* and *R. C. Anderson*: Eighth Internat. Symposium on Combustion. Williams and Wilkins, Baltimore 1962, p. 774.

[39] *R. Slysh* and *C. R. Kinney*, J. physic. Chem. *65*, 1044 (1961).

[40] *H. B. Palmer* and *F. L. Dormish*, J. physic. Chem. *68*, 1553 (1964).

[41] *F. Rössler*, Optik *10*, 533 (1953).

[42] *W. Pepperhoff*: Temperaturstrahlung. Steinkopff, Darmstadt 1956, p. 137.

[43] *A. Becker*, Ann. Physik *28*, 1017 (1909).

[44] *R. C. Millikan*, J. opt. Soc. America *51*, 698 (1961).

[45] *R. G. Siddall* and *I. A. McGrath*: Ninth Internat. Symposium on Combustion. Academic Press, New York 1963, p. 102; see also the discussion by *R. C. Millikan*.

[46] *U. Bonne*, Dissertation, Universität Göttingen, 1964.

ticle sizes from the emissivity of the soot, which is a function of the particle size for small particles. Finally, light scattered by the soot particles has also been used to determine particle sizes [47]. However, the accuracy of the optical methods cannot compare with that of the electron microscope.

The soot concentration at a given point in the flame can be measured by aspiration of a given volume of gas from the flame at this point, the soot then being removed from this gas and weighed [3] or burnt to form carbon dioxide [48]; absorption measurements *in situ* [12,46] provide a suitable direct method, particularly for flat flames and for exhaust gas. (This method has the disadvantage that the absorption coefficients of very small soot particles under the conditions prevailing in the flame are not very accurately known.) The average number of particles can be calculated from the quantity of soot and the average particle size.

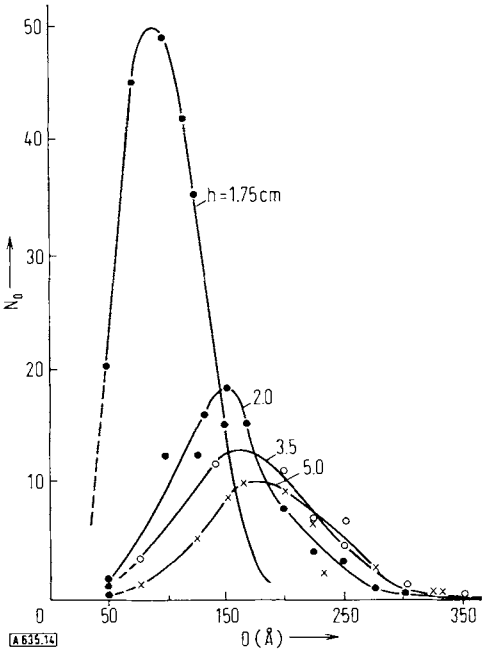


Fig. 14. Size distribution of soot particles at various heights (h = height over burner) in an acetylene-oxygen flame. C/O = 1.6, p = 20 torr.

Fig. 14 shows the size distribution of the soot particles (individual particles, no aggregation) at various heights in an acetylene-oxygen flame. The total number of particles falls off from the end of the oxidation zone (which is about 1.1 cm above the burner in this flame) rapidly at first and then more slowly, while the diameter of the particles increases up to a height of 6 cm, after which there is practically no further change in size. The curves correspond to approximately normal distributions. In this process the total quantity of soot at first increases steadily, until the first phase of the soot formation is complete at a height of $\approx$ 5 cm above the burner, and the concentration in low-pressure flames remains practically constant (Fig. 15); at higher pressures, this first phase takes place in a correspondingly narrower zone [48].

It can also be seen in Figure 15 that the acetylene and polyacetylene concentrations remain constant after the end of the first phase. The increase in the quantity of soot with richer fuel mixtures is almost exclusively due to an increase in the number of particles, the size of the particles remaining approximately the same up to the end of the first growth phase. The first phase of growth ends earlier in richer flames. In benzene-oxygen flames of the same C/O ratio, which form much more soot than acetylene flames, the particles have increased both in size and in number after the first phase.

[47] *W. D. Erickson*, Dissertation, MIT Cambridge/Mass., 1961; *W. D. Erickson, G. C. Williams*, and *H. C. Hottel*, Combust. and Flame *8*, 127 (1964).

[48] *C. P. Fenimore* and *G. W. Jones*, Combust. and Flame *12*, (1968), in press.

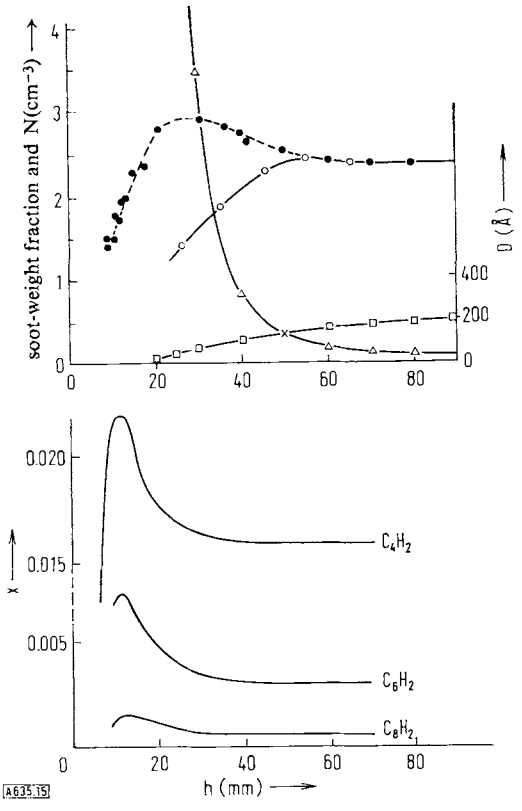


Fig. 15. Profiles of the soot concentration, number of particles, and particle size, as well as the polyacetylene concentrations, in an acetylene-oxygen flame (h = height over burner) C/O = 1.37, p = 20 torr. ● weight fraction of soot (10^{-3}; absorption), ○ weight fraction of soot (10^{-3}, electron microscope), Δ $N(10^{10}$ cm$^{-3})$, □ D(Å).

The soot concentration found by absorption is higher in the vicinity of the oxidation zone than the value found by removal of a sample (Fig. 15). The additional absorption is due to large hydrocarbon molecules and radicals, which absorb almost continuously at these temperatures, and which are probably identical with those found by mass spectrometry (Fig. 12).

An important indication of the source of soot particles is provided by the variation of their H/C ratio in the flame (Fig. 16). The first measurable soot has a high hydrogen content that corresponds approximately to the composition C_8H_2. The hydrogen content decreases rapidly at first, and then more slowly. The maximum rate of soot formation in the first phase agrees well

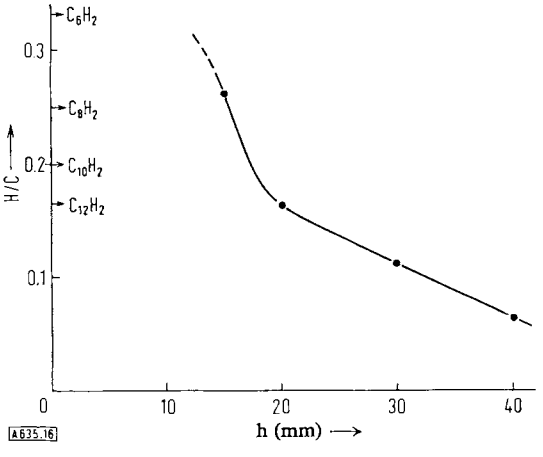


Fig. 16. Atomic ratio H/C in soot at various heights (h = height over burner) in an acetylene-oxygen flame. C/O = 1.7, p = 20 torr.

with that expected if the total concentration of soot grows through addition of higher polyacetylenes (C_8H_2 to $C_{10}H_2$) to soot particles by collisions with no activation energy [33]. The good agreement with the H/C ratio at this point is striking.

New, rapidly growing soot particles have a pronounced free-radical character as can be seen from the ESR signals of soot samples taken from close behind the oxidation zone. This free-radical character decreases rapidly with increasing age and growth of the particles. The subsequent slow growth of the particles in the second growth phase is due to heterogeneous decomposition of unsaturated hydrocarbons, *e.g.* of acetylene [49] and lower polyacetylenes, and probably partly of aromatic compounds, on their surface. This process requires an appreciable activation energy, and is slow in comparison with the first growth phase.

Very little is known about the forces that hold the larger soot particles together in chain networks. Electric forces may be involved. When sampled, these aggregates can be broken down again into the individual particles by ultrasonic radiation [50].

3. Discussion of the Soot Formation

3.1. General

There are numerous theories, or rather chemical models, for the mechanism of soot formation [*]. Individual points of many theories are also valid for the situation in premixed flames; however, the different hypotheses are mostly based on the observation of single phenomena, which could not always be seen in their true relation to the process as a whole, owing to lack of comprehensive information.

3.2. Differences from Condensation

In the theory of the condensation of a vapor, the concept of a nucleus leading to a particle of the new phase [53] is rigidly defined. This is not so in the formation of soot in the gas phase, though the word "nucleus" is often used in this connection. This concept is not very helpful in the consideration of soot formation, and really means nothing more than a small particle that is capable of further growth. There is no critical particle size above which the rate of growth (as in condensation) is greater than the rate of vaporization, and which could be correlated with a certain degree of supersaturation of "soot vapor". The growth of soot particles takes place under conditions that are far removed from an equilibrium state. At the temperatures in hydrocarbon flames, there is no evidence that existing soot particles, no matter how small, vaporize again; all that can happen to them is oxidation.

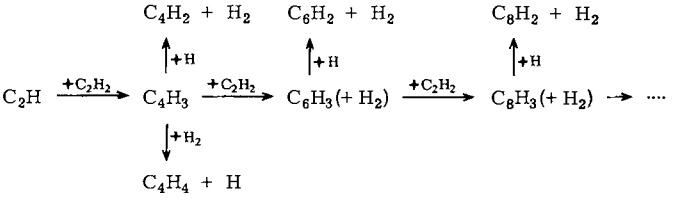
Johnson and *Anderson* [54] have shown that in the pyrolysis of acetylene, soot particles are not formed by condensation of high-boiling reaction products followed by "graphitization" [55]; such droplets are formed only when the reacting gases have cooled by several hundred degrees. Direct condensation of carbon vapor at very high temperatures, such as prevail *e.g.* in cyanogen-oxygen flames would be conceivable; however, the soot formation in these flames is slight in comparison with corresponding hydrocarbon flames [56–58].

3.3. Path of Soot Formation

The process as a whole is far from well enough known to allow a description of the "mechanism of soot formation" in the usual manner by a series of reactions. However, an attempt will be made to interpret the course of soot formation in premixed flames of lower hydrocarbons as far as is permitted by the essentially quantitative results obtained so far.

In the first, cooler portion of the oxidation zone, free-radical reactions lead to hydrocarbons containing more carbon atoms than the original fuel (*e.g.* $C_2H_2 + CH_2 \rightarrow C_3H_4$; $C_2H_2 + C_2H \rightarrow$ polyacetylenes). Those with relatively high hydrogen contents, such as propylene, methylacetylene, butadiene, or vinylacetylene, have no great direct importance in the formation of soot, since they disappear again before solid particles are formed.

Acetylene and the polyacetylenes predominate in the hotter part. The latter reach their maximum concentration at the end of the oxidation zone, where the oxygen supplied has been consumed; they are very probably formed by free-radical reactions



[49] *P. A. Tesner*: Seventh Internat. Symposium on Combustion. Butterworths, London 1959, p. 546; *P. A. Tesner, E. Ya. Robinowitsch*, and *L. A. Matyuschenko*, Trudy vsesoyuz. naučno-issled. Inst. prirodn. gazov *1961*, 49.

[50] *W. Rutsch*, Dissertation, Technische Universität Berlin, 1962.

[*] A short but critical review of the theories of soot formation is presented in [51]; results of measurements carried out up to 1958 are included. More recent views are discussed in [52], which gives a list of reviews on this subject that have appeared so far.

[51] *A. G. Gaydon* and *H. G. Wolfhard*: Flames, their Structure. Radiation and Temperature. Chapman and Hall, London 1960, p. 196.

[52] *H. B. Palmer* and *C. F. Cullis* in *P. L. Walker*: Chemistry and Physics of Carbon. Marcel Dekker, New York 1965, Vol. *1*, p. 265.

[53] *R. Becker* and *W. Döring*, Ann. Physik *24*, 719 (1935).

[54] *G. L. Johnson* and *R. C. Anderson*: Proc. fifth Conf. on Carbon. Pergamon, London, 1962, Vol. 1, p. 395.

[55] *W. G. Parker* and *H. G. Wolfhard*, J. chem. Soc. (London) *1950*, 2038.

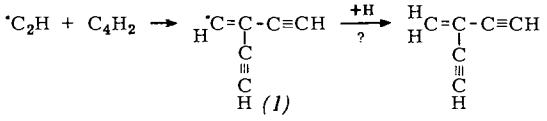
[56] *A. Reis*, Z. physik. Chem. *88*, 513 (1914).

[57] *N. Thomas, A. G. Gaydon*, and *L. Brewer*, J. chem. Physics *20*, 369 (1952).

[58] *E. A. Albers* and *K. H. Homann*, Z. physik. Chem. N.F. *58*, 220 (1968).

C_2H and C_4H_3 have been detected by mass spectroscopy [30]. C_2H can naturally also react directly with C_4H_2 to form C_6H_3 *etc.*

This mechanism for the formation of polyacetylenes and polyacetylene radicals is sufficiently fast only in the radical-rich oxidation zone, but no longer plays any great part in the burnt gas, despite the appreciable acetylene concentration in this region. Continuation of the growth of polyacetylenes cannot lead directly to soot particles, which are not giant chain molecules. However, there are other possible reactions besides chain growth. When C_2H or any other hydrocarbon radical reacts with a polyacetylene, the probability of attack on a terminal carbon atom decreases with increasing chain length; reaction on any other C-atom, if it does not result in cleavage of the chain, cannot lead again to a polyacetylene, since polyacetylenes cannot be branched, *e.g.* [33]:



(1)

The radical *(1)* can attain stability at low temperatures by formation of a methylene group, but such a substance, like vinylacetylene, is very unstable at the maximum temperature of the flame. It is therefore reasonable to assume that a radical such as *(1)* can add on further acetylene and polyacetylenes without loss of its free-radical character; the products are radicals with several branches, which can readily undergo ring closure to form five- or six-membered rings [*]. This leads to the formation of the relatively hydrogen-rich hydrocarbons with side chains found in the region of from about 100 to more than 500 mass units; at flame temperature many of these heavy cyclic hydrocarbons, which probably possess free-radical character [59], remain reactive and they add on further polyacetylenes and also combine with one another. Fast growth is caused in particular by the combination of larger particles.

There is practically no criterion of the size beyond which these particles are to be regarded as soot. As they grow, their free-radical character and their hydrogen content decrease. The decrease in the hydrogen content can be partly explained by the fact that the more reactive higher polyacetylenes add more readily if the free-radical character of the particles decreases.

The numerous heavy polycyclic hydrocarbons include the relatively inert pure aromatic compounds such as pyrene and phenanthrene. It must be concluded from their concentration profiles that these may be regarded as by-products rather than as reactive intermediates in the formation of soot [33, 38, 60]. Unlike the majority of the reactive polycyclic compounds, they continue to be formed in the burnt gases; it is therefore possible that they are also formed by heterogeneous reactions on the surface of soot particles, and evaporate off because of their relatively high vapor pressure.

Sharkey et al. [61] found a similar situation in investigations on the thermal stability of polycyclic aromatic compounds and their derivatives. Pure aromatic compounds such as naphthalene, phenanthrene, chrysene, pyrene, and anthracene were found to be relatively stable. However, compounds with side chains, such as methyl- and dimethylnaphthalene, methylphenanthrene, and substances having higher hydrogen contents, such as dihydroanthracene, indene, and indane reacted much more rapidly and gave products having four times the molecular weight of the starting material. Many of these aromatic compounds have free-radical character at higher temperatures [59].

The rapid decrease in the number of particles can be quantitatively explained if at each collision two particles remain together to form a larger particle. The shape of the particles is rounded off again by the simultaneous addition of hydrocarbons, so that they remain roughly spherical during the first growth phase. When this addition lags behind the association of the particles in the second phase, aggregates in the form of clusters or chains result (Fig. 13b). The heterogeneous decomposition of hydrocarbons, which now leads to a further increase in the quantity of soot, is slow in relation to the growth in the first phase. Since the concentration of hydrocarbon radicals in the burnt gas is low, the formation of new small particles in this zone is also very slow.

The soot formation in benzene flames differs from that in the flames of aliphatic fuels in that more benzene rings are involved from the outset in the formation of the reactive cyclic hydrocarbons in the region between about 100 to 600 mass units. Owing to the supply of larger "structural units", heavy hydrocarbons are formed even in the oxidation zone, and the soot formation zone partly overlaps with the radical-rich principal reaction zone of the flame [2]. Very many more hydrocarbon radicals can thus grow into larger particles, and the number of particles formed is much greater than *e.g.* in acetylene flames with the same C/O ratio. Thus benzene gives higher yields both of soot and of polycyclic aromatic compounds than lower aliphatic hydrocarbons [62].

3.4. Effect of Temperature

The decrease in the quantity of soot with rising flame temperature except for very rich flames is related to the reactions of the OH radical and the formation of water and carbon dioxide [63]. During the temperature rise in the first part of the oxidation zone, water and carbon dioxide are formed, mainly by the reactions

$$H_2 + OH \rightarrow H_2O + H \quad (1)$$

$$C_xH_y + OH \rightarrow H_2O + C_xH_{(y-1)} \quad (2)$$

$$CO + OH \rightarrow CO_2 + H \quad (3)$$

[*] However, the benzene found in flames of lower aliphatic compounds is formed earlier, together with C_4H_6 and C_3H_6. Its formation must be assumed to result from direct ring closure of a C_6-chain having a relatively high hydrogen content.

[59] *E. G. Janzen*, J. Amer. chem. Soc. *87*, 3531 (1965); *W. F. Forbes* and *J. C. Robinson*, Nature (London) *214*, 80 (1967).

[60] *R. Long* and *E. E. Tompkins*, Nature (London) *213*, 1011 (1967).

[61] *A. G. Sharkey jr.*, *J. L. Shultz*, and *R. A. Friedel*, Carbon (Oxford) *4*, 365 (1966).

[62] *W. Morgeneyer*, Dissertation, Universität Göttingen, to be presented 1968.

[63] *K. H. Homann*, Combust. and Flame *11*, 265 (1967).

Sufficient oxygen is bound in this way to make the formation of higher hydrocarbons initially faster than their oxidation. With rising temperature in the flame front and in the burnt gas, the reverse reactions (1) and (3) become significant; water and carbon dioxide are consumed (Fig. 11) with regeneration of OH, which can now oxidize the higher hydrocarbons. The higher the temperature in the burnt gas, the lower is the concentration of water and carbon dioxide[2], and the soot limit is displaced toward its theoretical value.

3.5. Effect of Electric Fields

The electric conductivity of a hydrocarbon flame is mainly due to chemi-ionization[*] in the oxidation zone. Ions are formed in concentrations of about 10^9–10^{10} ions/cm^3 at atmospheric pressure[64]. A considerable proportion of these ions consists of positive and of negative hydrocarbon ions with molecular weights of up to ≈ 100. In rich flames, the heavier negative ions in particular have masses similar to those of the uncharged higher unsaturated hydrocarbons (polyacetylenes). However, their concentrations are several orders of magnitude lower[65].

There is no doubt that a certain percentage of the soot particles in the flame is positively charged. The soot formation both in diffusion flames and in premixed flames is strongly influenced by electric fields in certain circumstances[66].

To determine the effect of ions on the soot formation we studied the action of electric fields on flat premixed flames at pressures of up to 100 torr. The burner surface was used as the cathode, and the anode was a wire gauze placed 15 cm above the burner[67,68]. The phenomena observed can be best explained with the aid of a current-voltage curve (Fig. 17).

In a non soot forming flame, the curve has the expected shape. After a steep increase in current, a saturation current (determined by the chemi-ion concentration) is reached, and when a discharge occurs, the current assumes very high values.

In a soot forming flame, on the other hand, the current increases much more slowly, since there is less chemi-ionization. When the voltage is raised above 500 V, there is a slight decrease, and with the rapid increase in current at 800 V the soot luminosity disappears almost instantaneously. On ignition of the regular gaseous discharge, which takes place at a much lower voltage in this flame, a band of soot luminosity extends with the discharge through the burnt gas to the anode.

These phenomena can be interpreted as follows. Below 800 V the current is transported by positive and negative ions and

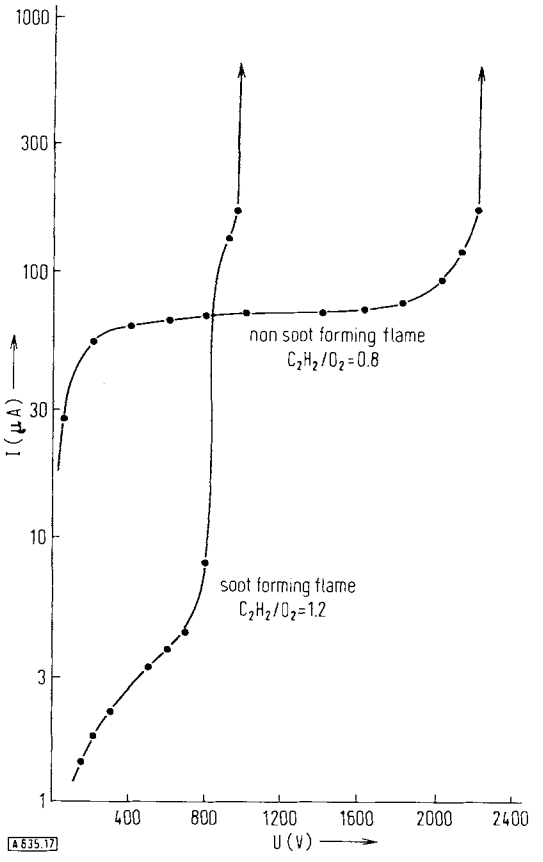


Fig. 17. Current-voltage curves of a soot forming and of a non soot forming flat acetylene-oxygen flame. $p = 30$ torr.

by electrons. At sufficiently high field strengths the few positively charged soot particles migrate back through the oxidation zone; a small portion is burnt, and the remainder is deposited on the negatively charged burner surface. This results in a slight decrease in the luminosity due to the soot between 500 and 800 V.

Above 800 V the soot particles, the ionization potential of which is very much lower than that of any other components of the flame, can be ionized by collisions with electrons. The new charge carriers formed by this "pre-discharge" cause the rapid increase in current. They can also ionize further soot particles until practically all the soot is positively charged and migrates to the negatively charged burner; the luminosity of the soot in the burnt gas is then almost completely extinguished. This also shows that soot particles are charged while still near to the oxidation zone and that practically no new small particles are formed within some distance from it. If such particles were formed they would continue to grow as they migrated, and would also emit light. New soot formation begins in the burnt gas only on establishment of a regular gaseous discharge. This leads to the formation of large quantities of free hydrocarbon radicals that promote soot formation.

The details of the process are difficult to understand, particularly since the variation of potential in the soot forming flame is unknown. However, it seems rather unlikely that ions play a decisive part as starting particles for soot formation so long as no suitable field is applied to the flame. The concentration of the ions in the absence of a field is several orders of magnitude lower than the concentration of hydrocarbon radicals. Moreover, if ions were important, the number of particles in the flames of rich mixtures should decrease as well as the ion concentration, but this is contrary to the observed facts. The ion concentration is increased

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by many orders of magnitude by the addition of salts of alkali metals to the flame, but the soot formation is unaffected.

However, it is interesting to note that soot containing very small quantities of finely divided alkali metal salts burns much more readily than ordinary soot on subsequent introduction of air. This is also true of the combustion of soot deposits on surfaces [69].

4. Conclusion

This review has been confined to pure hydrocarbon fuels, since these are the systems that have been most thoroughly studied. Soot formation in the flames of fuels containing oxygen, *e.g.* ethanol, is also largely due to acetylene and polyacetylenes, and not to compounds such as higher alcohols or aldehydes [30]. The question of the effect of hetero atoms (nitrogen, sulfur, halogens, *etc*) on the mechanism of soot formation [70] has been deliberately avoided, since the existing results in this connection are not yet sufficient to allow any interpretation.

The same is true of the action of foreign additives in the flame [4, 36]. The effects of many substances on soot formation have already been studied. For practical reasons, the question of primary interest was whether the additive promoted or inhibited soot formation or had no influence. Thus barium salts of organic acids have recently been used to reduce soot formation in diesel motors; however, ideas on the mechanism of this inhibition are still only conjecture [71, 73]. The intensification of soot formation by *e.g.* sulfur trioxide and halogens is also still only incompletely understood.

For lack of information, the question of the process of soot formation in hydrocarbon-fluorine and hydrocarbon-chlorine flames has also been avoided, as has the interesting fact that perchlorinated hydrocarbons burn with fluorine but do not form soot, provided that no hydrogen is supplied to the flame in any form [72].

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Dodecacarbonyltriruthenium

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Dedicated to Prof. H. J. Emeléus on the occasion of his 65th birthday

Since the pioneering work of Mond and his coworkers the metal carbonyls and their derivatives have been under active study, and, as in other areas of inorganic chemistry, research activity has greatly increased in the last twenty years. Whereas hitherto our knowledge of the carbonyls of the heavier transition metals has been seriously hampered by a lack of good methods of synthesis, new preparative methods have recently been developed for $Ru_3(CO)_{12}$, and many new ruthenium carbonyl complexes are being discovered as its chemistry is explored.

1. Introduction

Dodecacarbonyltriruthenium was discovered in 1910, but was not characterized as such. *Mond et al.* [1] observed the formation of volatile rose to orange crystals by the action of carbon monoxide on ruthenium metal at 300 °C and 350 to 450 atmospheres. Subsequently, a chocolate brown nonvolatile amorphous compound, insoluble in benzene but soluble in water, was claimed as a product of the same reaction and assigned the formula $Ru(CO)_2$ [2].

A more thorough investigation [3] of the ruthenium black-carbon monoxide system showed that $Ru(CO)_5$ was formed

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at 180 °C and 200 atmospheres, as a colorless volatile liquid, which, in the presence of sunlight or on warming to 50 °C in benzene, readily formed the orange crystalline complex referred to above. The orange compound was incorrectly assigned the formula $Ru_2(CO)_9$, mainly by analogy with $Fe_2(CO)_9$. A dichroic green-red product, insoluble in most solvents, but giving intensely green solutions with pyridine was also obtained, and was thought to be $Ru(CO)_4$. The synthesis of a ruthenium carbonyl by the action of carbon monoxide on ruthenium disulfide at 200 °C and 200–300 atmospheres in the presence of copper, zinc, or lead was also reported [4]. Much of this early work on ruthenium and other metal carbonyls was reviewed by *Emeléus* and *Anderson* [5] in a text which helped to stimulate the growth of modern inorganic chemistry by presenting the subject as offering unlimited opportunities for developing new experimental methods of a physicochemical nature, and the exploration, at that time, of little known fields.

2. Physical Properties of $Ru_3(CO)_{12}$

The reddish-orange colored crystalline ruthenium carbonyl was shown to be incorrectly formulated as $Ru_2(CO)_9$ as a result of an X-ray crystallographic study [6] on the presumed $Os_2(CO)_9$. The latter proved to be a trimeric tetracarbonyl $[Os(CO)_4]_3$ with a molecular structure involving a triangle of osmium atoms and no bridging carbonyl groups [7]. The ruthenium analog was shown to be isostructural, and the formulation was therefore revised to $[Ru(CO)_4]_3$ [6]. A detailed report of the molecular structure of dodecacarbonyltriruthenium has only recently been given [8]. As shown in Figure 1, $Ru_3(CO)_{12}$ has D_{3h} symmetry; its structure differs from that established for $Fe_3(CO)_{12}$ [9] in that none of the three metal-metal bonds is supported by bridging carbonyl groups.

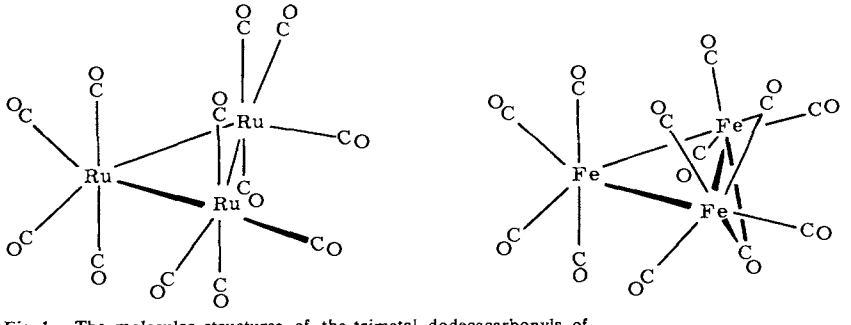

Fig. 1. The molecular structures of the trimetal dodecacarbonyls of ruthenium and iron in the crystalline state.

$Ru_3(CO)_{12}$ is soluble in benzene, toluene, chloroform, and carbon tetrachloride, but is insoluble in methanol or water. It is stable to air and to light, both as a solid and in solution. Some physical properties are given in Table 1.

Table 1. Physical properties of $Ru_3(CO)_{12}$.

M.p. (°C)	154–155 (decomp.)
IR	ν(CO) (cm^{-1}): 2059 (s), 2029 (s), 2010 (m); [a], [19] 2061 (s), 2032 (s), 2015 (m); [b], [10] 2066 (s), 2026 (s), 2004 (m); [c], [11] ν(RuC) (cm^{-1}): 544, 575, 589; [c], [11]
UV	λ_{max} (nm): 490 [d], 391, 310 [d], 275 [d], 238; [13] ε: 390, 5350, 1000, 10000, 24100; [13]
Unit cell constants	$a/b = 0.5496$, $b/b = 1.000$, $b/c = 0.9861$, $\beta = 100°46'$; [e], [3] 0.546, 1.000, 0.984, 100°47'; [f], [7]
Bond distances (Å) [8]	Ru—Ru: 2.85 ± 0.003 Ru—C: 1.92 ± 0.03 C—O: 1.15 ± 0.03
Bond angles (°) [8]	C^1—Ru—C^1: 178.2 ± 1.2 C^1—Ru—C^2: 90.1 ± 1.3 C^2—Ru—C^2: 103.3 ± 1.4 C^1 = C-Atom above and below the Ru_3-plane C^2 = C-Atom in the Ru_3-plane

[a] In C_6H_{12}; [b] in CCl_4; [c] in Nujol; [d] shoulder; [e] optical; [f] X-ray.

The color of the carbonyl has been discussed [12], and the absorption at 391 nm has been ascribed to the metal-metal interactions [13]. The high resolution mass spectrum shows successive loss of twelve carbonyl groups to give a stable Ru_3^+ cluster, and no migration of carbonyl groups to form $Ru(CO)_n^+$ ions ($n>4$) occurs, as is observed in the spectrum of $Fe_3(CO)_{12}$ [14, 15].

3. Synthesis

In the last few years a series of syntheses of $Ru_3(CO)_{12}$ have been reported which are of increasing simplicity and efficiency. Reduction of tris(acetylacetonato)ruthenium(III) with equimolar mixtures of carbon monoxide and hydrogen at 140–160 °C and 200–300 atmospheres in methanol affords $Ru_3(CO)_{12}$ in 76% yield [16]; the method was later modified to give $Ru(CO)_5$ [17]. Treatment of ruthenium stearate in hydrocarbon solutions with carbon monoxide and

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hydrogen at 200 °C and 240 atmospheres [18] leads to the formation of $Ru(CO)_5$, which on decomposition affords $Ru_3(CO)_{12}$ in 60% yield.

The simplest and most efficient preparation of the carbonyl is by low-pressure (< 10 atm) carbonylation of methanol solutions of ruthenium trichloride at about 65 °C in the presence of zinc as a halogen acceptor [19]; the $Ru_3(CO)_{12}$ obtained is essentially pure, large orange crystals forming on the surface of the zinc. Yields are around 70%, and can exceed 80% if the solutions are recycled. In the absence of zinc, the dimeric metal carbonyl chloride, $[Ru(CO)_3Cl_2]_2$ is formed in high yield, along with a small amount of $Ru_3(CO)_{12}$. Stirring a suspension of this carbonyl chloride in aqueous potassium carbonate solution also gives $Ru_3(CO)_{12}$, in a slow reaction which must involve disproportionation of $[Ru(CO)_3Cl_2]_2$ to give $Ru_3(CO)_{12}$ and perhaps $K_2[Ru(CO)_2Cl_4]$ [20].

Passage of carbon monoxide at ambient pressures into alcoholic solutions of $RuCl_3$ does not afford $Ru_3(CO)_{12}$, but addition of donor ligands yields carbonyl chloride complexes, *e.g.* $[C_6H_5(C_2H_5)_2P]_3RuCl_2(CO)$ or *cis*-$[(C_2H_5)_3P]_2RuCl_2(CO)_2$ [21]. In this way, complexes containing amines [22,23], phosphines [21,22], arsines [21,22], stibines [22], a variety of sulfur-containing ligands [23,24], and $SnCl_3$ [22–24] groups as ligands to ruthenium have been prepared, as well as some diene [25] complexes.

4. Chemical Reactions of $Ru_3(CO)_{12}$

Following the ready availability of $Ru_3(CO)_{12}$ many aspects of its chemistry and that of its derivatives have been explored. A summary of results is given in this section, with some comparison with analogous reactions of $Fe_3(CO)_{12}$ where appropriate.

Chlorine, bromine, or iodine react with $Ru_3(CO)_{12}$ affording four types of complex: mononuclear $Ru(CO)_4X_2$; binuclear $[Ru(CO)_3X_2]_2$; trinuclear $[Ru(CO)_4X_2]_3$; and polymeric $[Ru(CO)_2X_2]_n$ [26]. Iron appears to form only the mononuclear and the polymeric species, although the complex $Fe(CO)_3Br_2$ [27] may be dimeric and related to $[Ru(CO)_3Cl_2]_2$ [26].

$[Ru(CO)_2I_2]_n$ was first obtained by *Manchot* and *Manchot* [3]. The dimeric carbonyl halide $[Ru(CO)_3Br_2]_2$ [26a] has a molecular structure which is based on octahedral coordination for the ruthenium atoms with two octahedra sharing a common edge formed by bridging halogen atoms. Isomers are possible, and both white and yellow forms of $[Ru(CO)_3Cl_2]_2$ are known [19]. The trimeric complexes $[Ru(CO)_4X_2]_3$ probably have molecular structures in which the Ru_3 cluster is retained.

Reactions of $Ru_3(CO)_{12}$ with thiols also give several products, *viz.*, $[Ru(CO)_3SR]_2$, polymeric $[Ru(CO)_2(SR)_2]_n$ (R = CH_3, C_2H_5, *n*-C_4H_9, or C_6H_5), and $Ru(SC_6H_5)_3$ [26]. The iron complex $[Fe(CO)_3SC_2H_5]_2$ is known to have a structure with bridging SC_2H_5 groups, and in which the S and Fe atoms adopt a "butterfly"-like arrangement, as a consequence of metal-metal bonding [28]. The ruthenium analogs probably have similar structures. The polymeric derivatives $[Ru(CO)_2(SR)_2]_n$ are thought [26] to have a chain structure similar to that proposed for $[Ru(CO)_2X_2]_n$ [29].

Several studies have been made of the reaction between triphenylphosphine and $Ru_3(CO)_{12}$. Trinuclear complexes $Ru_3(CO)_9[P(C_6H_5)_3]_3$ are obtained [26, 30–32] but different accounts report different carbonyl stretching frequencies in the infrared spectra of the products. The metal atom cluster is preserved, but apparently mixtures of different isomers are formed, the composition of which depends on the solvent employed for the reaction [32]. Similar reactions with $Fe_3(CO)_{12}$ give only the mononuclear complexes $Fe(CO)_4P(C_6H_5)_3$ and $Fe(CO)_3[P(C_6H_5)_3]_2$ [33], except under the mildest conditions, when a complex $Fe_3(CO)_{11}P(C_6H_5)_3$ can be isolated in 2% yield [34]. Interestingly, crystals of this complex contain a 1:1 mixture of two isomers [35]. Prolonged refluxing of chloroform solutions of triphenylphosphine and $Ru_3(CO)_{12}$ gives an orange-yellow complex, $Ru(CO)_3[P(C_6H_5)_3]Cl_2$, which also appears to be a mixture of isomers [32].

Reactions between $Ru_3(CO)_{12}$ and tri-*n*-butylphosphine or triphenyl phosphite also afford trinuclear complexes $Ru_3(CO)_9(PR_3)_3$, but if the carbonyl is heated in solution with excess of the phosphine under CO pressure, mononuclear complexes $Ru(CO)_3(PR_3)_2$, of the type first reported by *Collman* and *Roper* [36], are produced [31]. The triphenylarsine complex, $Ru_3(CO)_{10}[As(C_6H_5)_3]_2$, has also been made. This compound reacts more readily than the triphenylphos-

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phine complex with carbon tetrachloride or chloroform [32]. Reaction of $Ru_3(CO)_{12}$ with the bidentate ligand, tetramethyldiphosphine, leads to the formation of $[(CH_3)_2PRu(CO)_3]_2$ [30] which appears to be similar in nature to $[(CH_3)_2PFe(CO)_3]_2$ [37]. Reaction of the ruthenium compound with iodine affords $[(CH_3)_2PRu(CO)_3I]_2$, presumably by cleavage of the ruthenium-ruthenium bond. Reactions between $Ru_3(CO)_{12}$ and the tetradentate ligands $[o\text{-}(C_6H_5)_2PC_6H_4]_3P$ (QP) and $[o\text{-}(C_6H_5)_2AsC_6H_4]_3As$ (QAS) have also been studied [38]. At 100 °C in chlorobenzene the complexes Ru(CO) (QP) and Ru(CO) (QAS) are produced; the Ru_3 cluster in $Ru_3(CO)_{12}$ does not survive reactions with these ligands.

The action of moist nitric oxide in dichloromethane on $Ru_3(CO)_{12}$ affords polymeric $[Ru(CO)_2(NO)_2]_n$ [30]. Earlier, an unstable red crystalline nitrosyl with the unlikely formulation $Ru(NO)_5$ had been claimed as the product of treating $Ru_3(CO)_{12}$ with nitric oxide at 120 °C [3].

Under appropriate conditions the metal-metal bonds in $Ru_3(CO)_{12}$ can be cleaved to give the $[Ru(CO)_4]^{2-}$ anion; this is best obtained by the action of sodium in liquid ammonia on the carbonyl, evaporation of the ammonia leaving a buff-colored residue, presumably $Na_2Ru(CO)_4$ [39]. Treatment of this solid with phosphoric acid yields $H_2Ru(CO)_4$ [40], a hitherto uncharacterized hydride analogous to the long known $H_2Fe(CO)_4$. $H_2Ru(CO)_4$ is a very unstable colorless liquid which rapidly decomposes to a red-brown solid, probably $H_2Ru_3(CO)_{12}$, at temperatures above −40 °C. In contrast $H_2Os(CO)_4$ is stable above 100 °C [41]. It is interesting to speculate that such a polynuclear hydride could have a molecular structure in which the three ruthenium atoms form a bent metal-metal sequence as in $HRe_2Mn(CO)_{14}$ [42]. Mononuclear $H_2Ru(CO)_4$ exhibits a high field proton resonance at $\tau = 17.6$ in its NMR spectrum, and a ruthenium-hydrogen stretching frequency $\nu(Ru-H) = 1980\ cm^{-1}$ in its IR spectrum. In $D_2Ru(CO)_4$, $\nu(Ru-D)$ occurs at 1380 cm^{-1}. $H_2Ru(CO)_4$ reacts with phosphines to give the complexes $H_2Ru(CO)_2(PR_3)_2$, which are more conveniently prepared by reduction of the readily available $(R_3P)_2Ru(CO)_2Cl_2$ (R = C_2H_5 or C_6H_5) with $LiAlH_4$ [40] (*e.g.* $H_2Ru(CO)_2[P(C_2H_5)_3]_2$; ^1H-NMR: $\tau = 18.48$, $J(P-H) = 24$ Hz (triplet)). These hydrides undergo the expected reactions, such as with chlorinated solvents ($CHCl_3$ or CCl_4) to give $(R_3P)_2Ru(CO)_2Cl_2$, and with Me_3SiCl or Me_3SnCl to give the corresponding $(R_3P)_2Ru(CO)_2[M(CH_3)_3]_2$ (M = Si or Sn) complexes.

Several polynuclear ruthenium carbonyl hydrides have been characterized. The action of carbon monoxide and hydrogen on carbonylated ruthenium trichloride solutions in the presence of silver powder gives $H_4Ru_4(CO)_{12}$ [43,44]. Another hydride characterized by mass spectrometry is $H_2Ru_4(CO)_{13}$ [44]. A mixed hydride $HRuCo_3(CO)_{12}$ has been prepared [45], in a similar manner to $HFeCo_3(CO)_{12}$ [46], by refluxing ruthenium and cobalt carbonyls in acetone, and acidifying the product.

The anion $[Ru(CO)_4]^{2-}$ has been used to prepare $[(C_6H_5)_3PAu]_2Ru(CO)_4$ [decomp. 170 °C; νCO: 2026, 1952, and 1935 cm^{-1} (CS_2)] by treatment with $(C_6H_5)_3PAuCl$ [47].

There is currently considerable interest in complexes wherein silicon, germanium, or tin atoms are σ-bonded to transition metals. Recently the chemistry of organotin-iron carbonyl compounds has been reviewed, and a number of new complexes described [48]. It was, therefore, of interest to extend this field by studying ruthenium carbonyl derivatives of the Group IV elements.

Treatment of the $[Ru(CO)_4]^{2-}$ anion with R_3SnCl (R = C_6H_5 or $C_6H_5CH_2$) affords air-stable *trans*-$(R_3Sn)_2Ru(CO)_4$ [49]. The stereochemistry is assigned on the basis of the single carbonyl stretching band observed in the infrared spectra of these complexes (*e.g.* *trans*-$[(C_6H_5CH_2)_3Sn]_2Ru(CO)_4$; m.p. 99 °C, νCO: 2021 cm^{-1}). In contrast Me_3SnCl and the anion afford *cis*-$[(CH_3)_3Sn]_2Ru(CO)_4$ (a yellow liquid, b.p. 80 °C/10^{-2} torr, νCO: 2084 (s), 2024 (s), 2012 (w), and 2003 (s) cm^{-1}). With R_3SnCl (R = C_2H_5, *n*-C_3H_7, or *n*-C_4H_9) mixtures of *cis* and *trans* compounds, $(R_3Sn)_2Ru(CO)_4$, are obtained. Similar complexes are formed from $Ru(CO)_4H_2$ and trimethyltin hydride or triphenyltin chloride [40].

The complexes $(R_3Sn)_2Ru(CO)_4$ are best obtained by reacting triorganotin hydrides with $Ru_3(CO)_{12}$ [49]. It had been shown earlier that the iron analogs can be prepared similarly from iron carbonyls [48]. However, with the ruthenium carbonyl a novel type of diamagnetic complex $R_{10}Sn_4Ru_2(CO)_6$ is also produced, albeit in low yield. These polynuclear tin-ruthenium compounds are probably formed in the reactions by thermal decomposition of the mononuclear ruthenium species, since pyrolysis of $[(CH_3)_3Sn]_2Ru(CO)_4$ produces some $(CH_3)_{10}Sn_4Ru_2(CO)_6$ *(I)* (νCO: 2036 (w), 2000 (s), and 1982 (m) cm^{-1}), which has the novel molecular structure shown, as established by an X-ray crystallographic study [50].

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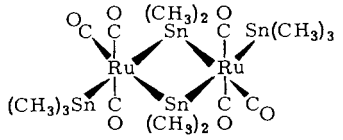
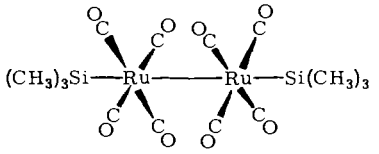
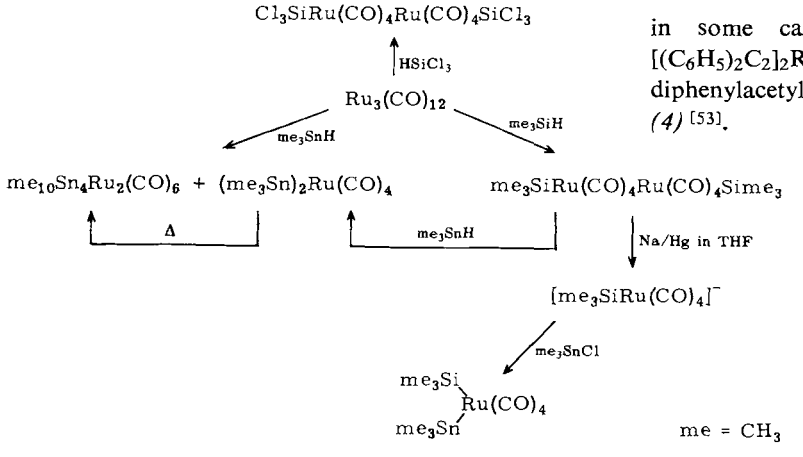


(1)



(2)

Reactions between $Ru_3(CO)_{12}$ and triorganosilanes follow a different course, complexes such as *(2)* (m.p. 129 °C; sublimes at 50 °C/10^{-3} torr) being produced in high yield. In contrast, under comparable conditions trimethylsilane and $Fe_3(CO)_{12}$ do not afford a stable silicon-iron complex. Moreover, with trichlorosilane $Ru_3(CO)_{12}$ gives $[Cl_3SiRu(CO)_4]_2$ *(3)* [51], whereas $Fe_3(CO)_{12}$ yields *cis*-$(Cl_3Si)_2Fe(CO)_4$ and $[Cl_2SiFe(CO)_4]_2$ [52]. Dimeric complexes $[R_2SnFe(CO)_4]_2$ analogous to $[Cl_2SiFe(CO)_4]_2$ are well known but iron complexes similar to *(1)* and *(2)* or *(3)* have not been prepared. Reaction of *(2)* with trimethylstannane gives $[(CH_3)_3Sn]_2Ru(CO)_4$ and $(CH_3)_3SiH$, but apparently the presence of the chlorine atoms in *(3)* enhances the stability of the silicon-ruthenium and ruthenium-ruthenium bonds since *(3)* does not react with trimethylstannane.



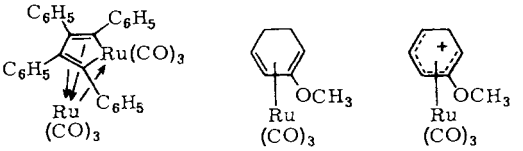
Scheme 1. Organosilicon and organotin complexes from $Ru_3(CO)_{12}$.

The discovery that an anion $[(CH_3)_3SiRu(CO)_4]^-$ can be obtained from *(2)* has led to the synthesis of a complex $(CH_3)_3Sn[(CH_3)_3Si]Ru(CO)_4$ in which two different group IV elements are bonded to ruthenium. Formation of $[(CH_3)_3SiRu(CO)_4]^-$ from *(2)* is reminiscent of the well known formation of $[(C_6H_5)_3PMn(CO)_4]^-$ from $[(C_6H_5)_3PMn(CO)_4]_2$. The infrared spectrum of *(2)* in the carbonyl region (νCO: 2040 (w), 2015 (vs), and 2010 (w, sh) cm^{-1}) is in accord with the structure proposed, being very similar to those of complexes of type $[R_3PMn(CO)_4]_2$. The high resolution mass spectrum of *(2)*, besides showing a molecular ion has a strong peak corresponding to $(CH_3)_3SiRu(CO)_4^+$.

Complex *(2)* undergoes a novel reaction with triphenylphosphine affording $[(C_6H_5)_3P]_2Ru(CO)_3$ and $[(CH_3)_3Si]_2Ru(CO)_2[P(C_6H_5)_3]_2$; under comparable conditions *(3)* does not react with the phosphine.

Reactions between $Ru_3(CO)_{12}$ and several hydrocarbons have been investigated. Unlike in the corresponding reactions involving $Fe_3(CO)_{12}$, several of the ruthenium complexes retain the metal atom cluster, for example, one product from cycloocta-1,3-diene is formulated as $C_8H_{12}Ru_3(CO)_{10}$ [30] and another from diphenylacetylene as $[(C_6H_5)_2C_2]_3Ru_3(CO)_9$ [53].

Diphenylacetylene affords several complexes, depending on the reaction conditions. In one study [54], in which the products were separated by thin-layer chromatography, complexes of formula $(C_6H_5)_2C_2Ru_3(CO)_9$, $[(C_6H_5)_2C_2]_2Ru_2(CO)_6$, $(C_6H_5)_2C_2Ru_2(CO)_6$, $[(C_6H_5)_2C_2]_2Ru_3(CO)_8$, $[(C_6H_5)_2C_2]_2Ru_2(CO)_7$, and $[(C_6H_5)_2C_2]_2Ru(CO)_4$ were obtained. The formulas of several of these complexes are similar to those of compounds obtained from acetylene and $Fe_3(CO)_{12}$ [55]. Structures may



(4) *(5)* *(6)*

in some cases be assigned by analogy, thus $[(C_6H_5)_2C_2]_2Ru_2(CO)_6$ formed from the carbonyl and diphenylacetylene in decalin at 200 °C is probably *(4)* [53].

The products obtained from similar reactions with other acetylenes depend on the substituents present [53]. 4,4'-Dichlorodiphenylacetylene gives dark red $[(ClC_6H_4)_2C_2]_3Ru_3(CO)_9$, analogous to $[(C_6H_5)_2C_2]_3Ru_3(CO)_9$ mentioned above, and orange $[(ClC_6H_4)_2C_2]_2Ru_3(CO)_8$ which probably has a structure similar to that of the black isomer of

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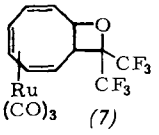
$[(C_6H_5)_2C_2]_2Fe_3(CO)_8$ [56]. 3-Hexyne [53] and hexafluoro-2-butyne [57] afford tetra-substituted cyclopentadienone-ruthenium tricarbonyl complexes, $(R_4C_4CO)Ru(CO)_3$ ($R = C_2H_5$ or CF_3) as the major products, along with trace amounts of what are probably polynuclear complexes. Dimethyl acetylenedicarboxylate is quantitatively trimerized to $C_6(CO_2CH_3)_6$ on heating with $Ru_3(CO)_{12}$ [53].

1,3-Cyclohexadienes react with $Ru_3(CO)_{12}$ to give the corresponding tricarbonylcyclohexadieneruthenium compounds [26]. The product from 2,5-dihydroanisole is a single isomer *(5)*, in contrast to the mixture of isomers formed from iron carbonyl. Proton abstraction with trityl tetrafluoroborate gives the cation *(6)*.

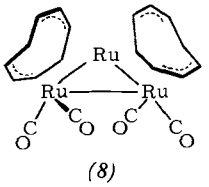
Tetracyclone and $Ru_3(CO)_{12}$ yield tricarbonyltetracycloneruthenium [57]. A ligand-exchange reaction occurs with tetraphenylcyclobutadienepalladium(II) bromide to give π-$(C_6H_5)_4C_4Ru(CO)_3$ [53]. Tricarbonylcyclobutadieneruthenium has been prepared [58] by treating 3,4-dichlorocyclobutene with the anion $[Ru(CO)_4]^{2-}$.

By refluxing cyclooctatetraene and $Ru_3(CO)_{12}$ in a hydrocarbon solvent at least four complexes are obtained. The compound π-$C_8H_8Ru(CO)_3$ [59,60] is the analog of π-$C_8H_8Fe(CO)_3$ [61], a complex which has been studied extensively on account of its being a stereochemically non-rigid molecule [62–65]. The ruthenium complex also exhibits a temperature-dependent ^1H–NMR spectrum but one capable of greater resolution at low temperatures. These studies [59,60] have established that the molecular structure of the ruthenium compound, and almost certainly that of the iron complex, in solution involves 1,3-diene to metal bonding [63,65] rather than 1,5-coordination of the C_8H_8 ring [64].

The compound $C_8H_8Ru(CO)_3$ undergoes 1,2-addition reactions [66] with suitably active molecules such as hexafluoroacetone or $(CF_3)_2C{=}C(CN)_2$ to give products such as *(7)*. These reactions are probably similar to the supposed Diels-Alder adduct of the corresponding iron complex and tetracyanoethylene [67,68].



(7)



(8)

Cyclooctatetraene is displaced from $C_8H_8Ru(CO)_3$ by iodine or phosphines to give the complexes $[Ru(CO)_3I_2]_2$ and *trans*-$(R_3P)_2Ru(CO)_3$, respectively. Mercuric halides or thiocyanate react with $C_8H_8Ru(CO)_3$ to afford the binuclear complexes $[Ru(CO)_3(HgX)X]_2$ (X = Cl, Br, or SCN), which further react with pyridine to give the complexes $Ru(CO)_3py(HgX)X$, which retain the Ru–Hg bond [69].

Other cyclooctatetraene-ruthenium complexes characterized so far include π-$C_8H_8Ru_2(CO)_6$ [69,70], π-$C_8H_8Ru_2(CO)_5$ [69,70], and $(\pi$-$C_8H_8)_2Ru_3(CO)_4$ [70]. The last named complex is particularly novel since it is both a metal atom cluster compound and a stereochemically non-rigid molecule. The molecular structure *(8)* has been established for this compound by an X-ray crystallographic study [71].

Prolonged heating of $Ru_3(CO)_{12}$ in benzene or cyclohexane at 150 °C gives a new cluster carbonyl formulated as $Ru_6(CO)_{18}$ [72]. Refluxing the carbonyl in toluene, xylene, or mesitylene gives other clusters such as red $Ru_6(CO)_{17}C$ and purple $Ru_6(CO)_{14}C$(arene) [73]. The hydrocarbons in these reactions may not be the source of the unique carbon atom but rather a CO group may have been degraded.

Ultraviolet irradiation of mixtures of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ has led to redistribution reactions affording $Ru_2Os(CO)_{12}$ and $RuOs_2(CO)_{12}$ [74].

Summary

A comparison of the chemistry of $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ indicates that in the former compound, the metal-metal bonds are easily broken, and it is only under the mildest conditions that compounds retaining the Fe_3 cluster are obtained. In contrast, the ruthenium cluster is much more robust, and many structurally new types of complexes with ruthenium-ruthenium bonds can be obtained, as is evident from the above review. For this reason further studies on $Ru_3(CO)_{12}$ and on the osmium analog are likely to be very worthwhile.

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The Oxidizing Properties of the Third Transition Series Hexafluorides and Related Compounds

BY NEIL BARTLETT[*]

Dedicated to Prof. H. J. Emeléus on the occasion of his 65th birthday

Some of the transition metal hexafluorides demonstrate an astonishing oxidizing power. In particular may be mentioned PtF_6, which is capable of oxidizing molecular oxygen or xenon, a process requiring an electron affinity, $E(PtF_6)$, > -156 kcal·mole^{-1}. From a comparative study of all of the hexafluorides of the third transition series the electron affinity is seen to increase regularly in the sequence $WF_6 < ReF_6 < OsF_6 < IrF_6 < PtF_6$. The increase in E with unit increase in atomic number of M appears to be ≈ -20 kcal·mole^{-1}. On the other hand the ability of the hexafluorides to accept F^- decreases along this series. This effect enables IrF_6 to be more effective than PtF_6 in the generation of nitrogen oxide trifluoride, ONF_3, by the oxidative fluorination of nitrosyl fluoride, ONF. Both PtF_6 and IrF_6 interact spontaneously with ONF or O_2NF to generate fluorine, at or below room temperature. The decrease in F^--acceptor ability along the series, which stands in sharp contrast to the increase in electron affinity, suggests that ligand crowding increases sharply across the series from WF_6 to PtF_6. This accords with the observed decrease in molecular volume along the series, both in the hexafluorides and in the MF_6^- salts. It is clear from this comparison that the species IrF_6 and PtF_6 are close to a minimum volume for this series. The oxide pentafluorides $ReOF_5$ and $OsOF_5$ are similar in oxidizing ability to their respective hexafluorides but are poorer F^- acceptors. Evidently the ligand crowding in MOF_5 molecules is greater than in MF_6.

1. Introduction

The discovery of dioxygenyl hexafluoroplatinate(v), O_2PtF_6[1,2], revealed the remarkable oxidizing properties of platinum hexafluoride. The crystal structure and magnetic, spectroscopic[**], and chemical properties of O_2PtF_6 all point to the ionic formulation $O_2^+[PtF_6]^-$.

The lattice energy was estimated from *Kapustinskii*'s equation[3],

$$U = 287.2\ \Sigma n\ \frac{z_1 z_2}{r_c + r_a}\left(1 - \frac{0.345}{r_c + r_a}\right)$$

where Σn is the number of ions in the molecule ($= y + x$ in $A_y(MF_6)_x$), z_1 and z_2 the ionic charges, and $r_c + r_a$ the sum of the ionic radii referred to coordination number six. In the case of $O_2^+[PtF_6]^{-1}$, $U = -125$ kcal·mole^{-1}. From the Born-Haber cycle, given in Figure 1, the electron affinity of the hexafluoride $E_{(PtF_6)}$ is required to be > -156 kcal·mole^{-1} in order that the oxidation of molecular oxygen (ionization potential $I_{(O_2)} = 281$ kcal·mole^{-1} [4]), by the hexafluoride, should occur spontaneously. Of course there is a considerable decrease in entropy for the process and for processes like it,

$$O_{2(g)} + PtF_{6(g)} \rightarrow O_2^+[PtF_6]_{(s)} \qquad (1)$$

hence $E_{(PtF_6)}$ needs to be considerably in excess of -156 kcal·mole^{-1} for spontaneous reaction.

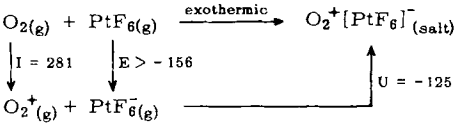

Fig. 1. A Born-Haber Cycle for $O_2^+(PtF_6)^-$. (Enthalpies in kcal·mole^{-1}.)

It may be argued that London dispersion forces and multipole forces[5] would add energy to that computed from *Kapustinskii*'s equation. This may be so, but this additional term is unlikely to exceed the enthalpy of formation of orthorhombic PtF_6 crystals from the vapor (*i.e.*, -11 kcal·mole^{-1})[6]. Furthermore it is probable that reaction (1) is more exothermic than -25 kcal·mole^{-1}, since the solid is not sublimable *in vacuo* below 90 °C[2]. Even allowing for additional lattice energy terms, it is probable that $E_{(PtF_6)}$ well exceeds -156 kcal·mole^{-1}.

Not only was it evident that PtF_6 should be capable of bringing about further spectacular oxidations but it seemed that other hexafluorides and related compounds could at least approach, or perhaps exceed it in oxidizing ability. A survey of the oxidizing properties of

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[**] The Raman spectrum of $O_2^+[PtF_6]^-$ obtained recently, at Princeton, by *P. A. Bulliner*, gives $\nu(O_2^+) = 1837$ cm^{-1}, which is close to the gas phase value of 1876.4 cm^{-1}.

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hexafluorides of the third transition series and a comparison of these fluorides with the oxide pentafluorides ($OsOF_5$ and $ReOF_5$), with ReF_7, and with hexafluorides of the second transition series was therefore undertaken.

2. Oxidation of Noble Gases

After having solved the O_2PtF_6 problem our attention was immediately focused on the possible oxidation of xenon, the ionization potential of which ($I_{(Xe)}$ = 280 kcal·mole^{-1}) [4] is almost identical to that of molecular oxygen. Further, in the case of an $[MF_6]^-$ salt the lattice energy is not greatly dependent on the cation size; it appeared probable, therefore, that PtF_6 would oxidize this noble gas. Indeed the lattice energy for $Xe^+[PtF_6]^-_{(c)}$ is unlikely to be less exothermic than -120 kcal·mole^{-1}, which is the appropriate value for an estimated Xe^+ radius of 1.5 Å. The predicted oxidation of xenon by PtF_6 did occur spontaneously at room temperature [7]. The product, however, is not as simple as first formulated [8].

This reaction has been repeated many times and followed tensimetrically as well as gravimetrically [9]. The combining ratio Xe: PtF_6 always lies between 1:1 and 1:2, with the former favored when the xenon is in excess and the concentration of the reactants is low. *Mahieux* [10] may well have produced similar material by exploding a platinum wire in Xe/F_2 gas, products of composition $XePtF_6$ and $Xe(PtF_6)_2$ being indicated. The product from $PtF_6 + Xe$ reactions is always plastic and, but for minor crystalline components, amorphous to X-rays. The product, irrespective of composition, is paramagnetic, and shows infrared absorption at 650 cm^{-1} (vs) and at 550 cm^{-1} (s), which spectra are similar to the spectra of $O_2^+[PtF_6]^-$ [2] and $NO^+[PtF_6]^-$ [11,12] and certainly characteristic of Pt(v) in a fluorine ligand environment.

If an excess of PtF_6 is used and the product, of composition $Xe(PtF_6)_2$, is warmed to ~ 60 °C a red solid is obtained which gives a characteristic X-ray diffraction pattern [9]. This product is structurally almost identical to the adduct XeF_2, 2 IrF_5 that was prepared recently by *Bartlett* and *Sladky* [13] by the reaction of XeF_2 with IrF_5 in BrF_5 and which probably is $XeF^+[Ir_2F_{11}]^-$. Furthermore, the faint pattern that frequently appears in X-ray photographs of $Xe(PtF_6)_x$ (x = 1–2) has been identified as that of XeF_2, PtF_5. This compound is structurally very closely related to the 1:1 adduct XeF_2, IrF_5, which is probably the salt $XeF^+[IrF_6]^-$ [13]. Incidentally, IrF_6 does not interact with xenon under the conditions of $Xe(PtF_6)_x$ formation.

Earlier work [8] had shown that the $Xe(PtF_6)_x$ contains Pt(v), since interaction with alkali fluoride ($A[IF_6]$, A = Rb, Cs) in IF_5 solution yielded $A^+[PtF_6]^-$ salts. A separate experiment established that XeF_4 in IF_5 solution does not oxidize Pt(IV) fluoride in the presence of alkali fluoride.

There are few solvents for $Xe(PtF_6)_x$ and recrystallization of the material from a solvent has not yet been achieved. When the solid is heated above 160 °C [*] a complicated redox reaction takes place, resulting in the formation of XeF_4 and a diamagnetic material, which contains xenon, has a composition approximating to $XePt_2F_{10}$ [8,9] and gives a distinctive X-ray powder pattern.

The interaction of PtF_6 with Xe may therefore be interpreted by assuming the following reactions:

$$Xe_{(g)} + PtF_{6(g)} \rightarrow Xe^+[PtF_6]^-$$

The cation is then fluorinated by excess PtF_6:

$$Xe^+PtF_6^- + PtF_6 \rightarrow XeF^+[PtF_6]^- + PtF_5.$$

Evidently the formation of the $XeF^+[Pt_2F_{11}]^-$ salt requires thermal activation:

$$XeF^+PtF_6^- + PtF_5 \rightarrow XeF^+[Pt_2F_{11}]^-$$

The initial product $Xe^+[PtF_6]^-$ could rearrange to form $Xe_2^{2+}[PtF_6]_2^-$ but the like charges of the Xe^+ would not be expected to encourage such a union and there is no evidence to support such a formulation.

The ionization potential of krypton $I_{(Kr)}$ is 323 kcal·mole^{-1} [4] and the lattice energy $U_{(Kr^+[MF_6]^-)}$ is approximately -125 kcal·mole^{-1}; hence, a minimum electron affinity $E_{(MF_6)}$ of -198 kcal·mole^{-1} is required to effect oxidation of krypton to $Kr^+[MF_6]^-$ by MF_6. Unfortunately PtF_6 will not oxidize krypton nor will RhF_6 [8], although AuF_6, should it be prepared, could possibly do so, since $E_{(AuF_6)}$ is estimated to be > -180 kcal·mole^{-1} [11].

Although RhF_6 will not oxidize Kr it does oxidize Xe [8].

The reaction product of two experiments had a composition close to $XeRhF_6$, the combining ratio Xe: RhF_6 being 1:1.05 and 1:1.0. Very faint sharp line patterns indicate the presence of $XeF^+[RhF_6]^-$ as a minor phase; this suggests that an excess of RhF_6, like PtF_6, interacts with the Xe^+ to produce XeF^+.

Clearly PtF_6 and RhF_6 (and possibly IrF_6) ought to be capable of oxidizing radon since $I_{(Rn)}$ = 246.6 kcal·mole^{-1}. With $U_{(Rn^+[MF_6]^-)} = -115$ kcal·mole^{-1}, $E_{(MF_6)}$ would have to be considerably more exothermic than -132 kcal·mole^{-1}

3. Oxidation of NO and ONF

None of the third transition series hexafluorides other than PtF_6 proved to be capable of oxidizing xenon or oxygen [9]. Since the hexafluoride anions are large and are similar in size, the lattice energy does not vary by

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[*] There is evidence that decomposition occurs as low as 110 °C.

Table 1. Products of NO + MF_6 and ONF + MF_6 reactions (all at ≈ 20 °C).

MF_6	Reagent	Conditions	Product: Gaseous	Product: Solid	Unit Cell of Salt S.G.; a, b, c (Å)	Refs.
WF_6	NO	g + g no reaction	—	—	—	[9, 11, 14]
	ONF	1:1, g + g	—	$NOWF_7$	(cub.); 5.197	[9, 11]
	ONF	1:2, g + g	—	$(NO)_2WF_8$	pattern not indexed	[11, 12]
ReF_6	NO	1:1 or excess NO, g + g	excess NO	$NOReF_6$	Ia 3; 10.151	[11, 12]
	ONF	1:1 g + g	ReF_6	$(NO)_2ReF_8$	isomorphous $(NO)_2WF_8$	[11, 12]
		1:2 g + g	—	$(NO)_2ReF_8$		[11, 12]
OsF_6	NO	1:1 or excess NO, g + g	excess NO	$NOOsF_6$	Ia 3; 10.126	[2, 9, 11]
	ONF	1:1 or excess ONF, g + g	excess ONF + trace ONF_3?	(a) $NOOsF_7$ + (b) some $NOOsF_6$	(a): (cub.); 5.145	[11, 12]
IrF_6	NO	1:1 or excess NO, g + g	excess NO	(a) $(NO)_2IrF_6$ + (b) $NOIrF_6$	(a): (hex.); $a = 10.01$; $c = 3.53$	[9, 11]
		IrF_6 in WF_6 (l) + NO (g)	—	$NOIrF_6$	Ia 3; 10.114	[9, 11]
	ONF	1:1, g + g	F_2 + minor ONF_3	$NOIrF_6$		[11, 12]
		1:3, g + g or c + g	ONF_3 + minor F_2	$NOIrF_6$		
PtF_6	NO	1:1 or excess NO, g + g	NO consumed to 1:2	(a) $(NO)_2PtF_6$ + (b) $NOPtF_6$	(a): (hex.); $a = 10.01$; $c = 3.53$	[9, 11, 15] [9, 11]
		PtF_6 in WF_6 (l) + NO (g)	—	(a) $(NO)_2PtF_6$ + (b) $NOPtF_6$		
	ONF	1:1, g + g	F_2 + trace ONF_3	$NOPtF_6$	Ia 3; 10.112	[11, 12, 15]
		1:≥ 3, g + g or c + g	F_2 + trace ONF_3	$NOPtF_6$		[11, 12]

S.G. = Space group (or Bravais lattice) g = gas, l = liquid, s = solid.

more than 1–2 kcal·mole^{-1} for a common cation. Furthermore, NO^+ is so similar in size to O_2^+ that the difference in lattice energy in salts of a common anion is negligible. Since the ionization potential $I_{(NO)}$ is 68 kcal·mole^{-1} less than $I_{(O_2)}$ [4], the electron affinity $E_{(MF_6)}$ for oxidation of NO need be that much less exothermic than for oxidation of O_2. On the other hand, the oxidation of nitrosyl fluoride with liberation of molecular fluorine requires a minimum $E_{(MF_6)}$ of −126 kcal·mole^{-1} (c.f. Fig 2).

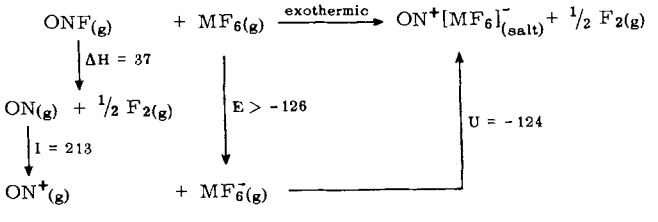

Fig. 2. A modified Born-Haber cycle for the reaction $ONF_{(g)} + MF_{6(g)} \rightarrow NO^+[MF_6]^-_{(s)} + {}^1/_2 F_{2(g)}$. (Enthalpies in kcal·mole^{-1}).

By employing NO or ONF as the reducing agent *Jha* and *Beaton* have established [2,9,11,12] a smooth increase in $E_{(MF_6)}$ in the series WF_6 to PtF_6 (cf. Table 1). Iridium hexafluoride is seen to be the only hexafluoride of this series, other than PtF_6, to be capable of oxidizing ONF to liberate fluorine. However, the ONF adduct with OsF_6 is readily reduced to $NOOsF_6$ and indeed on one occasion ONF_3 has been noted as a gaseous product. This contrasts with the marked stability of $(NO)_2ReF_8$. The nature of the products obtained by reaction of NO with MF_6 shows that WF_6 is the poorest oxidizer and that IrF_6 and PtF_6 are the best oxidizing agents. Evidently $E_{(MF_6)}$ increases (exothermally) regularly in the sequence $WF_6 < ReF_6 < OsF_6 < IrF_6 < PtF_6$ with $E_{(ReF_6)} > -90$ $E_{(IrF_6)} > -126$; and $E_{(PtF_6)} > -156$ kcal·mole^{-1} [11]. The increase in $E_{(MF_6)}$ with unit increase in atomic number of M appears to be ~ −20 kcal·mole^{-1}.

The change in volume of MF_6^-, indicated by the relative formula-unit volumes in the cubic crystalline $NO^+[MF_6]^-$ salts [2,9,11,12] is as follows: Ta, 133.4; Re, 130.7; Os, 129.8; Ir, 129.3; Pt, 129.2 Å^3.

The volume of the PtF_6 group is close to a limiting volume. The unit cell volumes of both the orthorhombic and cubic forms of the hexafluorides [16] reveal a similar limiting volume behavior (cf. Table 3). Presumably, therefore, $V_{(AuF_6)}$ ought to be similar in magnitude to $V_{(PtF_6)}$; however, the fluorine ligand electrons of the former would be more highly polarized than in the latter and consequently spontaneous liberation of fluorine would be more likely to occur. Undoubtedly the AuF_6 molecule would be more strongly oxidizing than PtF_6 and $E_{(AuF_6)}$ would probably be > −180 kcal·mole^{-1}. It is unlikely that it would be powerful enough to oxidize molecular nitrogen ($I_{(N_2)}$ = 358 kcal·mole^{-1} [4]) since this requires an $E_{(AuF_6)}$ greater than −233 kcal·mole^{-1}, but the oxidation of Kr (cf. Section 2) could be within range.

The products obtained on reaction of ONF with MF_6 not only reveal an increase in electron affinity from WF_6 to PtF_6 but also demonstrate a marked decrease in F^- acceptor ability – at least from ReF_6 to PtF_6. Although WF_6 cannot oxidize NO, it readily adds F^-:

$$ONF + WF_6 \rightarrow NOWF_7$$
$$2\,ONF + WF_6 \rightarrow (NO)_2WF_8$$

The $NOWF_7$ complex is simple cubic and must be a plastic crystal, the WF_7^- being rotationally disordered. The $(NO)_2WF_8$ salt is isomorphous with $(NO)_2ReF_8$

[14] *J. R. Gleichmann, E. A. Smith, S. S. Trond,* and *P. R. Ogle,* Inorg. Chem. *1*, 661 (1962).

[15] *F. P. Gortsema* and *R. H. Toeniskoetter,* Inorg. Chem. *5*, 1217 (1966).

[16] *S. Siegel* and *D. A. Northrop,* Inorg. Chem. *5*, 2187 (1966).

and it is probable that both contain MF_8^{2-} ions. Interestingly, although there is evidence that $NOReF_7$ can be prepared at temperatures lower than −30 °C, the compound dismutates below room temperature [12]:

$$ONF + ReF_6 \rightarrow [NOReF_7] \rightarrow ReF_6 + (NO)_2ReF_8$$

The interaction of NO with ReF_7 [12] involves the same intermediate:

$$2\,NO + ReF_7 \rightarrow NO + [NOReF_7] \rightarrow NOReF_6 + (NO)_2ReF_8$$

It seems that the enthalpy of the addition reaction $F^-_{(g)} + MF^-_{7(g)} \rightarrow MF^{2-}_{8(g)}$ is more exothermic for ReF_7^- than for WF_7^-; all other factors being neglected, this is at least consistent with the greater electron affinity of Re^{VI} over W^{VI}. The inability of OsF_6 to form $(NO)_2OsF_8$ is therefore ascribed to the greater ligand crowding in the Os^{VI} species. Presumably in ReF_7^- the ligands are not so tightly crowded as in OsF_7^-. The unimolecular unit cell volume of $NOWF_7$ (140.4 Å^3 [11,12]) is certainly much greater than in $NOOsF_7$ (136 Å^3); also, the latter volume is only 14 Å^3 greater than the molecular volume in the cubic OsF_6 (122 Å^3).

With IrF_6 the marginal ability to add F^- and the ability to oxidize F^- to $^1/_2F_2$ combine to render it a most effective oxidative fluorinating agent. When ONF and IrF_6 are mixed in approximately equimolar quantities at 20 °C, a reaction occurs, the overall stoichiometry of which approximates to

$$ONF + IrF_6 \rightarrow NOIrF_6 + {}^1/_2F_2$$

Some nitrogen oxide trifluoride [11,17–19] is formed, the yield of which is increased greatly when the ratio of ONF to IrF_6 is increased; with a 3:2 molar ratio, more than 60% of the theoretical yield of ONF_3 is obtained:

$$3\,ONF + 2\,IrF_6 \rightarrow 2\,NOIrF_6 + ONF_3$$

Since ONF will not interact with F_2 at ordinary temperatures and pressures without excitation [17], and since IrF_6 does not interact with ONF_3 [18], it is reasonable to suppose that these reactions involve an intermediate, probably $NOIrF_7$. Presumably this short lived complex salt can eliminate molecular F_2 concertedly.

$$2\,NOIrF_7 \rightarrow 2\,NOIrF_6 + F_2$$

Alternatively, it could interact with an excess of nitrosyl fluoride in a two step process.

$$ONF + NOIrF_7 \rightarrow ONF_2^{\bullet} + NOIrF_6$$
$$ONF_2^{\bullet} + NOIrF_7 \rightarrow ONF_3 + NOIrF_6$$

The ONF_2 radical reported by *Fox et al.* [18] is unlikely to be free in this reaction but is more likely to be fluorinated before it can leave the $NOIrF_6/NOIrF_7$ surface.

There is no evidence to suggest that a salt-like adduct is formed by the interaction of PtF_6 and ONF; such an intermediate – if it were formed – would have an extremely short lifetime, since, no matter what the concentration of ONF, the overall reaction is close to that represented by the equation:

$$ONF + PtF_6 \rightarrow NOPtF_6 + {}^1/_2F_2$$

Minor amounts of ONF_3 are produced [11,12]. It is a safe assumption that the ligand crowding is greater in PtF_6 than in the other hexafluorides of the third transition series, but this molecule also has the oxidizing power to liberate atomic fluorine from ONF, for which $E_{(MF_6)}$ must merely exceed −144 kcal·mole^{-1}. It is conceivable therefore that the shorter lifetime of $NOPtF_7$ compared to $NOIrF_7$ results from both the greater crowding and the ability to shed atomic fluorine.

The ability of PtF_6 to liberate fluorine on interaction with ONF was discovered independently by *Gortsema* and *Toeniskoetter* although their report [15] makes no mention of ONF_3 formation. The study by *Beaton* [11,12] gave no evidence to support the claim made by these authors that further interaction of ONF with $NOPtF_6$ takes place with liberation of more fluorine; indeed $(NO)_2PtF_6$, said to be formed in the reaction, and described as cubic, cannot be made in this way. $(NO)_2PtF_6$ is a diamagnetic salt, which has a hexagonal lattice (somewhat disordered) and can be prepared from NO (excess) + PtF_6 (cf. Table 1); it is isomorphous with $(NO)_2PdF_6$ [20].

Although the F_2 produced in these reactions is derived at normal temperatures and pressures from reagents which may be kept indefinitely at ordinary temperatures (in suitable containers), the preparation is nevertheless not a primary one. Fluorine (or presumably electrolytic syntheses) must be used to generate IrF_6 or PtF_6. Indeed there is still no definitive primary chemical preparation of this halogen.

4. Other Oxidations Involving MF_6

Attempts to oxidize Kr, N_2, NF_3, and F_2O by PtF_6 failed [9]. All are more difficult to oxidize than O_2 or Xe.

Although the lower ionization potential of hexafluorobenzene ($I_{(C_6F_6)}$ = 207.5 kcal·mole^{-1}) [21] favors its oxidation by PtF_6, it has not yet proved possible to prevent highly favored alternative reactions such as:

$$3\,PtF_6 + C_6F_6 \rightarrow 3\,PtF_4 + C_6F_{12}$$

[17] *N. Bartlett, J. Passmore*, and *E. J. Wells*, Chem. Commun. *1966*, 213.

[18] *W. B. Fox, J. S. MacKenzie, N. Vanderkoor, B. Sukomick, C. A. Wamser, J. R. Holmes, R. E. Eibeck*, and *B. A. Stewart*, J. Amer. chem. Soc. *88*, 2604 (1966).

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[21] *J. R. Majer* in *M. Stacey, J. C. Tatlow*, and *A. G. Sharpe*: Advances in Fluorine Chemistry. Butterworths, London 1961, Vol. 2, p. 83.

Similarly, although CO has an ionization potential close to that of N_2 and would not be expected to yield CO^+, it interacts instantly with PtF_6 to form COF_2, PtF_4, and even Pt; the CO here assuming its normal role as a strong reducer:

$$CO + PtF_6 \rightarrow Pt + PtF_4 + COF_2$$

The oxidation of Cl_2 with PtF_6 is feasible if one considers its ionization potential $I_{(Cl_2)} = 260$ kcal·mole^{-1} [4] and its lattice energy $U_{(Cl_2^+[PtF_6]^-)}$, which was estimated to be ≈ -115 kcal·mole^{-1}. Although the gases interact immediately at $\approx 20\,^\circ C$ and no free chlorine fluorides are produced, the combining ratio $Cl_2:PtF_6$ is $\approx 1:2.5$ [9]. The investigation of this interaction is incomplete, but it is evident that the product obtained is a mixture and may well contain PtF_5 and ClF_2PtF_6 [22].

Iridium hexafluoride also proved able to oxidize Cl_2 [9]. The molar combining ratio is closer to 1:1 and, as in the case of PtF_6, no evidence has been found for free chlorine fluorides in the product. Unfortunately the product is amorphous to X-rays; the yellow solid is unstable at room temperature and decomposes [9, 23] to iridium pentafluoride [24] and a gaseous decomposition product, other than chlorine, that has not been identified. Should the Raman and infrared studies presently being carried out prove the presence of $Cl_2^+[IrF_6]^-$ in the adduct then it would follow that $E_{(IrF_6)} > -144$ kcal·mole^{-1}.

Gibler has shown [23] that WF_6, as expected, does not oxidize I_2 ($I_{(I_2)} = 214$ kcal·mole^{-1}) spontaneously. OsF_6 does, but the reaction is complex. He established that nitryl fluoride interacts with IrF_6 according to the equation:

$$O_2NF + IrF_6 \rightarrow NO_2^+[IrF_6]^- + {}^1/_2F_2$$

The nitryl salt shows the usual [26] ν_3 infrared bands at 2360 cm^{-1} and IrF_6^- ν_3 at 630 cm^{-1} [27]. The unit cell is orthorhombic, but the alternative primitive monoclinic cell $a = b = 4.99$; $c = 5.55$ Å; $\alpha = 92.3\,^\circ$ $V = 138$ Å^3, shows a clear relationship to the primitive *pseudo* cell of $NOIrF_6$, $a = 5.057$ Å, $V = 129$ Å^3. Since the dissociation enthalpy for $O_2NF_{(g)} \rightarrow NO_{2(g)} + {}^1/_2F_{2(g)}$ [25] $= 27$, $I_{(NO_2)} = 228$ [4], and $U_{(NO_2IrF_6)} = -120$ kcal·mole^{-1}, $E_{(IrF_6)}$ must be > -135 kcal·mole^{-1}, which is ~ 9 kcal more exothermic than the $E_{(MF_6)}$ requirement in the oxidation of NOF with IrF_6.

The salt $NO_2^+[OsF_6]^-$, which was prepared in a slightly impure form (contaminated with $NOOsF_6$) by *Jha* [9] from NO_2 and OsF_6, is isomorphous with NO_2IrF_6. The spontaneity of this reaction implies an $E_{(OsF_6)} > 108$ kcal·mole^{-1}.

5. Oxidizing Properties of $ReOF_5$ and $OsOF_5$

Both $ReOF_5$ and $OsOF_5$ are of C_{4v} symmetry and are nearly octahedral [33, 38]. The molecular volume of $OsOF_5$ in both the orthorhombic and cubic forms is less than that of OsF_6 (see Table 3). At 20 °C $ReOF_5$ is isomorphous with orthorhombic $OsOF_5$. The interaction of the oxide fluorides with NO produces [9, 12] 1:1 salts spontaneously at ambient temperature:

$$NO_{(g)} + MOF_{5(g)} \rightarrow NOMOF_{5(s)}$$

It seems, then, that both $OsOF_5$ and $ReOF_5$ have an oxidizing capability similar to that of the respective fluorides. Clearly $OsOF_5$ is not so powerful as IrF_6, and $ReOF_5$ is not so weak as WF_6. The salts $NO^+[MOF_5]^-$ bear a close structural relationship to their $NO^+[MF_6]^-$ relatives (cf. Table 2).

Table 2. Structural Relationships of $NOMF_6$ and $NOMOF_5$ Salts.

Salt	Bravais lattice	Bravais lattice parameters (Å)		Mols./ unit cell	Mol. Vol. (Å^3)
		a	*c*		
$NOReOF_5$	tetragonal	5.083	10.00	2	129
$NOOsOF_5$	tetragonal	5.025	10.37	2	131
$NOReF_6$	body centered cubic	10.151		8	130.75
$NOOsF_6$	body centered cubic	10.126		8	129.79

When the NO + $OsOF_5$ reaction was carried out in WF_6 solution, a cubic phase of composition $(NO)_2OsWOF_{11}$ was obtained, which proved to be isomorphous but not isodimensional with $NOOsF_6$ [$(NO)_2OsWOF_{11}$: $a = 10.152$ Å; $NOOsF_6$: $a = 10.126$ Å] [9]. The magnetic susceptibility was measured over the 77–297 °K range and showed a Curie-Weiss law obedience, with $\theta = 24\,^\circ K$; the behavior closely parallels that of $NOOsF_6$ [9]. The product is presumably a solid solution of $NOWOF_5$ in $NOOsF_6$. The magnetic moment of $(NO)_2OsWOF_{11}$ obtained on this basis was $\mu_{eff} = 3.15$ B.M. (297 °K) which compares favorably with the value of $\mu_{eff} = 3.36$ B.M. (297 °K) obtained for the pure $NOOsF_6$ salt [9]. The overall reaction in this instance was therefore:

$$2\,NO + WF_6 + OsOF_5 \xrightarrow{HF\ catalyst} NOOsF_6 + NOWOF_5$$

with the oxygen ligand exchanging partners.

It is probable that the effective catalyst was HF but this has not been established. Exchange of oxo-ligand could take place by way of an oxygen-bridged intermediate; the hypothetical oxyfluoride WOF_5 with its unsaturated oxygen valence would be a better electron acceptor than WF_6.

The course of the reaction suggests that $E_{(OsF_6)} > E_{(OsOF_5)}$, although the soundness of this conclusion must await the outcome of an investigation of the reaction mechanism.

[22] *N. Bartlett* and *D. H. Lohmann*, J. chem. Soc. (London) *1964*, 619.

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[24] *N. Bartlett* and *P. R. Rao*, Chem. Commun. *1965*, 252.

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[26] *R. A. Marcus* and *J. M. Fresca*, J. chem. Physics *27*, 564 (1957).

[27] *R. D. Peacock* and *D. W. A. Sharp*, J. chem. Soc. (London) *1959*, 2762.

Table 3. Some physical properties of third transition series MF_6 and MOF_5.

	WF_6	ReF_6	OsF_6	IrF_6	PtF_6	$ReOF_5$	$OsOF_5$
Color solid	colorless	cream	yellow	deep yellow	purple	colorless	Emerald green
Color vapor	colorless	colorless	colorless	yellow	red	colorless	colorless (?)
m.p. (°C)	2.0 [28]	18.5 [29]	33.2 [30]	44.0 [28]	61.3 [31]	40.8 [32]	59.2 [33]
b.p. (°C)	17.1 [28]	33.7 [29]	45.9 [30]	53.6 [28]	69.14 [31]	73.0 [32]	100.5 [33]
Orth. cell (Å) a (Å)	9.68 [16]	9.61 [16]	9.59 [16]	9.58 [16]	9.55 [16]	not measured	9.54 [34]
Orth. cell (Å) b	8.81	8.76	8.75	8.73	8.71		8.67
Orth. cell (Å) c	5.09	5.06	5.04	5.04	5.03		5.02
Mol. Vol. (Å^3)	108.5	106.5	105.7	105.4	104.6		103.8
Cub. cell a (Å)	6.28 [16]	6.26 [16]	6.25 [16]	6.23 [16]	6.21 [16]	—	6.14 [33]
Mol. vol (Å^3)	123.8	122.6	122.1	120.9	119.7		115.7
Orth. → Cub. T (°C)	−8.2 [28]	−3.5 [29]	1.4 [30]	−1.2 [28]	3.0 [31]	30.0 [32]	32.5 [33]
ΔH trans. (Kcal·mole^{-1})	1.4 [28]	2.0 [29]	2.0 [30]	1.7 [28]	2.1 [31]	1.3 [32]	—
ΔS fus. (e.u.)	1.45 [28]	3.2 [29]	5.7 [30]	3.7 [28]	3.2 [31]	3.9 [32]	5.3 [33]
$\Delta H_{vap.}$ (kcal·mole^{-1})	6.33 [28]	6.87 [29]	6.72 [30]	7.38 [28]	7.06 [31]	7.72 [32]	8.75 [33]
$\Delta S_{vap.}$ (e.u.)	21.8 [28]	22.3 [29]	21.0 [30]	22.6 [28]	22.5 [31]	22.3 [32]	23.4 [33]
M—F (Å)	1.833 [35,36]	—	1.831 [36]	1.830 [36]	—	—	—
ν_1 (cm^{-1})	771 [37]	755 [37]	733 [37]	701 [37]	655 [37]	Re—O 992 [33]	Os—O 960 [33]
Ground State d electron conf.	d^0 [46]	dt_{2g}^1 [46]	dt_{2g}^2 [46]	dt_{2g}^3 [46]	dt_{2g}^4 [46]	d^0	dt_{2g}^1

Unlike ReF_6, $ReOF_5$ is not able to combine with 2 ONF, the sole product being $NOReOF_6$. This difference in F^- acceptance may again be ascribed to a steric cause. Similarly, although OsF_6 and ONF interact to give $NOOsF_7$, a mixture of ONF and $OsOF_5$ does not give an adduct. As is shown in Table 3, the molecular volume of $OsOF_5$ is significantly less than that of OsF_6.

The greater ligand crowding in the oxide pentafluorides compared with their hexafluoride relatives must in part be ascribed to the greater size of the oxygen ligand compared with the fluorine ligand, but there is probably an important electron configuration factor which will be referred to later.

6. Metal Hexafluorides of the Second Transition Series

Although attention has been focused upon the oxidative chemistry of the third transition series compounds it should be noted that a similar trend of increasing oxidizing power with increasing atomic number and decreasing molecular volume also occurs in the second transition series; however, information is much scarcer.

In particular, MoF_6 has been shown by *Geichmann et al.*[14] to be capable of oxidizing NO to give $NOMoF_6$, which establishes that MoF_6 is a stronger oxidizer than WF_6. *Seip*[35] determined the M—F distances in MoF_6 and WF_6 from electron diffraction studies; the values obtained were 1.820 and 1832 Å respectively. Furthermore, the MoF_6 molecular volume[16] in the orthorhombic (106.6 Å^3) and cubic (120.9 Å^3) phases is significantly less than in the case of WF_6 (Table 3).

As already mentioned, RhF_6 is capable of oxidizing Xe as also is RuF_6[39]. Both of these hexafluorides are less stable thermally than PtF_6[40] and both are much smaller than the platinum analog in size[16] (100.9 and 99.5 Å^3, respectively).

Clearly the trends noted in the third series are exaggerated in the second; however, TcF_6 is not very different from ReF_6[41,42] in its behavior toward NO or ONF since it forms $NOTcF_6$ with NO and $(NO)_2TcF_8$ with ONF, there being no indication of ONF_3 or of F_2 generation. It seems therefore that TcF_6 is not so powerful an oxidizing agent as OsF_6.

7. A Rationalization of the Properties of MF_6 and MOF_5

The relationship of oxidizing strength of MF_6 to high nuclear charge of M and to the smallness of the molecule is well established.

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[42] *N. Bartlett, R. A. Naumann*, and *R. Serfass*, unpublished.

It should also be remarked that, in each series, the more powerful MF_6 is as an oxidizer the less stable it is towards dissociation [43] to a lower fluoride and fluorine. However, this does not prevent efficient synthesis. Although PtF_6 rapidly decomposes to PtF_4 and F_2 at temperatures above 260 °C [31], it is conveniently prepared in $\approx 90\%$ yield by burning platinum (≈ 1000 °C) in a F_2 atmosphere adjacent to a cold finger (−196 °C). It is probable that the average bond energies in the more powerful oxidizers are less than in the weaker oxidizers, but all are highly exothermic compounds. *Hubbard et al.* [44] have measured the enthalpies of formation of MoF_6 and WF_6, and their data indicate average bond energies of 107.4 and 121.1 kcal·mole^{-1}, respectively. These values are almost double the average bond energies in the non-transition hexafluorides of the sixth main group (SF_6, 78.5; SeF_6, 72.6; and TeF_6, 81.2 kcal·mole^{-1}) [45].

The MF_6 molecules are octahedral, although some exhibit dynamic Jahn-Teller effects [37]. Both $ReOF_5$ and $OsOF_5$ are nearly octahedral [33]. All of the hexafluorides and $OsOF_5$ are dimorphic as solids (cf. Table 3).

The orthorhombic phase approximates to a close packed fluorine ligand array, with the metal atoms in octahedral hole sites. Undoubtedly the bonded octahedra (MF_6) are smaller than the nonbonded, but it is evident that the octahedra cannot be greatly distorted since the ratio $c:b:a$ is in all cases close to $1:3:4\ \sqrt{2}/\sqrt{3}$, which is that required for a hexagonal close packing with an *abac* layering sequence along *a*.

In the cubic phase there is plastic crystal disorder and as *Weinstock* has pointed out [40] the entropy of fusion of this phase is not very different from the value of 3.3 e.u. found for the noble gases.

In keeping with the rotational disorder in the cubic phase, its volume is greater than that in the orthorhombic form. There is, however, a significant decrease in volume across the series for each phase. Presumably this results from a decrease in the size of MF_6 with z rather than from an increase in the van der Waals forces. If so, the volume decrease may be due *either* to a M–F bond shortening *or* to a decrease in the ligand van der Waals radius, *or* both.

Results of electron diffraction investigations of gaseous MF_6 by *Schomaker* and *Weinstock* (Table 3) indicate that the M–F bond length remains approximately constant. This implies a significant decrease in the van der Waals ligand radii in this series of compounds. It is, furthermore, somewhat surprising at first sight that the totally symmetric MF_6 (A_{1g} symmetry) mode decreases along the series.

There is little reason to doubt the main conclusions of *Moffitt et al.* [46] that the *d* electron configurations in MF_6 in the ground state and in the low excited state are as given in Table 3. Excited states involving configurations $dt_{2g}^{n-x}e_g^x$ were assigned to expanded molecule states, since only the e_g^x electron density effectively screens the ligands from the nuclear charge. Since the t_{2g} electrons are ineffective in their screening, an increasing polarization of the F ligand σ bonding electrons will occur with increase in atomic number *i.e.* from WF_6 to PtF_6. Moreover, if π bonding occurs it is clear that its contribution to the total bonding will decrease with increase in the population of the t_{2g} orbitals (*i.e.* as the antibonding π orbitals are filled). Therefore, F ligands in WF_6 are more likely to be multiply bonded than in PtF_6 and because of the greater z and smaller π bonding in the latter, the σ bond electrons will be very strongly polarized towards the Pt atom. This last feature may well lead to a diminution of the electron density on the outside of the F ligands and in this way to a decrease in the van der Waals radius of the ligand. If this picture is true the approximate constancy of the M–F bond lengths in the series must arise from a coincidental matching of the lengthening due to loss of multiple bond character with a shortening from the transition series contraction.

This explanation would also account for the greater readiness of the F ligands in RuF_6, RhF_6, and PtF_6 to lose M–F bonding electrons, as required for the dissociation:

$$MF_6 \rightarrow MF_{(6-x)} + {}^{x}/_{2}F_2$$

It seems that the decrease in F^- acceptor ability with increase in z is associated with the decrease in t_{2g} orbital availability. As these orbitals are populated the MF_7^- and MF_8^{2-} ions become less favorable. Each added F^- requires one of the t_{2g} orbitals, and this further severely curtails M–F π bonding. As the π bonding becomes limited, so the polarization of the σ electrons increases. Simultaneously the repulsive interaction of neighboring F ligands will also increase as those F ligand electrons previously involved in π bonding become "nonbonding". The electron affinity can, of course, be simply attributed to the need of the F ligands to replace electron density lost to the highly polarizing central atom.

The oxide pentafluorides are significantly smaller than their related fluorides. This may in part be ascribable to the dipole moment, but the major factor must lie elsewhere – perhaps in increased π bonding. Since the t_{2g} electrons have a small screening effect on the ligands, the difference in the *d* electron configurations of $OsOF_5$ (d^1) and OsF_6 (d^2) is not expected to have a large effect on the polarization of the ligand σ electrons. The $OsOF_5$ ligands have a greater opportunity to π bond, therefore the polarization of the σ electron density will, on the whole, be less than in OsF_6. On this basis $OsOF_5$ would have less affinity than OsF_6 for an electron.

It is evident from the foregoing that much more research of a quantitative nature will have to be done before the many questions posed by these remarkable compounds can be adequately answered.

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Nitrogen Oxide Fluorides

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Dedicated to Professor H. J. Emeléus on the occasion of his 65th birthday

Oxyfluorides of nitrogen, i.e. compounds containing the grouping F–N–O, have been known for many years in the form of simple compounds, such as NOF and NO_2F. Detailed studies of physical, structural, and chemical aspects of this class of compounds have been conducted only in recent years, after the potential of N–F compounds as rocket propellants had been recognized. Several novel types of oxyfluorides of nitrogen, such as difluorohydroxyl amines, $RO-NF_2$, or trifluoroamine oxide, F_3NO, have been discovered recently. A further major development in O–N–F chemistry is indicated by the discovery that compounds of great chemical potential are formed between HF and NOF or NO_2F, respectively.

The compound O_2NOF, although not an oxyfluoride of nitrogen, will also be discussed in this review, because of its particular chemical relationship to NO_2F.

A. Introduction

Although the simplest oxyfluorides of nitrogen, NOF [1] and NO_2F [2], have been known for over 60 and nearly 40 years, respectively, the chemistry of these compounds has not been studied in any depth until very recently [3,4]. For a long time after their discovery NOF and NO_2F remained academic curiosities. It was not until the potential of such compounds as rocket propellants had been recognized – about 1960 – that a systematic study of the oxyfluorides was initiated. In addition to improvements in earlier syntheses of the known oxyfluorides of nitrogen, novel types of compounds were discovered, perhaps the most noteworthy being trifluoroamine oxide F_3NO, which was reported nearly simultaneously by several research groups in 1966/67.

B. Nitrogen Oxide Fluorides

1. Nitrosyl Fluoride, NOF

1.1. Preparation

NOF was first prepared by *Ruff* by the fluorination of NOCl with silver fluoride at room temperature [1]. *Ruff* also discovered that NOF is formed in the gas phase reaction between nitric oxide and fluorine [2]. This direct synthesis is usually conducted in reactors made of polytetrafluoroethylene, copper, or nickel [2,5,6]; the extremely fast and quantitative reaction [7]

$$2\,NO + F_2 \rightarrow 2\,NOF,\ \Delta H^0_{298} = -74.8\ \text{kcal/mole}\ [8]$$

takes place with emission of visible light [9]. The spectrum of ONF is continuous with a maximum at 6095 Å [8]. The following mechanism has been suggested [9]:

$$NO + F_2 \rightarrow ONF + F^{\cdot}\ (\text{slow})$$

$$NO + F^{\cdot} \rightleftharpoons [ONF]^{*} \rightarrow ONF + h\nu$$

$$[ONF]^{*} \xrightarrow{M} ONF\ [8,10]$$

Further methods of synthesis of NOF are based on the reaction of some readily accessible nitrosyl salts with alkali fluorides at high temperatures (200–300 °C) according to

$$[NO]^+X^- + F^- \xrightarrow{\Delta} ONF + X^-$$

where X = $[BF_4]^-$ [11] (c.f. also [7,12]), $[SbF_6]^-$ [13], $[S_2O_7]^{2-}$ [6]. N_2O_4 ($\approx [NO]^+[NO_3]^-$) also fits this scheme; it gives NOF upon interaction with $[N(CH_3)_4]F$ [14], KF, or CsF [15].

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NOF is obtained as the major product in a synthesis of tetrafluorohydrazine [16–19], which is represented by

$$2\,NF_3 + 2\,NO \rightarrow N_2F_4 + 2\,ONF$$

and which is carried out at 500–800 °C in a flow system.

Equimolar amounts of NOF and NF_3 are produced in the reaction of nitrous oxide N_2O with fluorine [20, 21], which may be conducted in the 300 to 800 °C range

$$N_2O + 2\,F_2 \rightarrow NF_3 + ONF$$

The reaction of N_2F_4 with nitrates, such as KNO_3 or $AgNO_3$, or with nitrites at elevated temperatures [22],

$$KNO_3 + N_2F_4 \rightarrow KF + 3\,ONF$$

$$2\,NaNO_2 + N_2F_4 \rightarrow 2\,NaF + 2\,ONF + 2\,NO$$

leads to the formation of NOF in 41–76 % yield.

The most economical method for the preparation of NOF is expected to be the dehydrofluorination of NOF/HF complexes which may be effected by passing these complexes as a vapor through NaF or KF; HF can be recovered by heating NaF·*x* HF or KF·*x* HF to 265–350 °C [23–28].

NOF is formed in a number of other reactions, most of which cannot be considered as synthetic methods. The following examples are representative:

$OF_2 + NO \rightarrow ONF\,(+\,O_2NF)$ [29–31]

$COF_2 + NO \rightarrow ONF\,(+N_2F_2,\ NF_3,$ and other products) [32]

$2\,N_2F_4 + OF_2 \rightarrow ONF + 3\,NF_3$ [33]

$N_2F_2 + NO \rightarrow ONF\,(+N_2O,\ NO_2,$ and other products) [34]

"$N_2O_5W_3F_{11}$" (from $WF_6 + N_2O_4$) $\rightarrow$ $ONF + ([NO][WOF_5],$ and other products) [35]

$3\,N_2O_4 + 2\,WF_6 \rightarrow ONF + 2\,[NO][WOF_5] + O_2NF + N_2O_5$ [35]

Nitrosyl fluoride is one of the products formed in a number of pyrolytic reactions of fluorocarbon derivatives, *e.g.* $C_3F_7NO_2$ [36], $O_2N(CF_2)_2ONO$, O_2NCF_2COF, $O_2N(CF_2)_2NO_2$, and $O_2NCF_2C(ONO)FCF_3$ [37].

Formation of NOF as an oxidation product of N_2F_4,

$$N_2F_4 + {}^1/_2O_2 \rightarrow ONF + NF_3$$

has been reported [38]; however, it has been shown in independent work that there is no direct reaction between N_2F_4 and O_2 [39]; the above observation must therefore be due either to wall reactions or to impurities.

NOF is also formed in the reaction of XeF_4 and XeF_2 with NO (130–180 °C, 0.1 to 30 torr) [40].

Formation of oxyfluorides of nitrogen, mainly NOF and NO_2F, upon irradiation of mixtures of numerous nitrogen- and oxygen-containing compounds with ionizing radiation between –196 °C and room temperature has been detected by mass spectroscopy. Examples for such systems include NF_3/O_2, NF_3/N_2O, NF_3/NO, NF_3/N_2O_4, OF_2/N_2F_4, OF_2/N_2, OF_2/N_2O, OF_2/NO, *etc.* [41]. Similar irradiation of NOF possibly gives rise to novel O–N–F systems.

1.2. Structure and Physical Properties

The structure of NOF is well established from its IR spectrum [42–46] and its microwave spectrum [43, 51]. IR fundamentals have been determined not only for $^{16}O^{14}NF$, but also for $^{16}O^{15}NF$, $^{18}O^{14}NF$, and $^{18}O^{15}NF$ [46]. According to these studies, NOF is a bent, unsymmetrical molecule (cf. Table 1).

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Table 1. Physical properties of nitrosyl fluoride.

Melting Point (°C)	-132.5 ± 0.3	[2]
Boiling Point (°C)	-59.9 ± 0.3	[2]
	-60 to -59	[5, 6]
Heat of Vaporization (kcal·mole^{-1})	4.6	[2]
Trouton Constant (cal·deg^{-1}·mole^{-1})	21.6	[2]
Liquid density (d_l)	$1.919-0.00278 \times T$ [a]	[2]
	1.326 [b]	[2]
Solid density (d_s)	1.719	[2]
IR Absorption (cm^{-1})	1844 (ν_1), 521 (ν_2), 766 (ν_3)	[42, 45]
	1843.4 (ν_1), 765.8 (ν_2), 519.9 (ν_3)	[46]
IR rotational spectrum (125–40 cm^{-1})		[47]
Force constants (mdyn·Å^{-1}) [c]	f_{N-O} 14.67; f_{N-F} 2.44	[48, 49]
	f_{N-O} 15.08; f_{N-F} 2.09	[50]
	f_{N-O} 15.9; f_{N-F} 2.3	[46]
Dipole Moment (D) [d]	1.81	[51]
Bond distances (Å)	N–O 1.13, N–F 1.52	[48, 51]
Bond Angle (°)	O–N–F 110	[48, 51]
^{19}F–NMR: δ_F (ppm) [e]	-479 ± 1	[53]
	-478	[54]
Thermodynamic data		[48]
Quadrupole Coupling Constants and Rotational Constants		[43, 50, 55]
ΔH^0_{298} (kcal·mole^{-1})	-15.8	[8]
Dissociation Energy (kcal·mole^{-1}) ONF → NO + F	$+55.4$	[8]
σ (Ω^{-1}·cm^{-1}) [f, g]	5.4×10^{-5}	[56]
	5.3×10^{-5}	[57]

[a] In the temperature range -125 to -67 °C. [b] At -59.9 °C. [c] In the NOX series (X = F, Cl, Br) $f_{NF} > f_{NCl} > f_{NBr}$. [d] The intrinsic dipole moment μ(N–F) = 2.72 D [52]. [e] Measured on liquid NOF (-70 ± 1 °C) relative to CCl_3F as external standard. [f] At -79 °C. [g] The temperature dependence of σ was determined for pure NOF and for solutions of NOF in BF_3, PF_5, and AsF_5 [58].

It was concluded from vibrational force constant calculations that the N–O bond order in NOF is 1.98 (*i.e.* very nearly the same as for NOCl or NOBr) [59]. Other evidence, such as the dipole moment [60], the very low N–F force constant [49], and the long N–F bond distance [48], suggests that the N–F bond has ionic character. This is also borne out by the fact that rapid exchange of fluoride ions with the solvent is observed in solutions of NOF in liquid HF [53]. Peculiarly, NOF shows one of the lowest ^{19}F chemical shifts ever reported in the NMR (well below F_2) and a large paramagnetic contribution to the shielding of the fluorine nucleus in NOF must be invoked to rationalize this finding [53]. A special technique has been developed to handle NOF in polytetrafluoroethylene NMR tubes [61].

In terms of MO theory, NOF is viewed as a loosely bound combination of a fluorine atom and a NO radical [62, 63]. This is also reflected, for example, in the low N–F force constant [46] and in the N–O force constant for NOF, which is virtually the same as in free NO; furthermore, recent SCF–MO calculations suggest that the values of the ONF equilibrium angle and of the N–F bond distance in NOF must be slightly revised [63].

1.3. Chemical Properties

Pure nitrosyl fluoride is a colorless gas which attacks glass, especially in the presence of moisture [1], and exhibits strongly corrosive properties towards various metals; tin, lead, and certain kinds of steel being particularly readily attacked [6]. The compound is tractable, however, in apparatus made of copper, nickel, or some nickel alloys [6].

As an acid fluoride, NOF is hydrolyzed as follows [1, 6, 11]:

$$\text{neutral: } 3\,ONF + 2\,H_2O \rightarrow 3\,HF + 2\,NO + HNO_3$$

$$\text{basic: } ONF + 2\,OH^- \rightarrow NO_2^- + F^- + H_2O$$

P_4O_{10} reacts with NOF to give POF_3 [11].

NOF is a strong oxidizing agent and reacts with a great variety of elements, both metallic and nonmetallic, but it is distinctly less reactive than elemental fluorine. Qualitative observations about such reactions, far too numerous to be listed here, have been reported since the first discovery of NOF [1, 2, 11]. Nitric oxide is formed as well as the respective fluoride in such reactions; however, the possibility exists of further reaction between NOF and the fluoride of the element concerned if the latter has acceptor properties (see Section B.3.). While some elements, such as B, Si, P, As, react with NOF with incandescence, others react only upon heating (*e.g.* Mg, Zn, Fe, W) or not at all (I_2, Br_2, C, O_2) [1, 2]. Chloryl fluoride will oxidize NOF to NO_2F quantitatively at room temperature [22]. A 10 % yield of N_2O is obtained in the reaction of NOF with azide ion, thus suggesting the formation of nitrosyl azide as an unstable intermediate [64].

NOF is presumably involved as an intermediate in a number of reactions of NF_3 [65], *e.g.*

$$SO_2 + NF_3 \rightarrow SOF_2 + ONF$$

$$SO_2 + 2\,ONF \rightarrow SOF_2 + NO + NO_2$$

SeO_2 behaves in an analogous fashion, $SeOF_2$ being the product. Nitrosyl salts of fluoroacids, $[NO]^+[MF_n]^-$ are obtained in similar reactions of NF_3 if the intermediate NOF can act as a fluorinating agent, giving rise to the formation of an acceptor fluoride which will then take up further NOF (see Section B.3. [65]).

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The reaction of NOF with SO_2 to give a 1:1 adduct (SeO_2 does not react) has long been known [11, 14, 66]. The adduct melts at −79 °C (+8 °C/3100 torr) and it is dissociated to an extent of 70 % at 19 °C. Chemically, $NOF{\cdot}SO_2$ behaves as a mixture of its components, *e.g.*

$$NOF{\cdot}SO_2 + BF_3 \rightarrow [NO][BF_4] + SO_2$$

$$NOF{\cdot}SO_2 + SO_3 \rightarrow [NO][SO_3F] + SO_2.$$

Like NOF itself, the adduct may act as a fluorinating, oxidizing, and complexing agent at the same time [14], *e.g.*

$$MCl_3 + 6\,NOF{\cdot}SO_2 \rightarrow [NO][MF_6] + 2\,NO + 3\,NOCl + 6\,SO_2\ (M = P, As)$$

No structural data on $NOF{\cdot}SO_2$ are available.

At high temperatures (125–600 °C), especially in the presence of an activated charcoal catalyst, SO_2F_2 is formed from SO_2 + NOF [67–70]. NOF also reacts with SCl_2 at ~50 °C to give SOF_2 [23, 71–74].

As a result of the strongly oxidizing character of NOF the scope of its organic chemistry is limited. Apart from a few qualitative observations [2], this field has only recently been investigated, the largest amount of work being concerned with the addition of NOF across double bonds, especially in perfluorinated systems. These reactions will be considered separately in Section B.4.

NOF is suitable as a gas phase fluorinating agent for CCl_4 or CH_2Cl_2, for example, giving rise to formation of chlorofluoromethanes [23, 75], sometimes in the presence of a CoF_2 catalyst [23, 76–80].

A potentially important type of reaction of NOF in organic chemistry involves its addition to steroids having olefinic bonds, such as cholesterol and some of its derivatives. Smooth reactions were observed between NOF and various such compounds in a CH_2Cl_2 or CCl_4 medium at 0 °C, with fluorine entering the 5-position, while either a nitrimine (=N–NO_2) group (from cholesteryl acetate and chloride) or a carbonyl group (from cholesterol) was in the 6-position of the steroid after working up [81].

1.4. The Hydrogen Fluoride – Nitrosyl Fluoride System

A very important development has arisen in recent years through the work of *Seel*, as well as that of research groups at Allied Chemical Corporation and at Brookhaven National Laboratory, in the study of the NOF/HF and NO_2F/HF systems. The existence of solvates such as $NOF{\cdot}3$ HF and $NO_2F{\cdot}5$ HF has been established. These compounds are potentially cheap sources of the oxyfluorides of nitrogen and may permit their use on a large scale.

The NOF/HF system has been dealt with in a review by *Seel* [54], and its discussion will be restricted here, attention being focused on recent developments.

Seel et al. [82, 83] found that solutions of N_2O_3, NOF, or alkali metal nitrites in liquid HF contain a species, $[NO]^+[F(HF)_x]^-$, from which defined products, especially $NOF{\cdot}3$ HF may be obtained. A cryoscopic study of the system NOF/HF revealed the existence of the complexes, $NOF{\cdot}HF$, 3 $NOF{\cdot}5$ HF, 2 $NOF{\cdot}5$ HF, $NOF{\cdot}3$ HF, and $NOF{\cdot}4$ HF, with melting points ranging in the −10 to +10 °C region [86, 87].

A seemingly homogeneous product of apparent composition $NOF{\cdot}6$ HF was reported by a number of workers [24–28, 85, 86, 88]. Later, however, it was shown that "$NOF{\cdot}6$ HF" has the composition $N_2O_3{\cdot}12.8$ HF or $NOF{\cdot}5.4$ HF$\cdot 0.5\ H_2O$ [54, 87]; its specific conductivity of 0.0129 Ω^{-1} cm^{-1} is comparable to that of a fused salt [24–28, 54].

A reaction has also been observed between N_2O_4 and liquid HF. Fractionation gave a product of constant b.p. 52 °C which corresponds to the composition N_2O_4 + 7.0 HF + 0.87 HNO_3 (or NOF + 6 HF + 1.87 HNO_3), along with $NOF{\cdot}3$ HF [54, 86, 89].

[66] *W. Kwasnik* in *G. Brauer*: Handbuch der präparativen anorganischen Chemie, Vol. I, Verlag F. Enke, Stuttgart 1960, p. 179.

[67] *L. G. Anello* and *C. Woolf*, French Pat. 1317920 (Jan. 7, 1963), Allied Chem. Corp.

[68] *L. G. Anello* and *C. Woolf*, Jap. Pat. Publ. 4051 (1963), Allied Chem. Corp.

[69] *L. G. Anello* and *C. Woolf*, US-Pat. 3107979 (Oct. 22, 1963), Allied Chem. Corp.

[70] *L. G. Anello* and *C. Woolf*, German Pat. 1160409 (Jan. 2, 1964), Allied Chem. Corp.

[71] *L. G. Anello* and *C. Woolf*, French Pat. 1309590 (Oct. 8, 1962), Allied Chem. Corp.

[72] *L. G. Anello* and *C. Woolf*, US-Pat. 3074781 (Jan. 22, 1963), Allied Chem. Corp.

[73] *L. G. Anello* and *C. Woolf*, Japan Pat. Publ. 3654 (1963), Allied Chem. Corp.

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[75] *L. G. Anello*, *J. Gordon*, and *C. Woolf*, German Pat. 1241427 (June 1, 1967), Allied Chem. Corp.

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[79] *J. Gordon*, *H. R. Nychka*, and *C. Woolf*, Jap. Pat. Publ. 10212 (1965), Allied Chem. Corp.

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[86] *F. L. Horn*, *C. B. Bartlett*, and *R. J. Tivers*, US Atomic Energy Commission Rep. BNL-6231 (1962).

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[88] *F. Seel*, *W. Birnkraut*, and *D. Werner*, Chem. Ber. *95*, 1264 (1962).

[89] *F. Seel*, *G. Fuchs*, and *D. Werner*, Chem. Ber. *96*, 179 (1963).

1.4.1. Preparation and Properties of NOF–HF Adducts.

The preparation of NOF·3 HF and "NOF·6 HF" is described in numerous reports, especially in the patent literature [23, 67–70, 72, 75, 90–97]. Usually, mixtures of HF and NOCl (molar ratio ≈ 6:1) were passed through a nickel reactor during 4 h, (contact time 18 sec). Fractional distillation of the reaction products gave "NOF·6 HF" (b.p. 68 °C) and NOF·3 HF (b.p. 95 °C).

The reaction of NOCl with HF may also be conducted in the liquid phase in polyethylene bottles; reaction commences at −40 °C. The HCl formed is finally removed by heating the system to +50 °C. Subsequent fractionation of the products must, because of their aggressive nature, be conducted in a nickel, gold, platinum, or polytetrafluoroethylene apparatus [84, 88, 91]. Although the standard free energy change for the gas phase reaction $NOCl + HF \rightarrow NOF + HCl$ is unfavorable, the reaction proceeds in the liquid phase because of complex formation between NOF and HF [54, 88]. Instead of NOCl, mixtures of $NO + Cl_2$ (or of $NO + Br_2$) may also be employed. Likewise, $NOCl{\cdot}AlCl_3$ or $[NO]^+[HSO_4]^-$ may serve as a source of NO [84, 88, 91].

NOF·3 HF is a colorless, hygroscopic liquid (b.p. 94–95 °C/760 torr; m.p. 1–5.6 °C [54, 84, 85, 88]; $d_4^{25} = 1.6$ [84, 85, 88]; $\sigma = 0.0503\ \Omega^{-1}cm^{-1}$ [24–28]) which may be stored in containers made of nickel or polytetrafluoroethylene.

A liquid of composition NOF·2.67 HF (m.p. 4.7 °C) is obtained when HF is pumped off from NOF·3 HF at room temperature. When heated, NOF·2.67 HF gives off NOF until finally NOF·3 HF distills. This observation suggests the existence of several nitrosyl fluoride-hydrogen fluoride complexes, which are in equilibrium with each other in the liquid and gas phase [54].

Very little is known concerning the structure of these products. *Seel et al.* suggested the possibility that the hydrogen fluoride in NOF·3 HF is present in the form of the cyclic associated trimer, and that NOF molecules are embedded between layers made up of such rings [88].

^{19}F–NMR spectra suggest that NOF·3 HF represents a highly associated system, in which all fluorine atoms are completely and rapidly exchanging, and that they have an environment more similar to that in HF than in NOF. The same is true for the products NOF·2.67 HF and $N_2O_3{\cdot}12.8$ HF [53, 54, 86].

Density determinations on the liquid phase in the NOF–HF system as a function of temperature and composition showed that a very remarkable volume shrinkage takes place on mixing of the pure components; in some ranges the volume of the complex mixture is very nearly the same as that of hydrogen fluoride [86, 87].

The N=O absorption in the IR spectrum of liquid NOF·3 HF (1797–1804 cm^{-1}) is shifted only slightly, compared to gaseous NOF (1844 cm^{-1}); no absorption due to $[N{\equiv}O]^+$ is detectable [88].

1.4.2. Chemistry of NOF·3 HF

NOF·3 HF is a versatile chemical reagent, whose chemical behavior is determined by both of its components, NOF and HF. It displays powerful oxidizing properties towards a great variety of nonmetallic and metallic elements. Whenever the fluoride, XF_n, formed has acceptor character, it is obtained in the form of a nitrosyl salt, $[NO]^+[XF_{n+1}]^-$ [54, 84, 88, 99]. The oxidative fluorination of certain metals, *e.g.* Mo and W, by their smooth and quantitative reaction with NOF·3 HF, can be directed so as to provide a straightforward synthesis of the hexafluorides [94, 97],

$$M + 6\ NOF{\cdot}3\,HF \rightarrow MF_6 + 6\ NO + 18\ HF$$

The oxides of all metals that react with NOF·3 HF will also react with this reagent to give fluorides, NO, and NO_2 [88]

$$MO + 2\ NOF{\cdot}3\,HF \rightarrow MF_2 + NO + NO_2 + 6\ HF$$

Particularly noteworthy is the rapid reaction of NOF·3 HF with quartz or natural silicates *e.g.* beryl,

$$Be_3Al_2[Si_6O_{18}] + 42\ NOF{\cdot}3\,HF \rightarrow$$
$$3\ [NO]_2[BeF_4] + 2\ AlF_3 + 6\ SiF_4 + 18\ (NO + NO_2) + 126\ HF$$

The significance of $NOF{\cdot}(HF)_n$ as a source of NOF, by its reaction with HF acceptors such as F^- (alkali fluorides), has already been mentioned,

$$NOF{\cdot}(HF)_n + F^- \rightarrow [F(HF)_n]^- + ONF$$

Lewis acids, such as BF_3, BrF_3, AsF_5, and SbF_5, will react with the NOF component, *e.g.*

$$NOF{\cdot}(HF)_n + BF_3 \rightarrow [NO][BF_4] + nHF$$

NOF·3 HF and other products obtained by dissolving NO, N_2O_3, N_2O_4 in HF will react with various metals and compounds which are of importance in nuclear technology (*e.g.* U, Pa, UO_2, UC, Zr, Fe, ceramics) to give the corresponding fluoro complexes, NO $[UF_6]$, $(NO)_2[ZrF_6]$, *etc.* [85, 86, 98, 101]. Such reactions are of practical significance in the recovery of uranium from spent fuel elements and in the separation of certain fission products. The complex $NO[UF_6]$ is volatile at 400 °C in the presence of NOF gas. Separation of uranium from other elements such as Pu, Nb, Mo, Te may be effected by virtue of the differences in volatility of the various complexes. Uranium may be recovered, ultimately, as UF_6, after treatment of $NO[UF_6]$ with a halogen fluoride [101].

In the electrolysis of the NOF–HF system the initial products are F_2 at the anode and NO at the cathode;

[90] *L. G. Anello* and *C. Woolf*, Belg. Pat. 611545 (Dec. 14, 1961), Allied Chem. Corp.

[91] *F. Seel*, German Pat. 1123297 (Febr. 8, 1962).

[92] *L. G. Anello* and *C. Woolf*, French Pat. 1310192 (Oct. 15, 1962), Allied Chem. Corp.

[93] *L. G. Anello*, *J. Gordon*, and *C. Woolf*, US-Pat. 3062902 (Nov. 6, 1962), Allied Chem. Corp.

[94] *H. Q. Trout* and *A. W. Yodis*, South African Pat. Appl. 0375 (1964); Allied Chem. Corp.

[95] *L. G. Anello* and *C. Woolf*, Brit. Pat. 963823 (July 15, 1964), Allied Chem. Corp.

[96] *L. G. Anello* and *C. Woolf*, US-Pat. 3160623 (Dec. 8, 1964), Allied Chem. Corp.

[97] *H. Q. Trout* and *A. W. Yodis*, US-Pat. 3185543 (May 25, 1965), Allied Chem. Corp.

[98] *F. L. Horn*, Sympos. inorg. Fluorine Chem., Argonne, Ill. 1963; US Atomic Energy Commission Rep. BNL-7572 (1963).

[99] *F. Seel*, *W. Birnkraut*, and *D. Werner*, Angew. Chem. *73*, 806 (1961).

[100] *H. H. Rogers*, *S. Evans*, and *J. H. Johnson*, J. electrochem. Soc. *111*, 704 (1964).

[101] *G. Strickland*, *R. Johnson*, *F. L. Horn*, and *C. B. Bartlett*, US-Pat. 3145078 (Aug. 18, 1964), US Atomic Energy Commission.

however, the two products will react with each other unless separated in the gas phase [100].

Finally it may be mentioned that NOF·3 HF (and also "NOF·6 HF") will convert the lower sulfur chlorides, SCl_2 and S_2Cl_2, to thionyl fluoride, SOF_2 [23, 71–74]. Sulfur dioxide reacts with NOF·3 HF to give sulfuryl fluoride [67–70].

NOF·3 HF and "NOF·6 HF" have some potential in organic chemistry (cf. [54]), *e.g.* in metathetical reactions involving exchange of fluorine for chlorine. A particular advantage over the use of pure HF is that such fluorination reactions may be conducted at higher temperatures without the necessity of employing sealed reaction vessels. The chlorine-fluorine exchange proceeds particularly smoothly if the chlorine is activated.

A typical example is the fluorination of halogenated benzene derivatives, a CoF_2 catalyst usually being employed [23, 76–80]. Chlorine-fluorine exchange has also been effected in aliphatic compounds, such as CCl_4 or CH_2Cl_2, which can be converted to chlorofluoromethanes [75, 93]. Unsaturated halogen compounds, such as tetrachloroethylene can also be fluorinated, the double bond not being affected [75, 93].

In some cases, oxidation of primary alcohols to aldehydes by NOF–HF complexes has been observed [54]. Especially noteworthy is the utilization of NOF–HF complexes in a Schiemann-type reaction with aromatic amines in a non-aqueous medium, whereby fluoroaromatic compounds can be prepared easily, and in high yields [23, 54, 88, 90, 92, 95, 96], *e.g.*

$$\text{Aryl–NH}_2 \xrightarrow{\text{NOF·(HF)}_n} \text{Aryl–F} + \text{N}_2$$

The diazonium compounds which are formed initially decompose in a readily controllable fashion at, or slightly above, room temperature.

2. Nitryl Fluoride, NO_2F

2.1. Preparation

Nitryl fluoride is believed to have been first obtained by *Moissan* by the reaction of NO with fluorine [102–104]. The compound was first characterized adequately by *Ruff* [2, 105] (cf. also [5]) who prepared it by the direct combination of NO_2 with fluorine. Here as well as in a number of other cases, the preparative methods for making NO_2F closely resemble those for making NOF; for example, in the reactions which involve heating a nitryl salt with alkali fluoride,

$$NO_2[X] + F^- \rightarrow O_2NF + [X]^-$$

X = BF_4, SiF_6 [12, 106–108], ClO_4 [109], PF_6 [110]. Syntheses of this type are attractive because elemental fluorine is not required. PF_5, for example, may be regenerated by heating $[PF_6]^-$ to 400–600 °C; since $NO_2[PF_6]$ is prepared from fuming nitric acid and PF_5, the above synthesis of NO_2F corresponds to the net reaction of NaF with HNO_3 [110].

The kinetics of the direct reaction of NO_2 with fluorine [108] was found to be first order both in NO_2 and F_2. The following two steps were proposed [111],

$$NO_2 + F_2 \rightarrow NO_2F + F^\bullet \text{ (slow)}$$

$$NO_2 + F^\bullet \xrightarrow{M} NO_2F + M \text{ (fast)}$$

A useful synthesis of NO_2F involves oxidation of N_2O_4 with CoF_3,

$$2\,CoF_3 + N_2O_4 \rightarrow 2\,O_2NF\ (90\%) + 2\,CoF_2$$

CoF_3 may be regenerated by reaction of CoF_2 with F_2 [112, 113]. CeF_4, MnF_3, and AgF_2 react with NO_2 at room temperature [113].

A further important method of preparation of NO_2F is based on the reaction of nitrite with fluorine [114, 115],

$$NO_2^- + F_2 \rightarrow O_2NF + F^-$$

which proceeds at temperatures slightly above room temperature. Elemental fluorine is avoided in a related synthesis, which involves the reaction of N_2O_5 with sodium fluoride [116],

$$F^- + N_2O_5\ (\approx NO_2[NO_3]) \rightarrow O_2NF + NO_3^-$$

N_2O_5 is the precursor of NO_2F in some other reactions, *e.g.*

$$BrF_5 + 2\,N_2O_5 \rightarrow BrO_2F \rightarrow 4\,O_2NF \quad [117]$$

$$BrF_3 + 3\,N_2O_5 \rightarrow Br(NO_3)_3 + 3\,O_2NF \quad [118]$$

Ruff's first successful synthesis of NOF, which involved fluorination of NOCl with silver fluoride, proved to be very unsatisfactory when applied to NO_2Cl; passage of NO_2Cl through AgF in a platinum tube at 240 °C leads to the formation of NO_2F in only 5 % yield [106, 107].

[102] *H. Moissan* and *P. Lebeau*, C. R. hebd. Séances Acad. Sci. *140*, 1573 (1905).

[103] *H. Moissan* and *P. Lebeau*, C. R. hebd. Séances Acad. Sci. *140*, 1621 (1905).

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[109] *M. M. Markowitz* and *P. F. Winternitz*, US-Pat. 3110558 (Nov. 12, 1963).

[110] *C. S. Cleaver*, US-Pat. 3092459 (June 4, 1963), duPont.

[111] *R. L. Perrine* and *H. S. Johnston*, J. chem. Physics *21*, 2202 (1953).

[112] *R. A. Davis* and *D. A. Rausch*, Inorg. Chem. *2*, 1300 (1963).

[113] *R. A. Davis* and *D. A. Rausch*, US-Pat. 3259460 (July 5, 1966), Dow Chem. Corp.

[114] *E. E. Aynsley*, *G. Hetherington*, and *P. L. Robinson*, J. chem. Soc. (London) *1954*, 1119.

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A potentially very cheap source of NO_2F is provided in the dehydrofluorination of the readily available compound, $NO_2F \cdot 5\,HF$ [119–123] with KF, NaF, or $KF \cdot xHF$,

$$NO_2F \cdot 5\,HF + y\,(KF \cdot xHF) \rightarrow$$

$$O_2NF + y\,KF \cdot (x + \tfrac{5}{y})HF$$

$$\downarrow \Delta$$

$$y\,(KF \cdot xHF) + 5\,HF$$

Finally, there are a number of reactions which also yield NO_2F but which cannot be considered suitable methods for the preparation of the compound [22, 29, 35, 36, 124–129].

The reaction of NO_2 with O_2F_2 to form NO_2F [129] might be expected to serve as a source of OF radicals which then might combine with NO_2 to form O_2NOF; however, formation of O_2NOF has not been observed.

NO_2F is also produced in the reaction of NO_2 with OF_2 [130].

2.2. Structure and Physical Properties

Nitryl fluoride, like nitrosyl fluoride, is a reactive, colorless gas at room temperature; both gases also exhibit a similar degree of volatility. A number of physical data for NO_2F are listed in Table 2.

The structure of NO_2F has been well established by a number of techniques. The ^{19}F–NMR spectrum consists of a 1:1:1 triplet (coupling between ^{19}F with nuclear spin $I = 1/2$, and ^{14}N with $I = 1$), with $J_{N-F} = 112.5$ Hz. The observation of N–F coupling of this order of magnitude proves the presence of a direct N–F bond [116]. The microwave spectrum of NO_2F [134] points to a planar molecule of point group C_{2v}; the pertinent bond parameters are listed in Table 2. The structure of NO_2F in terms of C_{2v} symmetry has been confirmed by a study of its vibrational

Table 2. Physical properties of nitryl fluoride.

Melting Point (°C)	-166.0 ± 0.5	[2, 115, 131]
	≈ -160	[114]
Boiling Point (°C)	-72.4 ± 0.2	[2, 115, 131]
	−70 to −65	[109]
	−73 to −72	[5, 114]
	−70	[105]
Heat of Vaporization (kcal·mole^{-1})	4.32	[2]
Trouton Constant	21.5	[2]
Liquid density (d_l)	$2.143 - 0.00323 \times T$	[2]
	1.571 [a]	[115, 131]
Solid density (d_s)	1.92	[2]
IR Absorption (cm^{-1})	1312 (ν_1); 822 (ν_2); 460 (ν_3); 1793 (ν_4); 570 (ν_5); 742 (ν_6)	[132]
	1309.6 (ν_1); 822.4 (ν_2); 567.8 (ν_3); 1791.5 (ν_4); 559.6 (ν_5); 742.0 (ν_6)	[133]
Force Constants		[49, 133, 135]
Dipole Moment (D)	0.47	[134]
Bond distances (Å)	N–O 1.23, N–F 1.35	[134]
Bond angles (°)	O–N–O 125; O–N–F 117.5	[134]
ΔH^0_{298} (kcal·mole^{-1})	-19 ± 2	[136, 137]
	−25.8	[115, 138]
Dissociation energy (kcal·mole^{-1})		
$O_2NF \rightarrow NO_2 + F$	46.0	[137]
	52.67	[133]
$O_2NF \rightarrow ONF + O$	62.8	[137]
	69.66	[133]
Thermodynamic data		[133, 137, 139]

[a] At −101 °C.

spectra (IR: vapor, solid; Raman: liquid) [132, 133]. The same structural features apply as for O_2NOH and O_2NCl [140, 141], both of proven planar C_{2v} configuration. The most recent IR study of NO_2F [133] also contains data for the isotopic species, $^{15}NO_2F$, and the results are compared to those obtained for $^{14}NO_2Cl$ and $^{15}NO_2Cl$.

Thermodynamic functions and force constants have been reported [133] (cf. also [140, 141]), which considerably revise earlier calculations [49, 139, 142–144]. The most recent value for the N–F bond dissociation energy in NO_2F, 52.67 kcal/mole [133] is of the same

[119] *A. W. Yodis*, Belg. Pat. 611546 (Dec. 14, 1961), Allied Chem. Corp.

[120] *F. Seel* and *H. Semmler*, Chimia *16*, 290 (1962).

[121] *A. W. Yodis*, French Pat. 1310893 (Oct. 22, 1962), Allied Chem. Corp.

[122] *A. W. Yodis*, Can. Pat. 686335 (May 12, 1964), Allied Chem. Corp.

[123] *A. W. Yodis*, US-Pat. 3185542 (May 25, 1965), Allied Chem. Corp.).

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[139] *P. G. Puranik* and *E. V. Rao*, Indian J. Physics *35*, 177 (1961).

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[144] *P. G. Puranik* and *E. V. Rao*, Current Sci. (Bangalore) *34*, 559 (1965).

order of magnitude as that for NOF, 55.4 kcal/mole[8]. Likewise, the N–O bond strengths in the two nitryl halides, NO_2F and NO_2Cl, are comparable (69.66 *vs.* 68.79 kcal/mole, respectively[133]).

2.3. Chemical Properties

The chemical characteristics of NO_2F are similar to those of NOF. Because of its high reactivity, NO_2F is best handled in apparatus made from quartz or nickel alloys.

As the fluoride of nitric acid, NO_2F is hydrolyzed quantitatively by 10 % NaOH[2].

$$O_2NF + 2\,OH^- \rightarrow F^- + NO_3^- + H_2O$$

The reactions of NO_2F with numerous elements were first studied qualitatively by *Ruff*[2] and, in much more detail, by *Aynsley*, *Hetherington*, and *Robinson*[114]. Like NOF, NO_2F may act both as a powerful oxidizing agent and as a fluorinating agent. Interaction of NO_2F with metals leads to the formation of either a mixture of oxide and fluoride, or of an oxyfluoride[114], *e.g.*,

$$2\,Zn + 2\,O_2NF \rightarrow ZnF_2 + ZnO + N_2O_3$$

$$Cr + 2\,O_2NF \rightarrow CrO_2F_2 + 2\,NO$$

A few metals, such as Be, Mg, Ca, Au do not react with NO_2F at temperatures up to 300 °C[115].

In the case of nonmetallic elements, formation of the nitryl salts of the corresponding fluoroanion is frequently observed. Presumably, the fluoride of the element is formed first and then reacts with NO_2F as a fluoride donor[114] (cf. Section B.3.).

As an acid fluoride, NO_2F will react with various oxides[114,115] thus

$$O_2NF + SO_3 \rightarrow [NO_2][SO_3F]$$

NO_2F behaves as an acid fluoride in the expected fashion towards ammonia or secondary amines[145]; nitramides are formed, both in the gas phase and in an inert solvent.

$$O_2NF + NH_3 \rightarrow O_2NNH_2$$

$$O_2NF + HNR_2 \rightarrow O_2NNR_2$$

A reaction has been observed between NO_2F and $BrO_2[NO_3]$ at −78 °C in CCl_3F[117].

$$O_2NF + BrO_2[NO_3] \rightarrow N_2O_5 + O_2BrF$$

The following reaction has also been observed to occur quantitatively[146],

$$O_2NF + Cl_2F[AsF_6]^- \rightarrow NO_2[AsF_6] + 2\,ClF.$$

[145] *H. C. Mandell*, US-Pat. 3071438 (Jan. 1, 1963), Pennsalt Chem. Corp.

[146] *K. O. Christe*, private communication.

O_2F_2 is very soluble in NO_2F but there is no reaction at −78 °C[31].

NO_2F reacts exothermally and irreversibly with sulfuric acid, with formation of a clear colorless liquid. At concentrations >70 mole-%, colorless crystals, believed to be $NO_2[HSO_4]$, are precipitated[147]. On the basis of electrical conductivity, density, viscosity, cryoscopic, and Raman-spectroscopic data[115,147], the following two steps are proposed for this reaction:

$$O_2NF + H_2SO_4 \rightarrow NO_2^+ + HF + HSO_4^-$$

$$HF + 2\,H_2SO_4 \rightleftharpoons H_3O^+ + HSO_3F + HSO_4^-$$

Selenic acid also absorbs NO_2F (>2 mole/mole acid), as does H_3PO_4; however, the reactions involved have not been investigated completely[115,147].

Reactions of NO_2F with a number of organic compounds have been studied. Aromatic hydrocarbons, for example, undergo fairly smooth nitration. Deactivated aromatic compounds such as $C_6H_5NO_2$, C_6H_5COOH, C_6H_5CHO remain largely unchanged, whereas highly reactive compounds, *e.g.* aniline, anisole, furan, *etc.*, give only tars. Ethanol reacts with formation of $C_2H_5ONO_2$, CH_3CHO, CH_3COOH[115,148].

Nitryl fluoride is much more powerful a nitrating agent than NO_2Cl and is of interest in mechanistic studies[149,150]. Nitration reactions involving NO_2F are strongly promoted by the addition of Lewis acid catalysts, *e.g.* BF_3, PF_5, AsF_5, SbF_5, all of which facilitate the heterolytic reaction

$$O_2NF + MF_n \rightarrow [NO_2]^+[MF_{n+1}]^-$$

by generating $[NO_2]^+$ ion. Reaction media employed include sulfolane and *sym*-difluorotetrachloroethane[149–151]. Nitration of benzotrifluoride with NO_2F at −100 °C leads to the formation of a 1:1:1 complex of NO_2F, $C_6H_5CF_3$, and BF_3, which decomposes at −50 °C without melting and with evolution of BF_3[149,151]. (For an account of the interaction of NO_2F with Lewis acids see Section B.3.)

Considerable attention has been given to the study of addition reactions of NO_2F across multiple bonds; these will be discussed, along with analogous reactions of NOF, in Section B.4.

2.4. The Nitryl Fluoride–Hydrogen Fluoride System

A compound having the composition $NO_2F \cdot 5\,HF$ (m.p. < −78 °C; b.p. ~ 62 °C) was found to be formed upon reaction of nitryl chloride with hydrogen

[147] *G. Hetherington*, *D. R. Hub*, and *P. L. Robinson*, J. chem. Soc. (London) *1955*, 4041.

[148] *G. Hetherington* and *P. L. Robinson*, J. chem. Soc. (London) *1954*, 3512.

[149] *G. Olah*, *L. Noszko*, and *A. Pavlath*, Nature (London) *179*, 146 (1957).

[150] *S. J. Kuhn* and *G. A. Olah*, J. Amer. chem. Soc. *83*, 4564 (1961).

[151] *G. A. Olah* and *S. J. Kuhn*, J. Amer. chem. Soc. *80*, 6541 (1958).

fluoride (molar ratio *ca.* 1:5 to 1:6; at −17 °C in the liquid phase, or at 30–100 °C in the gas phase) [119–123].

$$NO_2Cl + 6\,HF \rightarrow NO_2F{\cdot}5\,HF + HCl$$

Pure $NO_2F{\cdot}5$ HF does not conduct electricity; the electric conductivity observed in the presence of moisture is ascribed to formation of $[NO_3H_2]^+[F(HF)_n]^-$ [120].

Chemically, $NO_2F{\cdot}5$ HF behaves as a mixture of its constituents, the simplest type of reaction being with the Lewis acid SbF_5 or with the Lewis base, F^- [120].

$$NO_2F{\cdot}5\,HF + SbF_5 \rightarrow NO_2[SbF_6]$$

$$NO_2F{\cdot}5\,HF + F^- \rightarrow NO_2F + [F(HF)_n]^-$$

Like $NOF{\cdot}3$ HF, $NO_2F{\cdot}5$ HF is a powerful fluorinating and oxidizing agent, its reactions often being more complicated than those of the former because of secondary transformations, such as $2\,NO_2 + 4\,HF \rightarrow NOF{\cdot}3\,HF + HNO_3$, or NO_2Cl (formed as a product) $\rightarrow NO_2 + {}^1/_2\,Cl_2$, *etc.* [120].

Worthy of particular mention is the reaction of $NO_2F{\cdot}5$ HF with gold(I) iodide which affords elemental gold (while $NOF{\cdot}3$ HF does not react with AuI). The following overall reaction is envisaged [120],

$$5\,NO_2F{\cdot}5\,HF + AuI \rightarrow Au + IF_5 + 5\,NO_2 + 25\,HF$$

In summary, the system NO_2F/HF has not been studied extensively, and further work is clearly indicated.

3. Reactions of NOF and NO_2F with Acceptor Fluorides

NOF and NO_2F interact in a characteristic manner with a great variety of acceptor (Lewis acid) fluorides, the majority of these reactions involving the heterolytic cleavage of the N–F bond and formation of the corresponding fluoro anion,

$$O_nNF + XF_m \rightarrow [O_nNF{\cdot}XF_m] \rightarrow [NO_n]^+[XF_{m+1}]^-$$

The reactions take place under mild conditions, often at dry ice temperature. The interaction with acceptor fluorides, such as BF_3, PF_5, AsF_5 is also responsible for the increase in conductivity of liquid NOF or NO_2F when these fluorides are present [58, 152]. Nitrosyl and nitryl salts are formed upon interaction of NOCl or NO_2Cl, respectively, with acceptor fluorides and hydrogen fluoride in polar media such as liquid sulfur dioxide or nitroalkanes [153]

$$O_nNCl + XF_m + HF \rightarrow NO_n[XF_{m+1}] + HCl$$

The reaction probably proceeds *via* the NOF- or NO_2–HF complex.

In some instances, nitric oxide has been found to react with strongly oxidizing fluorides with formation of the corresponding nitrosyl fluoro salts as the ultimate products, and it seems reasonable to assume that NOF occurs as an intermediate and that *e.g.* the reaction:

$$3\,NO + 4\,BrF_3 \rightarrow 3\,NO[BrF_4] + {}^1/_2Br_2$$

takes place in two steps [154],

$$3\,NO + BrF_3 \rightarrow 3\,NOF + {}^1/_2Br_2$$

$$3\,ONF + 3\,BrF_3 \rightarrow 3\,NO[BrF_4].$$

Further, the reactions

$$NO + TcF_6 \rightarrow NO[TcF_6]\ [57]\ \text{and}$$

$$NO + UF_6 \rightarrow NO[UF_6]\ [155]$$

may well proceed *via* formation of NOF which then reacts with the pentafluoride, TcF_5 or UF_5. Similar considerations probably apply to the well-investigated reactions of NO with WF_6, ReF_6, OsF_6, IrF_6, and PtF_6; in all reactions except that of NO with WF_6, nitrosyl salts of the various fluoro acids are obtained [156]. An interesting trend in the reactivity of the same hexafluoride series towards NOF has also been observed [156]. A regular increase in the oxidizing power of these fluorides is reflected in the observation that for WF_6 and ReF_6 the sole products formed are the adducts (1:1 and 1:2 for WF_6, 1:2 for ReF_6) while in the case of OsF_6 a trace of ONF_3 (see Section B.5.) is obtained. IrF_6 gives $NO[IrF_6]$, besides F_3NO and F_2, while $NO[PtF_6]$ and F_2 result from PtF_6 + NOF. $[PtF_7]^-$ is not formed, even in the presence of an excess of fluorine [156, 157].

In the case of NO_2F, a mode of reaction with oxides is known in which the ultimate product is the nitryl salt of a fluoro acid [114, 115], undoubtedly as a result of Lewis acid-base interaction between NO_2F and an intermediate acceptor fluoride. The following example is typical:

$$V_2O_5 \xrightarrow{NO_2F} VOF_3$$

$$VOF_3 \xrightarrow{NO_2F} NO_2[VOF_4]$$

The role of NOF as an intermediate which subsequently acts either as a fluoride ion donor or as an oxidizing agent, is also evident in numerous reactions of NF_3 [65], as illustrated in the following example,

$$B_2O_3 + 3\,NF_3 \rightarrow 2\,BF_3 + 3\,NOF$$

$$B_2O_3 + 6\,NOF \rightarrow 2\,BF_3 + 3\,NO + 3\,NO_2$$

$$BF_3 + NOF \rightarrow NO[BF_4]$$

Likewise, $(NO)_2[SiF_6]$, $NO[PF_6]$, and $(NO)_2[S_2O_5F_4]$ are the ultimate products of the reaction of NOF with SiO_2, P_2O_5, and SO_3, respectively [65].

[152] *M. S. Toy* and *W. A. Cannon*, Abstr. 151st Meeting, Amer. chem. Soc. *1966*, H47.

[153] *S. J. Kuhn*, Canad. J. Chem. *45*, 3207 (1967).

[154] *P. Bouy*, Ann. Chimie *4*, 853 (1959).

[155] *J. R. Geichman*, *E. A. Smith*, *S. S. Trond*, and *P. R. Ogle*, Inorg. Chem. *1*, 661 (1962).

[156] *N. Bartlett*, *S. Beaton*, and *N. K. Iha*, Chem. Commun. *1966*, 168.

[157] *F. P. Gortsema* and *R. H. Toeniskoetter*, Inorg. Chem. *5*, 1217 (1966).

A further case in this connection is the light-induced reaction of POF_3 with N_2F_4, in which NOF is believed to occur as intermediate [158]

$$POF_3 + F^{\cdot} \longrightarrow F_4PO^{\cdot} \xrightarrow{{}^{\cdot}NF_2} F_4PONF_2$$

$$F_4P(O)(O)N(F)F \longrightarrow PF_5 + ONF \longrightarrow NO[PF_6]$$

NO_2 may react with an oxidizing fluoride such as UF_6 in an entirely analogous way to that of NO and thus give the nitryl salt of a complex fluoro acid; the occurrence of NO_2F as an intermediate is indicated by the observation that identical compounds are obtained from the two reactions, $UF_5 + NO_2F$ and $UF_6 + NO_2$ [159].

$$NO_2 + UF_6 \rightarrow [O_2NF + UF_5] \rightarrow NO_2[UF_6] \rightarrow O_2NF + UF_5$$

A fairly general method of preparation of the nitryl salts of non-metals (as fluoro anions) involves the reaction of the element with NO_2F, which almost certainly proceeds *via* the fluoride of the respective element [115], *e.g.*

$$B + 3\,O_2NF \rightarrow BF_3 + 3\,NO_2$$

$$BF_3 + O_2NF \rightarrow NO_2[BF_4]$$

Other elements behaving similarly include Si, Ge, P, As, Sb, Se, I_2, Te, *etc.* [115].

While NOF and NO_2F evidently often behave in an identical fashion towards Lewis acid acceptor molecules, a notable difference has been observed for $C_6H_5PF_4$ as the acceptor fluoride.

At temperatures as low as −78 °C, NOF forms a 1:1 adduct with $C_6H_5PF_4$ in a Freon ® medium. This adduct decomposes irreversibly at ~ 0 °C. Chemical evidence suggests it to be the expected nitrosyl salt, $NO[C_6H_5PF_5]$. In contrast to NOF, NO_2F will attack the aromatic ring of $C_6H_5PF_4$ at −30 °C (in Freon ®) to give a nitrophenyltetrafluorophosphorane which upon hydrolysis gives *p*-nitrophenylphosphonic acid; this is contrary to the expectation that the PF_4 group should be *meta*-directing [160],

$$ONF + C_6H_5PF_4 \rightarrow [NO][C_6H_5PF_5]$$

$$O_2NF + C_6H_5PF_4 \xrightarrow{-HF} O_2NC_6H_4PF_4 \xrightarrow{H_2O} p\text{-}O_2NC_6H_4P(O)(OH)_2$$

The known reactions between NOF or NO_2F and acceptor fluorides are summarized in Tables 3 and 4.

The great majority of the NO_nF-acceptor fluoride adducts are stable salts at room temperature and contain the $[NO]^+$ or $[NO_2]^+$ cation; however, the possibility of the existence of molecular complexes, $NO_nF{\cdot}XF_m$, must be considered in some instances.

Table 3. Reactions of nitrosyl fluoride with acceptor fluorides.

Fluoride	Product	Ref.
BF_3	$NO[BF_4]$	[11]
$C_6H_5PF_4$	$NO[C_6H_5PF_5]$	[160]
$S_2O_5F_2$	$(NO)_2[S_2O_5F_4]$	[65]
ClF_3	$NO[ClF_4]$	[161, 162]
	$(NOF{\cdot}ClF_3?)$	
ClF	$NO[ClF_2]$	[56]
VF_5	$NO[VF_6]$	[163]
GeF_4	$(NO)_2[GeF_6]$	[154]
AsF_3	$NO[AsF_6]$	[13]
BrF_3	$NO[BrF_4]$	[154, 164]
MoF_5	$NO[MoF_6]$	[155]
MoF_6	$NO[MoF_7] + NOF{\cdot}MoF_6$	[159, 165 166]
TcF_6	$(NO)_2[TcF_8]$	[57]
SbF_5	$NO[SbF_6]$	[13]
IF_5	$NO[IF_6]$	[14]
XeF_6	$(NO)_2[XeF_8]$	[167]
$XeOF_4$	$NOF{\cdot}XeOF_4$	[167]
WF_6	$NO[WF_7] + NOF{\cdot}WF_6$	[159, 165, 166]
	$(NO)_2[WF_8]$	[57, 156]
ReF_6	$(NO)_2[ReF_8]$	[57, 156]
OsF_6	$(NO)_2[OsF_8]$ [a]	[57]
	$NO[OsF_6] + NO[OsF_7]$ [b]	[156]
PtF_6	$NO[PtF_6]$ [c]	[156, 157, 168]
	$(NO)_2[PtF_6] + F_2$ [d]	[57]
UF_5	$NO[UF_6]$ [e]	[155]
UF_6	$NO[UF_7]$	[159, 165, 166, 169]

[a] Adduct loses NOF on pumping at −30 °C and $NO[OsF_7]$ is formed; [b] Traces of ONF_3 were also found; [c] From $ONF + PtF_6 \rightarrow NO[PtF_6] + {}^1/_2\,F_2$; [d] with large excess of NOF; [e] Same product obtained from $UF_6 + NO$.

Table 4. Reactions of nitryl fluoride with acceptor fluorides.

Fluoride	Product	Ref.
BF_3	$NO_2[BF_4]$	[114, 170]
PF_5	$NO_2[PF_6]$	[114, 170]
ClF_3	[a]	[161]
VF_5	$NO_2[VF_6]$	[163]
GeF_4	$(NO_2)_2[GeF_6]$	[114]
AsF_5	$NO_2[AsF_6]$	[114]
SeF_4	$NO_2[SeF_5]$	[114]
BrF_3	$NO_2[BrF_4]$	[114]
BrF_5	[a]	[161]
MoF_6	$NO_2[MoF_7] + NO_2F{\cdot}MoF_6$	[159, 166]
SbF_5	$NO_2[SbF_6]$	[114, 170]
IF_5	$NO_2[IF_6]$	[114]
WF_6	$NO_2[WF_7] + NO_2F{\cdot}WF_6$	[159, 166]
UF_5	$NO_2[UF_6]$	[159]
UF_6	$NO_2[UF_7] + NO_2F{\cdot}UF_6$	[159, 166, 169]

[a] No reaction.

4. Addition of NOF and NO_2F across Double Bonds

Nitrosyl fluoride and nitryl fluoride add across the double bond of fluoroolefins, alkyl perfluorovinyl ethers, fluoroketones, and fluoroketenes; addition to

[158] *M. Lustig, C. L. Bumgardner,* and *J. K. Ruff,* Inorg. Chem. *3,* 917 (1964).

[159] *J. R. Geichman, L. R. Swaney,* and *P. R. Ogle,* US Atomic Energy Commission Rep. GAT-T-971 (1962).

[160] *R. Schmutzler* and *G. S. Reddy,* Inorg. Chem. *4,* 191 (1965).

[161] *E. D. Whitney, R. O. MacLaren, T. J. Hurley,* and *C. E. Fogle,* J. Amer. Chem. Soc. *86,* 4340 (1964).

[162] *J. W. Dale,* US-Pat. 3167908 (Febr. 2, 1965), Monsanto Co.

[163] *H. C. Clark* and *H. J. Emeléus,* J. chem. Soc. (London) *1958,* 190.

[164] *A. Chretien* and *P. Bouy,* C. R. hebd. Séances Acad. Sci. *246,* 2493 (1958).

[165] *J. R. Geichman, P. R. Ogle,* and *L. R. Swaney,* US Atomic Energy Commission Rep. GAT-T-809 (1961).

[166] *J. R. Geichman, E. A. Smith,* and *P. R. Ogle,* Inorg. Chem. *2,* 1012 (1963).

[167] *G. J. Moody* and *H. Selig,* Inorg. nuclear Chem. Letters *2,* 319 (1966).

[168] *N. Bartlett* and *S. Beaton,* Chem. Commun. *1966,* 167.

[169] *P. R. Ogle,* US-Pat. 3039846 (June 19, 1962), US Atomic Energy Commission.

[170] *D. Cook, S. J. Kuhn,* and *G. A. Olah,* J. chem. Physics *33,* 1669 (1960).

a C=N bond (in $CF_3-N=CF_2$) is also known [171]. NOF and NO_2F are usually employed as such; however, NOF, for example, may also be generated *in situ* by treating a fluoroolefin with a mixture of N_2O_4 ($\approx NO[NO_3]$) and KF in sulfolane [172].

4.1. Fluoroolefins and Alkoxyfluoroolefins

Addition of NOF to fluoroolefins with formation of the corresponding perfluoronitroso compound *e.g.*,

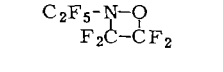
$$CF_3-CF=CF_2 + ONF \rightarrow CF_3-CF(NO)-CF_3$$

has been observed in a number of cases (cf. Table 5), yields and reaction conditions being very variable. Sometimes the perfluoronitroso compound occurs as by-product only, and there are numerous side reactions as a result of oxidation, fluorination, and nitration of the fluoroolefin; this is particularly true for the simplest fluoroolefin, $CF_2=CF_2$.

Table 5. Addition of nitrosyl fluoride to fluoroolefins.

Fluoroolefin	Product	Ref.
$CF_2=CF_2$	CF_3CF_2NO	[174]
$CF_2=CFCl$	$CF_3CF(NO)Cl$	[172, 176]
$CF_3CF=CF_2$	$CF_3CF(NO)CF_3$	[171–173, 175]
$(CF_3)_2C=CF_2$	$(CF_3)_3CNO$	[171, 173]
F_2C-CF F_2C-CF	$F_2C-CF(NO)$ F_2C-CF_2	[172, 175]
Cf. $CF_3N=CF_2 + ONF \rightarrow$	$(CF_3)_2NNO$	[171]
$CF_3N=CF_2 + O_2NF \rightarrow$	$(CF_3)_2NNO_2$	[171]

In the first study of the C_2F_4/NOF reaction (in a glass tube at −78 or −100 °C), *Barr* and *Haszeldine* [174] observed a multitude of products, C_2F_5NO being only a minor by-product (1%). The main products at −100 °C were O_2NCF_2CFO (17%), *N*-perfluoroethyltetrafluorooxazetidine



(13%), $(CF_2NO_2)_2$ (7%), and $C_2F_5NO_2$ (1%). A small amount of polymer, $[-N(C_2F_5)-O-CF_2CF_2-]_n$, was also formed.

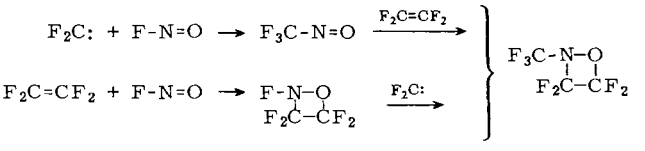
The formation of these products was rationalized on the assumption of C_2F_5NO being the primary product; however, the possibility must be considered that, as a result of attack of NOF on glass, nitrogen oxides were present which could also give rise to products such as $(CF_2NO_2)_2$ and O_2NCF_2CFO [171].

N-pentafluoroethyltetrafluorooxazetidine was also found as a major product in *Knunyants'* independent study [173], under rather different conditions, which involved heating the C_2F_4/NOF mixture over activated carbon/$CaSO_4$ at 70–80 °C for 10 hours. Upon aqueous workup, by-products such as O_2NCF_2COOH and C_2F_6 were detected. *Andreades* [171, 177] obtained *N*-pentafluoroethyltetrafluorooxazetidine in 55% yield by heating C_2F_4 and NOF (molar ratio 2:1) at 100 °C in an autoclave. It was concluded that the initial addition of NOF to C_2F_4 is rate-determining since no more than trace amounts of C_2F_5NO can be isolated. Also, it is known that the addition of the primary C_2F_5NO to C_2F_4 occurs rapidly at low temperatures in the absence of light.

A major by-product in the 100 °C reaction was perfluorocyclobutane; small amounts of polymerization products of the type already mentioned were also formed [171, 177].

The main products of the reaction at 200 °C were COF_2 and $CF_2NC_2F_5$, the latter presumably originating from the initial rupture of the N–O bond of the oxazetidine [171, 177].

Evidence for the insertion of CF_2 (originating from C_2F_4) into an N–F bond has been obtained in a study of the reaction of C_2F_4 with NOF under UV irradiation [178]. One of the products was found to be *N*-trifluoromethyltetrafluorooxazetidine which may be formed in either of two ways:

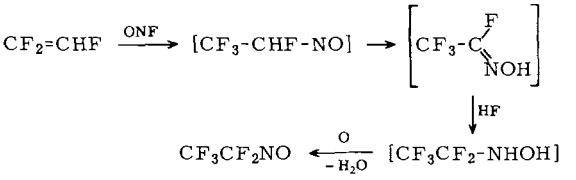


Hexafluoropropane was also observed. Neither the oxazetidine nor C_3F_6 are formed in the absence of UV irradiation [178].

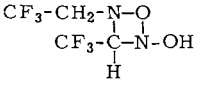
When NOF and higher fluoroolefins or chlorofluoroolefins are heated under pressure at 120 °C for long periods the major product is usually a perhalogenated derivative of 1-oxa-2-azacyclohexane [171, 177]. The positions of the substituent groups in these compounds have not yet been established [177].

When the reaction of NOF with $CF_3CF=CF_2$ is carried out at 200 atm, $(CF_3)_2CFONO$, $(CF_3)_2CO$, and $(CF_3)_2C=NCF(CF_3)_2$ are the main products formed [171].

The reaction of a hydrogen-containing olefin, *e.g.* trifluoroethylene, with NOF [173] takes a different course, the final product being C_2F_5NO. This may be accounted for by the following sequence,



The reaction between vinylidene fluoride and NOF [173] is still more complex, and a product of b.p. 80 °C, believed to have the following structure, has been isolated.



Both $CF_2=CClF$ and $CF_2=CH_2$ react explosively with NOF, and the reaction must therefore be conducted in an inert solvent.

The addition of NOF and NO_2F to alkyl perfluorovinyl ethers in the absence of catalysts proceeds smoothly and with high yields [176, 179, 180] (cf. Table 6).

[171] *S. Andreades*, J. org. Chemistry *27*, 4163 (1962).

[172] *B. L. Dyatkin, E. P. Mochalina, R. A. Bekker, S. R. Sterlin,* and *I. L. Knunyants*, Tetrahedron *23*, 4291 (1967).

[173] *I. L. Knunyants, E. G. Bykhovskaya, V. N. Frosin, Ya. M. Kisel*, Doklady Akad. Nauk SSSR *132*, 123 (1960).

[174] *D. A. Barr* and *R. N. Haszeldine*, J. chem. Soc. (London) *1960*, 1151.

[175] *B. L. Dyatkin, E. P. Mochalina, R. A. Bekker*, and *I. L. Knunyants*, Izvest. Akad. Nauk SSSR, Ser. chim. *1966*, 585.

[176] *B. L. Dyatkin, E. P. Mochalina, R. A. Bekker, S. R. Sterlin,* and *I. L. Knunyants*, Ž. vses. chim. Obšč. im D. I. Mendeleeva *11*, 598 (1966).

[177] *S. Andreades*, US-Pat. 3248394 (April 26, 1966), duPont.

[178] *S. Andreades*, Chem. and Ind. *1962*, 782.

[179] *B. L. Dyatkin, R. A. Bekker, Yu. S. Konstantinov*, and *I. L. Knunyants*, Doklady Akad. Nauk SSSR *165*, 1305 (1965).

[180] *B. L. Dyatkin, R. A. Bekker*, and *I. L. Knunyants*, Doklady Akad. Nauk SSSR *168*, 1319 (1966).

Table 6. Addition of nitrosyl fluoride and nitryl fluoride to alkoxyfluoroolefins.

Alkoxyfluoroolefin	Product with ONF	Ref.	Product with O_2NF	Ref.
$CF_2=CFOCH_3$	$CF_2(NO)CF_2OCH_3$	[179]	$CF_2(NO_2)CF_2OCH_3$	[180]
$CF_2=CFOC_2H_5$	$CF_2(NO)CF_2OC_2H_5$	[179]	$CF_2(NO_2)CF_2OC_2H_5$	[180]
$CF_3CF=CFOCH_3$	$CF_3CF(NO)CF_2OCH_3$	[179, 181]	$CF_3CF(NO_2)CF_2OCH_3$	[180]
$CF_3CF=CFOC_2H_5$	$CF_3CF(NO)CF_2OC_2H_5$	[179]	$CF_3CF(NO_2)CF_2OC_2H_5$	[180]
$(CF_3)_2C=CFOC_2H_5$	$(CF_3)_2C(NO)CF_2OC_2H_5$	[179]	$(CF_3)_2C(NO_2)CF_2OC_2H_5$	[180]
$CFCl=CF_2OCH_3$			$CF(NO_2)ClCF_2OCH_3$	[180]
$CFCl=CF_2OC_2H_5$			$CF(NO_2)ClCF_2OC_2H_5$	[180]

As was suggested by *Knunyants* [182], observations on the addition of NOF and NO_2F to various other derivatives of fluoroolefins provides an insight into the mechanism of this reaction. An inversion of reaction mechanism from electrophilic to nucleophilic is observed as the electron-accepting properties of the double bond increase. Thus, addition of NOF to fluoro derivatives of ethylene (including perfluorovinyl ethers) proceeds by an electrophilic mechanism and, accordingly, is catalyzed by Lewis acids, such as BF_3 in a sulfolane medium [172, 175, 176]. Starting with perfluoropropene, the reaction mechanism becomes nucleophilic and is catalyzed by fluoride ion.

$$CF_3\text{-}\overset{\delta-}{C}F=\overset{\delta+}{C}F_2 \xrightarrow{F^-} [CF_3\text{-}\overset{\ominus}{C}F\text{-}CF_3] \xrightarrow[-F^-]{ONF} (CF_3)_2CFNO$$

A similar inversion of reaction mechanism is known to occur in other reactions of fluoroolefins and their derivatives, *e.g.* in halogenation, hydrohalogenation, acylation, *etc.* [182].

The addition of nitrosyl fluoride and nitryl fluoride to difluoromethylenetrifluoromethylamine (cf. Table 5) proceeds rapidly and quantitatively at low temperature, presumably by a nucleophilic mechanism *via* the resonance-stabilized anion, $CF_3-\overset{\ominus}{N}-CF_3$ [171].

4.2. Fluoroketones and -ketenes

A few reactions of this type are listed in Table 7. At low temperature, the equilibrium

$$\text{>}C=O + ONF \rightleftharpoons F-\overset{|}{C}-ONO$$

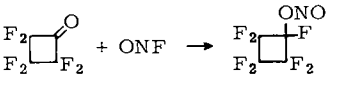
is rapidly established, the stability of the α-fluoronitrite thus formed depending markedly upon the nature of the substituents and upon the temperature [12, 183]. $(C_3F_7)_2C=O$, for example, at 0 °C absorbs an equimolar amount of NOF; the mixture shows the characteristic nitrite absorption band in the IR spectrum. At 20 °C, however, the mixture reverts to the starting compounds [12, 183]. Likewise, the compounds $(ClCF_2)_2C(F)ONO$ and $(ClCF_2)_2C(F)ONO_2$ revert to $(ClCF_2)_2C=O$ and NOF or NO_2F, respectively, on warming to room temperature [183].

The most stable fluoronitrite thus prepared is heptafluorocyclobutyl nitrite.

Table 7. Addition of nitrosyl fluoride and nitryl fluoride to fluoroketones and -ketenes.

Reaction	Product	Ref.
$(CF_3)_2C=O + ONF$	$(CF_3)_2CF(ONO)$	[12]
$CF_3(CF_2NO_2)C=O + ONF$	$CF_3CF(ONO)CF_2NO_2$	[186]
$(ClCF_2)_2C=O + ONF$	$(ClCF_2)_2CF(ONO)$	[183]
$F_2C(-CF_2)C=O + ONF$	$F_2C(-CF_2)CF(ONO)$	[12, 183]
$F_2C(-CF_2)C=O + O_2NF$	$F_2C(-CF_2)CF(ONO_2)$	[12, 183]
$(CF_3)_2C=C=O + ONF$	$(CF_3)_2C(NO)CFO$ [a]	[184]

[a] Also obtained by the addition of NOF to $CF_2=C(CF_3)CFO$ [185].



Perfluorocyclobutanone also reacts readily at low temperature with NO_2F to give heptafluorocyclobutyl nitrate, the first example of a fluoroalkyl nitrate. The NOF and NO_2F addition products of fluoroketones not only decompose readily into their components but also undergo a variety of secondary reactions, such as thermal ring opening in the case of heptafluorocyclobutyl nitrite and nitrate. The ring-opening products are 4-nitroso- or 4-nitrohexafluorobutyryl fluoride which can be made directly if the reaction between perfluorocyclobutanone and NOF or NO_2F is conducted at 100 °C, instead of at or below room temperature [183].

5. Trifluoroamine Oxide, F_3NO

Trifluoroamine oxide is the most recently discovered compound containing the O–N–F grouping. It was first disclosed in 1966/67 by several independent research groups, its synthesis having been achieved by a number of approaches [187–192], most of which involve

[181] *B. L. Dyatkin, R. A. Bekker,* and *I. L. Knunyants,* Izvest. Akad. Nauk SSSR, Ser. chim. *1965,* 1121.

[182] *B. L. Dyatkin, E. P. Mochalina,* and *I. L. Knunyants,* Usp. chim. *35,* 979 (1966).

[183] *S. Andreades,* US-Pat. 3032400 (June 19, 1962), duPont.

[184] *N. Mukhamedaliev, Yu. A. Cheburkov,* and *I. L. Knunyants,* Izvest. Akad. Nauk SSSR, Ser. chim. *1965,* 1982.

[185] *Yu. A. Cheburkov, N. Mukhamedaliev,* and *I. L. Knunyants,* Doklady Akad. Nauk SSSR *165,* 127 (1965).

[186] *I. L. Knunyants, A. V. Fokin,* and *V. A. Komarov,* Izvest. Akad. Nauk SSSR Ser. chim. *1966,* 466.

[187] *N. Bartlett, J. Passmore,* and *E. J. Wells,* Chem. Commun. *1966,* 213.

[188] *W. B. Fox, J. S. MacKenzie, N. Vanderkooi, B. Sukornik, C. A. Wamser, J. R. Holmes, R. E. Eibeck,* and *B. B. Stewart,* J. Amer. chem. Soc. *88,* 2604 (1966).

[189] *W. B. Fox, J. S. Mackenzie,* and *R. K. Vitek,* Brit. Pat. 1054330 (Jan. 11, 1967), Allied Chem. Corp.

[190] *W. B. Fox, J. S. Mackenzie,* and *R. K. Vitek,* Brit. Pat. 1066679 (April 26, 1967), Allied Chem. Corp.

[191] *W. B. Fox, J. S. MacKenzie,* and *R. K. Vitek,* US-Pat. 3306834 (Febr. 28, 1967), Allied Chem. Corp.

[192] *W. Maya,* US-Pat. 3320147 (May 16, 1967), North American Aviation.

the oxidative fluorination of either NO or NOF (the latter being the initial reaction product between NO + F_2), *e.g.*

$$3\,NOF + 2\,IrF_6 \rightarrow 2\,[NO][IrF_6] + ONF_3$$

$$NF_3/O_2 \xrightarrow[-196\,^\circ C]{\text{electr. discharge}} ONF_3$$

$$2\,NO + 3\,F_2 \rightarrow 2\,ONF_3$$

$$ONF + F_2 \rightarrow ONF_3$$

$$N_2/F_2/O_2 \xrightarrow{\text{electr. discharge}} ONF_3$$

Pyrolysis of $(NO)_2[NiF_6]$ (prepared from NiF_2, F_2, and NOF) at 350 °C in an atmosphere of fluorine also gives rise to formation of ONF_3 [187]. Finally, according to as yet unpublished work by *Pilipovich et al.* (quoted in [193]) ONF_3 is obtained by the action of a mixture of ClF_3/ClO_2 on HNF_2.

In comparison with the starting materials required for its synthesis, ONF_3 is chemically very inert and somewhat similar to carbon tetrafluoride, CF_4, with which it is isoelectronic. ONF_3 is stable towards glass and many metals at room temperature and its reaction with water is only very slow. When heated in nickel or Monel® vessels, ONF_3 is thermally stable up to 300 °C [188, 192]. It is a strong oxidizing agent towards various organic and inorganic materials [188].

The structure of ONF_3 could be established quite readily from its IR [187, 188, 193] and ^{19}F–NMR spectra (Table 8), both ruling out a hypofluorite, F_2NOF formulation. IR fundamentals have been assigned in terms of C_{3v} symmetry.

Table 8. Physical properties of trifluoroamine oxide.

M.p. (°C)	−161,5 ± 1,0	[192, 196]
	−160	[188]
B.p. (°C)	≈ −89	[192, 196]
	−85	[188]
^{19}F–NMR	1:1:1 Triplet, J_{NF} = 136 Hz, $\delta_F(CCl_3F)$ = −363 ± 2 ppm (liquid at −90 °C)	[188]
	1:1:1 Triplet, J_{NF} = 135.5 Hz, $\delta_F(CCl_3F)$ = −365.7 ± 0.2 ppm (solution in CCl_3F at −82 °C)	[187]
IR		[187, 188, 193]
Thermodynamic Data		[193]

Little is known, as yet, about the chemistry of ONF_3. Addition reactions with fluoroolefins lead to the formation of $RONF_2$ derivatives [188]. The radical, F_2NO is produced in the photolysis of ONF_3 (at −196 °C) and is identified by its ESR spectrum [188].

Trifluoroamine oxide reacts with acceptor fluorides, such as BF_3 [194, 195], AsF_5 [187, 188, 195], or SbF_5 [188, 195]. Formation of the $F_3NO{\cdot}BF_3$ adduct has been claimed as a means of purifying ONF_3, removing impurities such as N_2O, SiF_4, NO_2F, NOF, NF_3, *etc.* The $F_3NO{\cdot}BF_3$ adduct dissociates quantitatively into its components on warming to room temperature [194]. At −126 °C formation of a 2:1 adduct between BF_3 and F_3NO has been observed [195]. The thermal stability of these adducts decreases in the order $F_3NO{\cdot}SbF_5 > F_3NO{\cdot}AsF_5 > F_3NO{\cdot}BF_3 > F_3NO{\cdot}2\,BF_3$ [187, 188, 195]. Hydrolysis of $F_3NO{\cdot}AsF_5$ leads to formation of $[NO_2][AsF_6]$. According to IR and ^{19}F–NMR spectra the solid 1:1 adducts are ionic and contain the $[F_2NO]^+$ cation (point group C_{2v}) whose structure is similar to that of the isoelectronic COF_2 [195].

IR spectra of thin films of the complexes exhibit strong bands at 1857, 1162, and 905 cm^{-1} which are assigned to ν(NO), ν_s(NF), and ν_{as}(NF) [188] for the ion $[F_2NO]^+$; this is supported by ^{19}F–NMR spectra for the solution state, of $F_3NO{\cdot}AsF_5$ and $F_3NO{\cdot}SbF_5$ (HF solvent). The compounds are apparently ionic and have the formulation $[F_2NO]^+[MF_6]$; in both cases, a 4:5:4 triplet N–F resonance at −331 ± 3 ppm (from CCl_3F) with J_{N-F} = 250 Hz, as well as the high field resonance of $[AsF_6]^-$ (+60 ppm.) or $[SbF_6]^-$ (+135 ppm.), is observed [188].

A high-yield fluorination reaction for haloolefins under mild conditions is based on the following reaction of F_3NO-Lewis acid adducts,

$$F_3NO \cdot BF_3 + \rangle C{=}C\langle \rightarrow \underset{|}{\overset{|}{F\overset{|}{C}-\overset{|}{C}F}} + NO[BF_4]$$

6. Oxydifluoroamines (*N,N*-Difluorohydroxylamines), $RONF_2$

A few members of a new class of compounds, containing the oxydifluoroamine grouping, $-ONF_2$ have been reported in recent years. Tetrafluorohydrazine, F_2NNF_2 or, sometimes, NF_3, CF_3NF_2, and $SO_2(F)NF_2$ served as a source of NF_2 radicals in their preparation. UV irradiation was required to initiate some of the reactions while others, *e.g.* $F_5SOF + N_2F_4 \rightarrow F_5SONF_2 + NF_3$, start immediately upon mixing the reactants. Since compounds such as F_5SOF, CF_3OF, CF_3OOCF_3, *etc.* may act as oxidative fluorinating agents towards N_2F_4, numerous by-products (NF_3, NO, SF_6, SO_2F_2, SOF_4, NO_2, COF_2, CF_4, *etc.*) are frequently formed, and an involved separation procedure, *e.g.* by VPC, may be required.

Fully characterized compounds containing the $-ONF_2$ grouping are listed in Table 9. A number of further compounds have been obtained by reaction of CF_3O radicals (generated by fission of CF_3OOCF_3) with N_2F_4; characterization of these compounds was by mass spectroscopy and IR only [199].

Mention has been made of the formation of $RONF_2$ by reaction of F_3NO with fluoroolefins [188], but no details are available, as yet.

The reaction of N_2F_4 with $(FSO_2)_2O_2$, which is homogeneous and proceeds without change in pres-

[193] *E. C. Curtis, D. Pilipovich*, and *W. H. Moberly*, J. chem. Physics *46*, 2904 (1967).

[194] *W. B. Fox, J. S. Mackenzie*, and *R. K. Vitek*, Brit. Pat. 1055190 (Jan. 18, 1967), Allied Chem. Corp.

[195] *K. O. Christe, W. Maya*, and *W. Sawodny*, to be published; *K. O. Christe*, private communication.

[196] *D. Pilipovich*, US-Pat. 3346652 (Oct. 10, 1967), North American Aviation.

[197] *M. Lustig* and *G. H. Cady*, Inorg. Chem. *2*, 388 (1963).

[198] *G. N. Sausen*, US-Pat. 3214465 (Oct. 26, 1965), duPont.

[199] *G. von Ellenrieder, E. Castellano*, and *H. J. Schumacher*, Z. physik. Chem. N.F. *57*, 19 (1968).

Table 9. Oxydifluoroamino compounds.

Compound	Preparation	Bp (°C)	Characterized by	Ref.
CF_3ONF_2	$CF_3OF + N_2F_4$/UV	-60 ± 1	^{19}F–NMR	[201]
	$CF_3OF + N_2F_4$/UV or $CF_3OSF_4NF_2$ + NaOH	−59.8	^{19}F–NMR	[204]
	$CF_3OOCF_3 + N_2F_4$/130 °C or UV	−53	IR (gas), ^{19}F–NMR	[198, 202]
$FC(O)ONF_2$	$FC(O)OOC(O)F + N_2F_4$	≈0	IR (gas), ^{19}F–NMR	[202]
FSO_2ONF_2	$(FSO_2)_2O_2 + N_2F_4$	-2.5 ± 0.5	m.p. = -128.5 ± 0.5 °C	[198, 203]
			IR (gas), ^{19}F–NMR	
	$SO_3 + N_2F_4/h\nu$ (2537 Å)			[158]
	$FSO_2OF + N_2F_4$			[198]
F_5SONF_2	$F_5SOF + N_2F_4$	−10.0	IR (gas), ^{19}F–NMR	[200]
	$F_5SOF + N_2F_4$/UV		Fp = -139 ± 1 °C	[201]
			IR (gas), ^{19}F–NMR	
$CF_3ON(F)CF_3$	$CF_3OOCF_3 + CF_3NF_2$	−25	IR (gas), ^{19}F–NMR	[198]
$(CF_3)_2NONF_2$	$(CF_3)_2NOH + NF_2Cl/CsF$	[a]	^{19}F–NMR	[205]

[a] Not determined, since product cannot be separated from accompanying $(CF_3)_2NO$.

sure, has been studied kinetically at temperatures between −15 and +15 °C. The following steps are proposed [199]:

$$(FSO_2)_2O_2 \rightarrow 2\ FSO_2O^{\bullet} \text{ (rate-determining)}$$

$$FSO_2O^{\bullet} + N_2F_4 \rightarrow FSO_2ONF_2 + {}^{\bullet}NF_2$$

$$N_2F_4 \rightleftharpoons 2\ {}^{\bullet}NF_2$$

FSO_2ONF_2 is also formed in the reaction of FSO_2OF with N_2F_4 by a similar radical mechanism [199].

Only a few reactions of oxydifluoroamines have been described as yet. Thus, the compound FSO_2ONF_2 undergoes an addition reaction which can be initiated thermally with fluoroolefins such as tetrafluoroethylene or hexafluoropropene [197].

$$F_2NOSO_2F + CF_2{=}CF_2 \rightarrow F_2NCF_2CF_2OSO_2F$$

$$F_2NOSO_2F + CF_3{-}CF{=}CF_2 \rightarrow CF_3CF(OSO_2F)CF_2NF_2 + CF_3CF(NF_2)CF_2OSO_2F$$

A few oxydifluoroamines react with both electrophilic and nucleophilic reagents [200] *e.g.*

$$F_2NOSF_5 + BF_3 \rightarrow SF_6 + NO[BF_4]$$

However, FSO_2ONF_2 does not react with BF_3.

A differentiation between F_5SONF_2 and FSO_2ONF_2 with regard to their reactivity towards nucleophiles is also evident: F_5SONF_2 is not attacked by Cl^- or F^- at 150 °C; however, FSO_2ONF_2 reacts with Cl^- (90 % yield).

$$F_2NOSO_2F + Cl^- \rightarrow FSO_3^- + F_2NCl$$

F^- reacts with FSO_2ONF_2 in a different fashion [200].

$$FSO_2ONF_2 + F^- \rightarrow FSO_2F + ONF$$

[200] *J. K. Ruff*, Inorg. Chem. *4*, 1788 (1965).

[201] *W. M. Hale* and *S. M. Williamson*, Inorg. Chem. *4*, 1342 (1965).

[202] *W. B. Fox*, *G. Franz*, and *L. R. Anderson*, Inorg. Chem. *7*, 382 (1968).

[203] *M. Lustig* and *G. H. Cady*, Inorg. Chem. *2*, 388 (1963).

[204] *J. M. Shreeve*, *L. C. Duncan*, and *G. H. Cady*, Inorg. Chem. *4*, 1516 (1965).

[205] *D. Babb* and *J. M. Shreeve*, unpublished work; *J. M. Shreeve*, private communication.

C. Nitryl Hypofluorite (Fluorine Nitrate), O_2NOF

Cady [206, 207] obtained O_2NOF in the reaction of dilute nitric acid with elemental fluorine. He noted that both concentrated and very dilute HNO_3 gave rise to explosions while the reaction proceeded fairly safely when 4 N HNO_3 was employed. Subsequently, other authors reported that it was safer to pass elemental fluorine at room temperature into conc. HNO_3 [208] or even into 100 % HNO_3 [209]; a detailed preparative procedure for NO_3F has been given by *Kwasnik* [210]. A further synthesis of NO_3F involves reaction of KNO_3 with fluorine [211, 212].

Varying amounts of NO_3F are produced in the reaction of OF_2 with NO_2 [130]. Finally, formation of NO_3F has been observed upon electrolysis of mixtures of HF with NO or N_2O, using nickel electrodes. NO_3F is formed at the anode at lower potentials while OF_2 is the predominant product at higher potentials [100, 213, 214].

Structure: Although the hypofluorite structure O_2NOF was proposed on the basis of chemical evidence, early parachor studies [208] led to the suggestion of a cyclic structure,

However, an electron diffraction study [215], reported at about the same time, gave the following structure and bonding parameters.

[206] *G. H. Cady*, J. Amer. chem. Soc. *56*, 2635 (1934).

[207] *G. H. Cady*, US-Pat. 2076364 (April 6, 1937).

[208] *D. G. Hill* and *L. A. Bigelow*, J. Amer. chem. Soc. *59*, 2127 (1937).

[209] *O. Ruff* and *W. Kwasnik*, Angew. Chem. *48*, 328 (1935).

[210] *W. Kwasnik* in *G. Brauer*: Handbuch der präparativen anorganischen Chemie, Vol. I, Verlag F. Enke, Stuttgart 1960, p. 181.

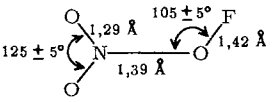
[211] *D. M. Yost* and *A. Beerbower*, J. Amer. chem. Soc. *57*, 782 (1935).

[212] *L. Viscido*, *J. E. Sicre*, and *H. J. Schumacher*, Z. physik. Chem. N.F. *32*, 182 (1962).

[213] *S. Evans*, *H. H. Rogers*, and *J. H. Johnson*, Rep. R-5077 (1963); Rocketdyne, Canoga Park, Calif.

[214] *H. H. Rogers*, *S. Evans*, and *J. H. Johnson*, J. electrochem. Soc. *111*, 701 (1964).

[215] *L. Pauling* and *L. O. Brockway*, J. Amer. chem. Soc. *59*, 13 (1937).



More recently, the IR spectrum of NO_3F has been analyzed and compared with that of NO_3Cl [216, 217] (see also [126]). Eight out of the expected 9 fundamentals could be observed. A planar structure of symmetry C_s (see above) is believed to be most likely, and the presence of an N–F bond can be ruled out with certainty on the basis of the spectroscopic evidence.

Physical and *chemical properties*: Various physical data pertinent to NO_3F are set out in Table 10.

Table 10. Physical properties of nitryl hypofluorite.

M.p. (°C)	-181 ± 0.2	[208]
	−175	[209, 210]
B.p. (°C/torr)	≈ −42	[206, 207, 211]
	−80 to −78/103	[208]
	−79/99	[209, 210]
	−45.9/760	[209, 210]
Heat of vaporization (kcal·mol^{-1})	4.726	[209, 210]
Trouton Constant (cal·deg^{-1}·mol^{-1})	20.8	[209, 210]
Critical Temperature (°C)	67.2	[209, 210]
d_{liquid}	$2.2148-0.003114 \times T$	
	1.507 [a]	[209, 210]
d_{solid}	1.951 [b]	[209, 210]
Thermodynamic data		[218]

[a] At the boiling point; [b] at −193.2 °C.

Fluorine nitrate is a toxic, colorless gas which is dangerously explosive in the gaseous, liquid, and solid state [206, 207, 209, 211]. NO_3F is a powerful oxidizer, and spontaneous explosions occur upon its contact with various organic compounds, such as ethanol, ether, aniline, *etc*; however, it does not attack dry glass. NO_3F is moderately soluble in water and on dissolution oxygen is evolved slowly; oxygen formation is more rapid in aqueous alkali [206, 207, 209].

$$O_2NOF + 2\,OH^- \rightarrow {}^1/_2\,O_2 + F^- + NO_3^- + H_2O$$

The following reaction takes place in aqueous solutions of iodide:

$$O_2NOF + 3\,I^- \rightarrow I_3^- + F^- + NO_3^-$$

NO_3F reacts with Ag^+ to form a black precipitate, formulated as "Ag_2O_3". In the presence of Ag^+, Mn^{2+} is oxidized to MnO_4^- [211].

Yellow solid addition compounds of unknown structure are formed on reaction of NO_3F with $TiCl_4$ or $SbCl_5$ [209].

In a recent study of the chemistry of NO_3F [219] it was found that the compound appears to add across the double bond of ethylene to give what is believed to be $FCH_2CH_2ONO_2$. The reaction of NO_3F with tetrafluoroethylene leads to the formation of COF_2 and CF_3NO_2; these products possibly originate from an unstable species $C_2F_5ONO_2$. A variety of products, including SF_6, NO_2F, SOF_2 NO_2, O_2, SiF_4, but not F_5SONO_2, are formed in the thermal or UV-initiated reactions of SF_4 with NO_3F. NF_3, NO_2, NO_2F, and NOF are obtained on reaction of NO_3F with N_2F_4 [219].

Considerable attention has been given to the study of the thermal decomposition of NO_3F which, as has been pointed out, forms the link between NO_3F and the simple oxyfluorides of nitrogen, NOF, and especially NO_2F. NO_3F decomposes into NO_2F and oxygen at temperatures between 80 and 130 °C, and at pressures varying between 0.6 and 400 torr [125–127]. The reaction is homogeneous and monomolecular; its rate varies with the addition of various foreign gases, such as Ar, N_2, O_2, CO_2, NO_2, OF_2, *etc.*

The primary process and rate-determining step during the thermal decomposition of NO_3F is believed to be the cleavage of the O–F bond [125–127, 130].

$$O_2NOF \rightarrow NO_3^\bullet + F^\bullet$$

The activation energy of this reaction which is a measure of the strength of the O–F bond in NO_3F, has been reported as 29.7 kcal/mole [125, 126] and 32.3 kcal/mole [127]. The subsequent, relatively fast steps are [125–127]

$$NO_3^\bullet + NO_3^\bullet \rightarrow 2\,NO_2 + O_2$$

$$NO_2 + F^\bullet \xrightarrow{M} O_2NF$$

In an earlier study of the kinetics of this reaction [220], the primary process was formulated as

$$O_2NOF \rightarrow NO_2 + {}^\bullet OF$$

followed by

$$O_2NOF + NO_2 \rightarrow O_2NF + NO_3^\bullet$$

$$NO_3^\bullet + {}^\bullet OF \rightarrow O_2NF + O_2$$

Further kinetic studies on the bimolecular reaction of NO_3F with NO_2 [221] have been carried out at temperatures between 80 and 100 °C.

$$NO_2 + O_2NOF \rightarrow O_2NF + NO_3^\bullet \text{ (rate-determining)}$$

$$NO_2 + NO_3 \rightleftharpoons N_2O_5 \rightarrow 2\,NO_2 + {}^1/_2\,O_2$$

The above study was conducted after the effect of added NO_2 upon the rate of the unimolecular decomposition of NO_3F had been observed [127]. For the same reason, the effect of added fluorine upon the decomposition of NO_3F was studied between 90 and 110 °C at partial pressures of 0.3–400 torr and 25–100 torr for fluorine and for NO_3F, respectively. Fluorine is believed to produce OF radicals which immediately react with further NO_3F [222].

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$$F_2 + O_2NOF \rightarrow NO_2F + F^\bullet + {}^\bullet OF$$

$$^\bullet OF + O_2NOF \rightarrow O_2NF + F^\bullet + O_2$$

$$F^\bullet + F^\bullet \xrightarrow{M} F_2$$

Addition of small quantities of F_2 (as little as 0.1 torr) was found to double the rate of decomposition of NO_3F.

Finally, the kinetics of the reaction between NO and NO_3F were investigated in the range −110 to +42 °C; the reaction is essentially second order and homogeneous, especially at high temperatures. The sole products are NOF and NO_2.

$$O_2NOF + NO \rightarrow ONF + NO_3^\bullet \text{ (rate-determining)}$$

$$NO_3^\bullet + NO \rightarrow 2\,NO_2 \rightleftharpoons N_2O_4$$

D. Uses of Oxide Fluorides of Nitrogen

Numerous examples illustrating the chemical significance of the oxyfluorides of nitrogen have already been discussed in the previous Sections. The role of these compounds as oxidizers in rocket propellants is of particular importance, and it is safe to assume that much relevant information is still classified. Attention has been focused on the potential of NOF, NO_2F[223,224] (and NO_3F[189,190]) in this field[223], since as far back as 1950.

Furthermore, it has been suggested that NOF might be used as a stabilizing agent for liquid SO_3 (in the α-form) against polymerization, small amounts of NOF (0.1–3 %) being sufficient[225]. NOF has also been claimed as a nitrosating agent for cycloaliphatic hydrocarbons in the presence of UV irradiation[226,227], but this has not been confirmed by other authors[4].

It has been reported that oxydifluoroamines, $RONF_2$, act as polymerization initiators, especially in the case of fluoroolefins[198].

Finally, it may be noted that one of the more curious uses proposed for NO_3F is as a war gas[228].

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COMMUNICATIONS

A Versatile Method for Preparation of *C*-Deuterated Compounds

By *K. Kühlein, W. P. Neumann,* and *H. Mohring* [*] [1]

Dedicated to Professor Fritz Kröhnke on the occasion of his 65th birthday

The possibilities for preparation of specifically deuterated compounds are limited[2]. Organotin deuterides have been used for deuteration of individual alkyl and cycloalkyl halides[3,4] and have been added to alkynes[5], but the need to use $LiAlD_4$[3] or R_2AlD[6] in their preparation has restricted their wider application.

We have now found a simple and prolific method of preparing organotin deuterides, namely, by preparing stannyl alkali compounds from distannanes by means of naphthalene sodium and treating the products with D_2O.

$$R_3SnNa + D_2O \rightarrow R_3Sn{-}D + NaOD$$

$$R_2SnNa_2 + 2\,D_2O \rightarrow R_2SnD_2 + 2\,NaOD$$

$R = CH_3, C_2H_5, C_3H_7, C_4H_9$, *sec*-$C_4H_9$, C_6H_5, cyclo-C_6H_{11}

Whether the resulting deuterides contain also Sn–H groups depends only on the purity of the D_2O used.

This result and the numerous possibilities of transferring hydrogen to carbon by using organotin hydrides in radical or

$$RR^1C{=}O + R_3^2Sn{-}D \longrightarrow RR^1CD{-}OSnR_3^2$$

$$RR^1CD{-}OSnR_3^2 \xrightarrow[-1/2\,(R_3^2Sn)_2O]{+1/2\,D_2O} RR^1CD{-}OD \quad (a)$$

$$RR^1CD{-}OSnR_3^2 \xrightarrow[-1/2\,(R_3^2Sn)_2O]{+1/2\,H_2O} RR^1CD{-}OH \quad (b)$$

$$RR^1C{=}O + R_2^2SnD_2 \longrightarrow RR^1CD{-}OD + 1/n\,(R_2^2Sn)_n \quad (c)$$

Carbonyl compound	Deuteride	Catalyst	Route	Conditions (h/ °C)	Deuterated alcohol [a]	ν_{C-D} (cm^{-1})
C_6H_5–CHO	$(C_4H_9)_3SnD$	Ni	(a)	20/140	C_6H_5CHD–OD	2108
CH_3–CH=CH–CHO	$(C_4H_9)_3SnD$	Pt	(a)	15/0–20	CH_3–CH=CH–CHD–OD	2142
C_6H_5–CO–C_6H_5	$(C_4H_9)_3SnD$	Ni	(a)	4/40 (in cyclohexane)	C_6H_5–CDOD–C_6H_5	–
C_6H_5–CO–CO–C_6H_5	$(C_4H_9)_3SnD$	Pt	(b)	2/40 (in ether)	C_6H_5–CDOH–CO–C_6H_5	2143
C_6H_5–CO–CO–C_6H_5	2 $(C_4H_9)_2SnD_2$	Pt	(c)	2/40 (in ether)	C_6H_5–(CDOD)$_2$–C_6H_5 (*meso*)	2130

[a] The products have no measurable optical activity.

polar additions or substitutions[7] induced us to test the wider use of organotin deuterides for deuteration.

Using powerful catalysts such as Raney nickel, palladium, platinum[8], or anhydrous $ZnCl_2$[9], we obtained both *C*-deuterated and *C,O*-bisdeuterated alcohols smoothly from organotin deuterides and aldehydes or ketones. To save deuteride we liberated the alcohol by deuterolysis (a) or hydrolysis (b), as required. However, a second equivalent of deuteride also effects this liberation, and is best used in the form of the more active compounds $R^2_2SnD_2$ which react in one step (c).

Working up is by fractional distillation. Yields are 70–95%.

Alkyl chlorides, bromides, and iodides, aryl iodides, and acid chlorides can be deuterated even without a catalyst. Carbonyl, nitro, and nitrile groups, which are often attacked by the usual deuterating agents, are unchanged in this reaction. Acid chlorides afford [1-D]aldehydes[10], and also the dideuterated esters. The ratio of the yields [1-D]aldehyde:ester can be varied according to the experimental technique and the concentration of the reactants, as is recorded[7,11] for the analogous reaction with hydrides.

Starting material	Conditions (h/°C)	Deuterated product, prepared by use of $(C_2H_5)_3SnD$ unless otherwise stated	ν_{C-D} (cm^{-1})	Yield (%) of pure compound
CH_3-CH_2I	0.2/0	CH_3-CH_2D	–	99 [a]
$C_6H_5-CO-CH_2Br$	9/20	$C_6H_5-CO-CH_2D$	2180	98 [a]
$CH_3-CHBr-CN$	0.1/70	$CH_3-CHD-CN$ [b]	2246	71
$C_6H_5-CH_2Cl$	2/110	$C_6H_5-CH_2D$	2189	79
$C_6H_5-CH_2-CH_2Br$	5/80	$C_6H_5-CH_2-CH_2D$	2171	74
C_6H_5-I	0.5/150	C_6H_5-D	2268	65
p-$O_2N-C_6H_4-CO-CH_2Br$	2/50 (in Benzene)	*p*-$O_2N-C_6H_4-CO-CH_2D$	2172	71
CH_3-COCl	3/0	$CH_3-CDO + CH_3-CD_2-OCOCH_3$	–	25 + 63
C_6H_5-COCl	3/60 (in Benzene)	C_6H_5-CDO + $C_6H_5-CD_2-OCOC_6H_5$	2101 2129	31 + 53
p-$O_2N-C_6H_4-COCl$	3/70	*p*-$O_2N-C_6H_4-CDO$ + *p*-$O_2N-CD_2-OCO-C_6H_4-NO_2$-*p*	2125 –	16 + 54
p-$O_2N-C_6H_4-COCl$	24/90	*p*-$O_2N-C_6H_4-CDO$	2125	73 [c]
p-$NC-C_6H_4-COCl$	24/80 (in Xylene)	*p*-$NC-C_6H_4-CDO$ + *p*-$NC-C_6H_4-CD_2-OCO-C_6H_4-CN$-*p*	2109 –	47 + 32

[a] By use of $(C_6H_5)_3SnD$. — [b] Since the product is formed in a radical reaction no optical activity is to be expected. — [c] By use of $(C_2H_5)_3SiD$.

As shown for the case of *p*-nitrobenzoyl chloride, even the more sluggishly reacting $(C_2H_5)_3SiD$ [easily obtained from the bromide and $(C_6H_5)_3SnD$ by distillation from the equilibrium mixture] acts as deuterating agent for particularly reactive starting materials.

The deuteride is usually added dropwise to the other reactant. The resulting products have been characterized by m.p. or b.p., elemental analysis, NMR spectra, ν_{C-D}, and sometimes ν_{O-D} in the IR spectra.

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A New Route to 1,1-Disubstituted Cyclopropanes

By *J. Gosselck* and *G. Schmidt*[*]

Dedicated to Professor F. Kröhnke on the occasion of his 65th birthday

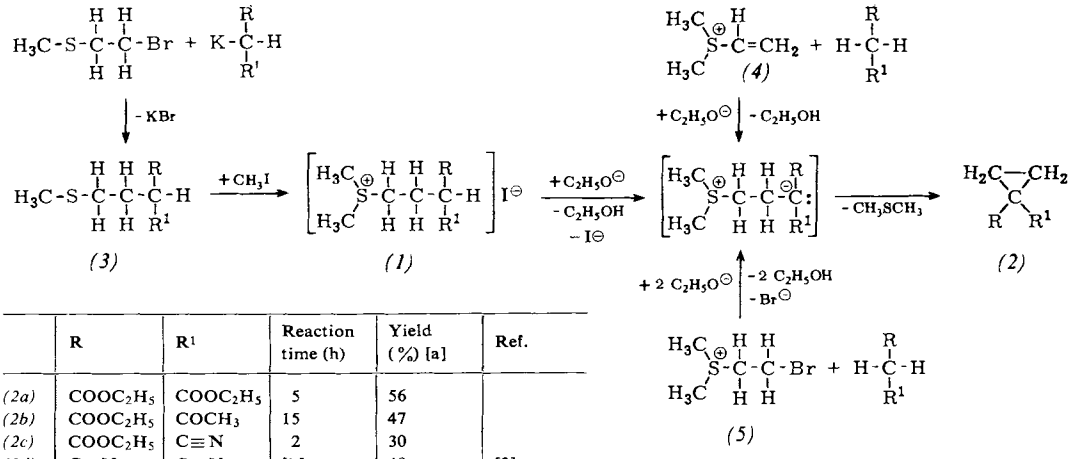
Treatment of substituted dimethylvinylsulfonium salts with the sodium salts of CH-acidic compounds in anhydrous ethanol leads stereospecifically to H^1,H^2-*trans*-cyclopropanes[1]. We have postulated a 1,4-sulfonium betaine as intermediate which closes the three-membered ring in a S_Ni reaction with loss of dimethyl sulfide. To test this assumption we synthesized the sulfonium salts *(1)* and treated them in anhydrous ethanolic solution or suspension with an equivalent amount of sodium ethoxide. Dimethyl sulfide was split off even at 20 °C. After 2–15-hours' stirring, the mixture was treated with ice and dilute sulfuric acid and then extracted with ether; the extract was worked up by distillation [*(2a)–(2d)*] or recrystallization [*(2f)*].

As expected, 1,1-disubstituted cyclopropanes *(2)* were obtained. They were identified by analysis of their NMR spectra, by gas-chromatographic studies, and by comparison of the results with recorded data.

1,1-Dibenzoylcyclopropane *(2f)* was a new compound. It crystallized from 4 parts of ethanol at −50 °C as pale yellow crystals (m.p. 56–58 °C).

As a result of alcoholysis of one nitrile group, *(1d)* (R = R^1 = CN) affords *(2c)* (R = $COOC_2H_5$, R^1 = CN) and not the dinitrile *(2d)*. To obtain *(2d)*, *(1d)* must be suspended in anhydrous ether and refluxed for 24 h with an equivalent amount of *N*-ethyldiisopropylamine.

In order to prepare the sulfonium salts *(1)* we first synthesized the β-substituted ethyl sulfides *(3)* by adding 2-(methylthio)-ethyl bromide[5] dropwise to a suspension of the potassium salts of CH-acidic compounds in *tert*-butyl alcohol[6]. The mixture was boiled until neutral (1–3 h). After removal of the



	R	R¹	Reaction time (h)	Yield (%) [a]	Ref.
(2a)	$COOC_2H_5$	$COOC_2H_5$	5	56	
(2b)	$COOC_2H_5$	$COCH_3$	15	47	
(2c)	$COOC_2H_5$	$C\equiv N$	2	30	
(2d)	$C\equiv N$	$C\equiv N$	[b]	48	[2]
(2e)	C_6H_5CO	C_6H_5	3	76 [c]	[3, 4]
(2f)	C_6H_5CO	C_6H_5CO	5	29	

[a] Calculated on *(3)*. — [b] Modified procedure (see text). — [c] Crystallized on addition of ice-water to the reaction mixture and recrystallized from 20 parts of 65% ethanol.

	R	R¹	Reaction time (h)	B.p. (°C/ 10^{-3} torr)	n_D^{20}	Yield (%)	Ref.
(3a)	$COOC_2H_5$	$COOC_2H_5$	2	83—89	1.4622	57 [a]	[7]
(3b)	$COOC_2H_5$	$COCH_3$	3	88—100	1.4723	32 [a]	[8]
(3c)	$COOC_2H_5$	$C\equiv N$	1.5	76—90	1.4750	33	[9]
(3d)	$C\equiv N$	$C\equiv N$	1	81—91	1.4912	39	
(3e)	C_6H_5CO	C_6H_5	2	136—143	1.6035	70	[10]
(3f)	C_6H_5CO	C_6H_5CO	2	166—176	1.6320	23	
(3g)	C_6H_5CO	$COOC_2H_5$	2	150—158	1.5530	56	
(3h)	$COCH_3$	$COCH_3$	1	90—100	1.5055	49	

[a] With Na ethoxide in anhydrous ethanol.

tert-butyl alcohol under vacuum the residue was treated with ice and dilute sulfuric acid and extracted with ether; the extract was then fractionated.

The sulfides *(3)* were treated with the calculated amount of methyl iodide and set aside at 0 °C for 1—8 days. This afforded the sulfonium salts in almost quantitative yield. They were purified by washing with anhydrous ether and were analyzed as iodides, picrylsulfonates, or tetraphenylborates.

	R	R¹	Reaction time (days)	M.p. (°C) [b]
(1a)	$COOC_2H_5$	$COOC_2H_5$	8	152 (P) [a], 129 (T)
(1b)	$COOC_2H_5$	$COCH_3$	3	146 (P)
(1c)	$COOC_2H_5$	$C\equiv N$	8	144 (P), 170 (T)
(1d)	$C\equiv N$	$C\equiv N$	2	142—144 (P), 108 (I)
(1e)	C_6H_5CO	C_6H_5	2	151—153 (P), 130—131 (I)
(1f)	C_6H_5CO	C_6H_5CO	1	123—124 (P)
(1g)	C_6H_5CO	$COOC_2H_5$	4	127 (P)
(1h)	CH_3CO	CH_3CO	2	165 (P), 125—126 (I)

[a] M.p. of the picrylsulfonate given in [11] is 168—169 °C.
[b] P = picrylsulfonate, T = tetraphenylborate, I = iodide.

The procedure described here has the advantage over synthesis of 1,1-disubstituted cyclopropanes from CH-acidic compounds and ethylene dibromide that the products are obtained in appreciably purer form. Further, the reaction occurs under very mild conditions.

As expected, 1,1-disubstituted cyclopropanes *(2)* are also formed on treatment of dimethylvinylsulfonium bromide *(4)* with the sodium salts of CH-acidic compounds in anhydrous ethanolic solution. Reaction of 2-bromoethyldimethylsulfonium bromide *(5)* with one equivalent of a CH-acidic compound and two equivalents of sodium ethoxide or *N*-ethyldiisopropylamine as proton acceptor also leads to cyclopropanes *(2)*. However, yields are lower in these two reactions.

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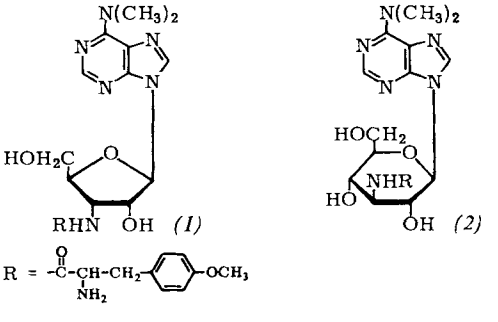
Synthesis of a Puromycin Analog[1]

By *F. W. Lichtenthaler* and *H. P. Albrecht*[*]

Dedicated to Professor F. Kröhnke on the occasion of his 65th birthday

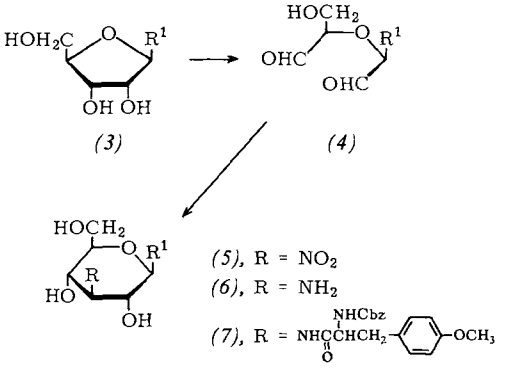
Attempts to improve the pharmacological properties of the nucleoside antibiotic puromycin *(1)*[2] have led to the synthesis of analogous compounds[3] largely based on the principle that the biological activity is due to the presence of an aminopentofuranose unit[4].

Although the activity of the puromycin analog *(2)* that is derived from 3-amino-3-deoxy-D-glucopyranose and whose



synthesis we describe below is not comparable with that of puromycin against *E. coli* and *S. faecalis*, it interferes with the transfer of [^{14}C]phenylalanine from t-RNS to the polypeptide (Nierenberg system)[5].

On cyclization with nitromethane in the presence of sodium methoxide in methanol and subsequent neutralization the nucleoside dialdehyde *(4)* that is obtained by periodate oxidation of 6-(dimethylamino)-9-(β-D-ribofuranosyl)purine *(3)*[6] affords a crystalline mixture of isomers (75 % yield), whence (3-deoxy-3-nitro-β-D-glucopyranosyl)-6-(dimethylamino)purine can be separated by fractional crystallization from methanol/water in 23 % yield [calculated on *(3)*] m.p. 202–204 °C (decomp.), $[\alpha]_D^{20} = -13°$ (c = 0.6, CH_3OH)[7]. Hydrogenation over 10 % palladium-animal charcoal affords 9-(3-amino-3-deoxy-β-D-glucopyranosyl)-6-(dimethylamino)purine *(6)*, m.p. 145–147 °C, $[\alpha]_D^{20} = -10°$ (c = 0.5, CH_3OH). This is converted by acetic anhydride/pyridine into the tetraacetate, m.p. 235–237 °C, $[\alpha]_D^{20} = -43°$ (c = 0.5, CH_3OH), whose NMR spectrum measured in $(CD_3)_2SO$ [9-Hz doublet for H-1′ at τ = 4.00, acetyl resonances at τ = 8.00, 8.03 (C-4′- and C-6′-OAc, respectively), 8.25 (NHAc), and 8.33 (C-2′-OAc)] proves the *gluco* configuration[8].



R^1 = 6-Dimethylaminopurin-9-yl

Treatment of *(6)* in dimethylformamide with the mixed anhydride prepared from *N*-(benzyloxycarbonyl)-*p*-methoxy-L-phenylalanine and ethylchloroformate/triethylamine[9] affords the amide *(7)*, m.p. 205–207 °C, $[\alpha]_D^{20} = +14°$ (c = 0.6, DMF), in 72 % yield. Hydrogenolysis of the benzyloxycarbonyl group over 10 % palladium-animal charcoal leads to the puromycin analog *(2)*, m.p. 135–137 °C, $[\alpha]_D^{20} = -26°$ (c = 0.8, CH_3OH), in 86 % yield. Its dihydrochloride crystallizes in well-formed needles of m.p. 188–190 °C.

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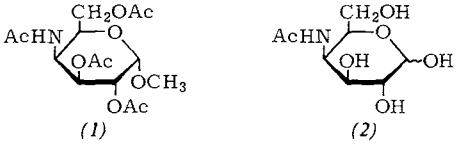
Synthesis of Derivatives of 4-Amino-4-deoxy-D-galactose

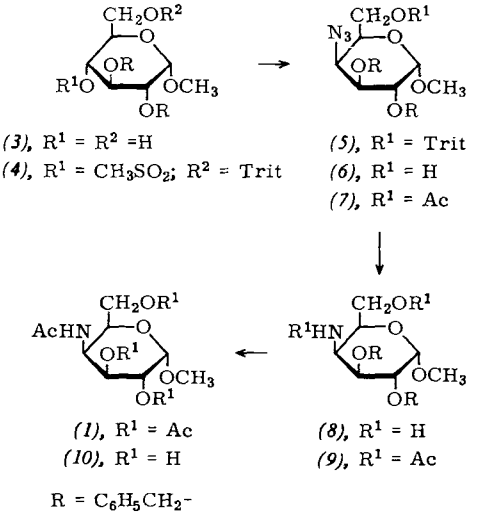
By *F. W. Lichtenthaler* and *P. Heidel*[*]

The structure proposed[2] for the nucleoside antibiotic gougerotin[1] is based on studies of periodate oxidation and some NMR data, and particularly on the physical constants of two degradation products *(1)* and *(2)*[2,3] to which the 4-amino *galacto* configuration is ascribed[2].



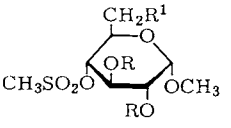
The syntheses described below afford compound *(1)* as a syrup with $[\alpha]_D^{25} = +119°$ in $CHCl_3$. Since the gougerotin degradation product has other constants (m.p. 193 °C, $[\alpha]_D^{20} = +87°$ in $CHCl_3$), the validity of the 4-amino-*galacto* structure is doubtful.

The 4-*O*-methanesulfonate *(4)*, m.p. 146–147 °C, $[\alpha]_D^{25} = +24°$ (c = 0.5 in $CHCl_3$), is obtained in 79 % yield from methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside *(3)*[4] by tritylation and subsequent methanesulfonylation; it is converted into the 4-azido galactoside *(5)*, m.p. 50–52 °C, $[\alpha]_D^{25} = +13°$ (c = 2 in $CHCl_3$), when heated with sodium azide in dimethylformamide for 30 h at 100 °C (yield 93 %). Detritylation by acid affords *(6)*, which does not crystallize but can be characterized as the 6-*O*-acetate *(7)*, m.p. 76–78 °C, $[\alpha]_D^{25} + 8°$ (c = 0.7 in $CHCl_3$). $LiAlH_4$ reduces *(6)* to the 4-amino galactoside *(8)* (a syrup, $[\alpha]_D^{25} = +49°$, c = 1 in $CHCl_3$), and acetylation then yields the diacetyl derivative *(9)* (a syrup, $[\alpha]_D^{25} = +51°$, c = 1 in $CHCl_3$). After thin layer chromatography on silica gel PF_{254} [development with ethyl acetate-ethanol-water (15:2:1) or chloroform-ethyl acetate-ethanol (10:2:1)] both these products were analytically pure (combustion analysis) and gave the expected NMR values. Reaction of *(6)* with sodium in liquid ammonia and subsequent acetylation led to the tetraacetate *(1)*, which after column chromatography on silica gel [elution with ethyl acetate-ethanol-water (15:2:1)] is obtained analytically and chromatographically pure, as a syrup, R_F = 0.6[5], $[\alpha]_D^{25} = +119°$ (c = 1 in $CHCl_3$), in 43 % yield calculated on *(6)*. Removing the *O*-acetyl groups by methanolic ammonia affords the *N*-acetate *(10)*, which crystallizes as needles, m.p. 203–205 °C, $[\alpha]_D^{25} = +182°$ (c = 1 in CH_3OH).



(10) can also be synthesized in five steps from methyl 2,3-di-*O*-benzoyl-4,6-di-*O*-mesyl-α-D-glucopyranoside *(11)*[6a] [m.p. 150–151 °C, $[\alpha]_D^{25} = +143°$ (c = 2, $CHCl_3$)]. In com-

pound *(11)*, the primary *C*-6 mesyloxy group can be solvolyzed selectively: sodium azide in dimethylformamide (3 h, 75 °C) gives the 6-azido compound *(12)* [m.p. 148–150 °C, $[\alpha]_D^{25} = +162°$ (*c* = 1, $CHCl_3$), yield 84 %]; similarly, sodium benzoate in dimethylformamide (5h, 80 °C) gives analytically and chromatographically[5] pure methyl 2,3,6-tri-*O*-benzoyl-4-*O*-mesyl-α-D-glucopyranosyl *(13)* in amorphous form [$[\alpha]_D^{25} = +139°$ (*c* = 1, $CHCl_3$), yield 92 %]. Solvolysis of the *C*-4 mesyloxy group in *(13)* by heating with sodium azide in dimethylformamide (60 h, 100 °C) and subsequent de-*O*-benzoylation with methanolic ammonia affords methyl 4-azido-4-deoxy-α-D-galactopyranoside *(6)*, R = H [m.p. 153–155 °C, $[\alpha]_D^{25} = +120°$ (*c* = 0.5, CH_3OH), yield 64 %]. Hydrogenation of *(6)*, R = H, followed by *N*-acetylation yields a product whose melting point, $[\alpha]_D$, and IR spectrum are identical with those of *(10)*.



(11), $R^1 = OSO_2CH_3$; R = C_6H_5CO
(12), $R^1 = N_3$; R = C_6H_5CO
(13), R^1 = R = C_6H_5CO

The *galacto* configuration of *(1)* and *(5)–(10)* follows from the method of preparation[6b] and from NMR spectroscopic data. The acetyl resonances obtained for *(1)* [τ = 7.91, 7.94 (2), and 8.01 in $CDCl_3$; 7.96, 7.98, and 8.08 (2) in [D_6]-DMSO] indicate[7] the absence of axial acetoxy and equatorial acetylamino groups. Analysis of the ring CH protons effected at 100 MHz in $CDCl_3$[8] gave for H-4 at τ = 5.27 a quartet with J_{34} = 4.0 and J_{4NH} = 10.0 Hz, each line being broadened by coupling with H-5 ($J_{45} \approx 1$ Hz). This quartet is simplified to a 4-Hz doublet by irradiation at the resonance frequency of the NH doublet (τ = 3.61, 10 Hz) and to a 10 Hz doublet by irradiation at the resonance frequency of the H-3 quartet (τ = 4.72).

Attempts to obtain *(2)* by acid hydrolysis of *(1)* or *(10)* [4 N HCl, 100 °C] and subsequent *N*-acetylation have so far failed. Apparently ring contraction giving the pyrrolidine sugar occurs under the conditions necessary for glycoside cleavage[9].

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[1] *T. Kanzaki, E. Higashide, H. Yamamoto, M. Shibata, K. Nakazawa, H. Iwasaki, T. Takewaka*, and *A. Miyake*, J. Antibiotics (Tokyo), Ser. A, *15*, 93 (1962); *J. M. Clark jr.* in *D. Gottlieb* and *P. D. Shaw*: Antibiotics. Springer, Berlin, Heidelberg, New York 1967, Vol. 1, p. 259.

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[5] Thin-layer chromatography on silica gel HF_{254} (E. Merck AG., Darmstadt) with ethyl acetate-ethanol-water (15:2:1) as eluant. Detection by iodine vapor or spraying with 2 % methanolic perchloric acid and heating to 100 °C.

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[6b] For the steric course of solvolysis of equatorial C-4-methanesulfonyloxy groups see *Y. Ali* and *A. C. Richardson*, Chem. Commun. *1967*, 554; also ref. [6a, 9].

[7] *F. W. Lichtenthaler* and *P. Emig*, Tetrahedron Letters *1967*, 577; Carbohydr. Res. *6* (1968), in the press.

[8] We thank Dr. *U. Scheidegger*, Varian AG., Zürich, for measurement of the 100 MHz spectrum.

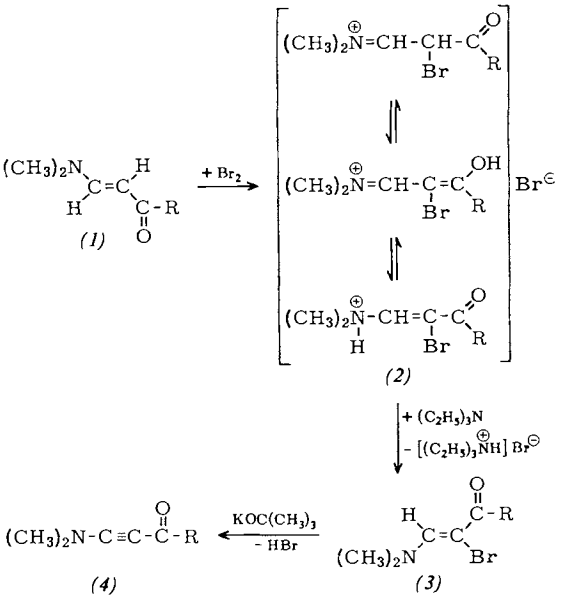
[9] *C. L. Stevens, P. Blumbergs*, and *D. H. Otterbach*, J. org. Chemistry *31*, 2817 (1966).

Ethynylogous Amides and Urethanes[**]

By *K. Hafner* and *M. Neuenschwander*[*]

Vinylogous amides have proved useful as starting compounds for the preparation of polycyclic conjugated, nonbenzenoid π-electron systems[1]. The hitherto unknown ethynylogous amides should provide a synthetic route to novel unsaturated ring systems; the study of the chemical and physical properties of these compounds was therefore of interest.

Ethynylogous amides and urethanes can be prepared easily and in good yields from the corresponding vinylogous compounds *(1)*. The bromination of 3-(dimethylamino)prop-



(1) *(2)* *(3)* *(4)*

(a), R = H
(b), R = CH_3
(c), R = OCH_3

	R	Yield (%)	M.p. (°C)	UV (CH_2Cl_2) λ_{max} (nm); log ε	IR (CCl_4) $\nu_{C\equiv C}$ (cm^{-1})	NMR ($CDCl_3$) (τ)
(3a)	H	95	54–56	294; 4.39	–	1.23/S/1 H; 2.78/S/1 H; 6.69/S/6 H.
(3b)	CH_3	95	63–65	305; 4.01	–	2.30/S/1 H; 6.77/S/6 H; 7.67/S/3 H.
(3c)	OCH_3	90	31–32	293; 4.05	–	2.23/S/1 H; 6.27/S/3 H; 6.82/S/6 H.
(4a)	H	70	–	282; 4.26	2165 2145	0.92/S/1 H; 6.95/S/6 H.
(4b)	CH_3	75	–	277; 4.23	2165	7.02/S/6 H; 7.79/S/3 H.
(4c)	OCH_3	70	35–37	255; 4.08	2195	6.33/S/3 H; 7.10/S/6 H.

2-en-1-al *(1a)*[2], 4-(dimethylamino)but-3-en-2-one *(1b)*[3], and methyl 3-(dimethylamino)acrylate *(1c)*[4] leads almost quantitatively to the hydrobromides *(2)*, which react with triethylamine to give the bromine derivatives *(3)* in yields of more than 90 %[5]. The acetylenes *(4)* are obtained from *(3)* in yields of about 70 % by elimination of HBr with potassium *tert*-butoxide[6]. Compound *(4a)*, a pale yellow oil, is stable for long periods only below −50 °C, whereas *(4b)* and *(4c)* can be kept for several hours at room temperature.

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[**] *M. N.* is grateful to the *Schweizerische Stiftung für Stipendien auf dem Gebiete der Chemie* for a grant. We thank Fräulein *M. Ruppert* for her skilful experimental assistance.

[1] *K. Hafner* and *J. Schneider*, Liebigs Ann. Chem. *624*, 37 (1959); *K. Hafner* and *G. Schneider*, *ibid. 672*, 194 (1964); *K. Hafner* and *M. Kreuder*, Angew. Chem. *73*, 657 (1961); *K. Hafner*, *R. Fleischer*, and *K. Fritz*, Angew. Chem. *77*, 42 (1965); Angew. Chem. internat. Edit. *4*, 69 (1965).

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[3] *E. Benary*, Chem. Ber. *63*, 1573 (1930).

[4] Propiolic acid after *V. Wolf*, Chem. Ber. *86*, 735 (1953); methyl ester by refluxing for two days with 10 % conc. H_2SO_4 in anhydrous methanol; *(1c)* by addition of dimethylamine to methyl propiolate in tetrahydrofuran at 20 °C.

[5] Correct analytical data were obtained for all the compounds described.

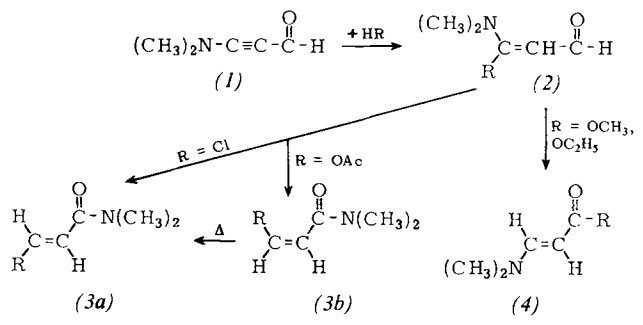
[6] Overall yield for all the steps. The acetylenes were purified by distillation in a bulb tube at 10^{-4} torr and oven temperatures of 20 °C *(4a)*, 40 °C *(4b)*, and 30 °C *(4c)*. The yields decrease rapidly at higher temperatures.

A New Rearrangement of Substituted 3-Aminopropenals[**]

By *M. Neuenschwander* and *K. Hafner*[*]

3-(Dimethylamino)prop-2-yn-1-al *(1)* reacts with an equimolar quantity of HCl in anhydrous tetrahydrofuran at 0 °C to give the reactive aldehyde *(2)*, R = Cl[1], which rearranges during isolation to form isomer-free[2] *trans*-3-chloro-*N,N*-dimethylacrylamide *(3a)*, R = Cl (yield 80 %)[3]. The strong band in the UV spectrum of *(3a)*, R = Cl, occurs at 216 nm (*n*-hexane), a position characteristic of amides of similar structure, and the AB system of the vinyl protons in the NMR spectrum occurs at τ = 2.77 and 3.32 (J = 13 Hz[4]); hydrogenation of *(3a)*, R = Cl, with Pd black (20 °C in benzene) yields *N,N*-dimethylpropionamide. The aldehyde *(2)*, R = OAc, cannot be isolated in the analogous reaction of *(1)* with glacial acetic acid; the product obtained (80 % yield) is isomer-free[2] *cis*-3-acetoxy-*N,N*-dimethylacrylamide *(3b)*, R = OAc [NMR in $CDCl_3$: τ = 2.58/D (J = 7.5 Hz)/1 H; τ = 4.43/D/1 H; τ = 6.90 and 6.94/2S/6 H; τ = 7.75/S/3 H], which rearranges when heated to 60 °C to give the thermodynamically more stable *trans* isomer *(3a)*, R = OAc [NMR in $CDCl_3$: τ = 1.73/D (J = 12 Hz)/1 H; τ = 3.73/D/1 H; τ = 6.93/S/6 H; τ = 7.79/S/3 H]. Compound *(3b)*, R = OAc, can be converted into 3-acetoxy-*N,N*-dimethylpropionamide by hydrogenation (Pd/H_2, 20 °C in benzene).

Compound *(1)* reacts highly stereoselectively[6] with an equimolar quantity of diethylamine or with an excess of methanol or ethanol[5] to give the aldehydes *(2)*, R = $N(C_2H_5)_2$, OCH_3, and OC_2H_5 respectively, which can be isolated since their tendency toward rearrangement is less pronounced than that of the adducts of *(1)* with HCl or acetic acid, and decreases in the order OCH_3 > OC_2H_5 > $N(C_2H_5)_2$.



Whereas only traces of 3-(diethylamino)-3-(dimethylamino)-prop-2-en-1-al *(2)*, R = $N(C_2H_5)_2$, rearrange at 60 to 80 °C, 3-methoxy-3-(dimethylamino)prop-2-en-1-al *(2)*, R = OCH_3, [yellow oil, yield 90 %, NMR in $CDCl_3$: τ = 0.72/D (J = 8 Hz)/1 H; τ = 5.46/D/1 H; τ = 6.16/S/3 H; τ = 7.06/S/6 H] is converted when heated at 60 °C in $CHCl_3$ into the isomeric methyl *trans*-3-(dimethylamino)acrylate *(4)*, R = OCH_3 [57 % yield, m.p. 46–47 °C, λ_{max} in CH_2Cl_2: 278 nm, log ε = 4.28, NMR in $CDCl_3$: τ = 2.57/D (J = 13 Hz)/1 H; τ = 5.50/D/1 H; τ = 6.35/S/3 H; τ = 7.09/S/6 H], the constitution of which was verified by comparison with *(4)*, R = OCH_3, prepared from methyl propiolate and dimethylamine.

The new rearrangement of 3-aminopropenal derivatives *(2)* evidently proceeds with high stereoselectivity; a four-membered ring intermediate or a corresponding transition state is probably involved. The configuration of the aldehyde *(2)*, which is important for the elucidation of the mechanism[7], cannot be established from the above results. We are now proceeding with the further study of this reaction.

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[**] *M. N.* is grateful to the *Schweizerische Stiftung für Stipendien auf dem Gebiete der Chemie* for a grant. We thank Fräulein *M. Ruppert* for her skilful experimental assistance.

[1] The aldehyde *(2)*, R = Cl, can be obtained in the impure state by careful working-up [UV in CH_2Cl_2: λ_{max} = 297 nm; NMR in $CDCl_3$: τ = 0.45/D/1 H and τ = 4.80/D (J = 7 Hz)/1 H; τ = 6.81/S/6 H].

[2] Purity checked by NMR spectra.

[3] Similarly, the addition of HCl to 3-(*N*-methylanilino)prop-2-yn-1-al (NMR in $CDCl_3$: τ = 0.73/S/1 H; τ approx. 2.75/M/5 H; τ = 6.62/S/3 H; IR in CCl_4: $\nu_{C\equiv C}$ = 2170 cm^{-1}) leads by rearrangement to *trans*-3-chloro-*N*-methylacrylanilide [NMR in $CDCl_3$: τ = 2.3–2.9/M/6 H, including τ = 2.64/D/(J = 13 Hz); τ = 3.78/D (J = 13 Hz)/1 H; τ = 6.63/S/3 H].

[4] For coupling constants of similar compounds, cf. *E. Winterfeldt* and *H. Preuss*, Chem. Ber. *99*, 450 (1966).

[5] Since the reaction rate in dilute equimolar solutions is too slow, the reactions was carried out in the corresponding alcohol.

[6] According to the NMR spectra, the adducts *(2)*, R = $N(C_2H_5)_2$, OCH_3, OC_2H_5, are formed with a stereoselectivity of about 90 %.

[7] For the steric course of additions to C≡C bonds, cf. *R. Huisgen*, *B. Giese*, and *H. Huber*, Tetrahedron Letters *1967*, 1883 (further references cited); *E. Winterfeldt*, Angew. Chem. *79*, 389 (1967) (further references cited); Angew. Chem. internat. Edit. *6*, 423 (1967).

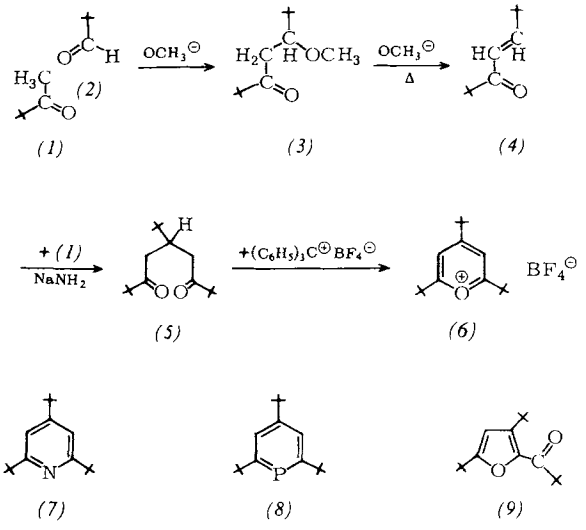
Preparation of 2,4,6-Tri-*tert*-butylpyrylium Tetrafluoroborate, 2,4,6-Tri-*tert*-butylpyridine, and 2,4,6-Tri-*tert*-butylphosphorin

By *K. Dimroth and W. Mach*[*]

Pyrylium salts substituted by *tert*-butyl groups in the 2,4,6-positions have not previously been known. The synthesis of such a salt, which we describe here, made possible the prepa-

ration of 2,4,6-tri-*tert*-butyl-pyridine and 2,4,6-tri-*tert*-butyl-phosphorin, the first phosphorin derivative containing only aliphatic substituents.

We obtained 2,4,6-tri-*tert*-butylpyrylium tetrafluoroborate *(6)* in a total yield of 42% by the route shown in the following scheme. The methoxy ketone *(3)* is converted mainly into the unsaturated ketone *(4)* when boiled in a basic medium, whereas it is converted by acids into a cyclic carboxonium salt[1].



(1) *(3)* *(4)*

(5) *(6)*

(7) *(8)* *(9)*

2,4,6-Tri-*tert*-butylpyridine *(7)*, m.p. 69 °C, is formed quantitatively by the action of alcoholic ammonia on the pyrylium salt *(6)*. NMR: singlet $\delta = -7.02$ ppm (2 H), $\delta = -1.34$ ppm (18 H), and $\delta = -1.30$ ppm (9 H). The base *(7)* can be isolated and purified by recrystallization from ethanol/water.

Tri-*tert*-butylphosphorin *(8)*[2] is formed in 37% yield from *(6)* and $P(CH_2OH)_3$; it has m.p. 88 °C, and in the NMR shows $\delta = -7.77$ ppm (2 H), $J_{P-CH} = 6$ Hz, doublet $\delta = -1.46$ ppm (18 H), $J_{P-CH} = 2$ Hz, singlet $\delta = -1.37$ (9 H) *(8)* is isolated and purified by recrystallization from methanol/water.

With H_2O_2 in ethanol[3], compound *(8)* affords a 30% yield of *tert*-butyl 3,5-di-*tert*-butyl-2-furyl ketone *(9)*, which can also be obtained from *(6)* by use of hydroxylammonium chloride.

Experimental:

Compounds *(2)* (86 g, 1 mole) and *(1)* (100 g, 1 mole) are boiled for 4 h in 10% $NaOCH_3$ solution (540 g, 1 mole of $NaOCH_3$), whereupon *(3)* and *(4)* are formed in approximately equal amounts in a total yield of about 67%. To 18.2 g of this mixture and 10 g of *(1)* (0.1 mole) is added 20 g of a 30% sodamide suspension in benzene (0.15 mole of $NaNH_2$). Compound *(5)*, m.p. 53 °C, is formed in 85% yield; this is boiled with an equimolar amount of triphenylmethyl tetrafluoroborate in glacial acetic acid, then treated with ether, whereupon the salt *(6)* crystallizes in 75% yield. It is recrystallized from ethylene dichloride/ether. M.p. 216 °C. NMR: $\delta = -7.82$ ppm (2 H), $\delta = -1.46$ ppm (9 H), $\delta = -1.53$ ppm (18 H).

Independently of us, *W. Rundel* (Tübingen) has prepared 2,4,6-tri-*tert*-butylpyrylium perchlorate by a different route[4].

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[1] *K. Dimroth* and *W. Mach*, Angew. Chem. *80*, 490 (1968); Angew. Chem. Internat. Edit. *7*, 462 (1968).

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[3] *A. T. Balaban* and *C. D. Nenitzescu*, Chem. Ber. *93*, 599 (1960).

[4] *W. Rundel*, private communication.

Stable Cyclic Carboxonium Salts

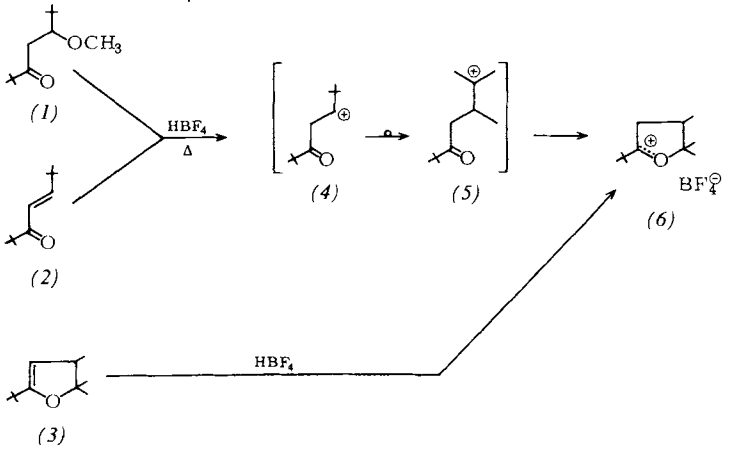
By *K. Dimroth* and *W. Mach*[*]

Whereas carbonium salts having two ethereal oxygen atoms in the α-position are known to exist as stable carboxonium salts[1], the corresponding cyclic carboxonium salts with only one ethereal oxygen in the α-position have hitherto only been detected kinetically or by NMR measurements at low temperature[2].

We have now succeeded in isolating the carboxonium salt *(6)*, whose stability can be ascribed to the formation of a heterocyclic five-membered ring. There are three ways in which this salt can be synthesized: a) by cleavage of methoxide from 5-methoxy-2,2,6,6-tetramethyl-3-heptanone *(1)*[3]; b) by addition of a proton to 2,2,6,6-tetramethyl-3-hepten-5-one *(2)*[3]; and c) by addition of a proton to 2-*tert*-butyl-4,5,5-trimethyl-4,5-dihydrofuran *(3)*.

In methods a) and b) the formation of *(6)* takes place on boiling the reactants with a 50% solution of water-free HBF_4 in 1,2-dichloroethane; the carbonium ion *(4)* is probably formed first, and migration of a methyl group leads to the formation of *(5)* and subsequently to *(6)*. Compound *(6)* can be isolated by precipitation with ether (yield 75%).

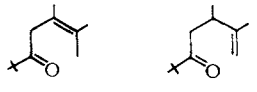
In method c) the cyclic carboxonium salt *(6)* is formed immediately, in quantitative yield, on addition of ethereal HBF_4 in the cold.



(1) *(2)* *(3)* *(4)* *(5)* *(6)*

The new carboxonium salt *(6)* melts, with decomposition at 190 °C (sealed tube). It is non-hygroscopic; however, on standing for a few days it changes color. Repurification can be achieved by recrystallization from 1,2-dichloroethane with ether. Its constitution is established by elemental analysis and from its NMR data (in liquid SO_2 at −30 °C): multiplet (AB part of an ABX spectrum) at $\delta = -3.27$ ppm (2H); multiplet at $\delta = -2.25$ ppm (1H); singlets at $\delta = -1.32$ ppm (3H), $\delta = -1.08$ ppm (3H), $\delta = -0.90$ ppm (9H); doublet at $\delta = -0.62$ ppm [$J = 7$ Hz, (3H)].

If potassium *tert*-butoxide or sodium methoxide is added to a solution of *(6)* in *tert*-butanol at room temperature, compound *(3)* is formed almost exclusively; on warming, a mixture of *(3)*, *(7)*, and *(8)* is formed that can be resolved into its components by gas chromatography (ratio *(3)*:*(7)*:*(8)* = 9:2:3).



(7) *(8)*

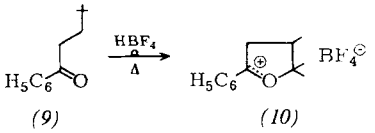
The constitution of each of these compounds is established by CH analysis, by mass spectrometry, and from the following NMR spectroscopic data:

(3): Doublet at $\delta = -4.27$ ppm [$J_1 = 3$ Hz, (1H)]; octet at $\delta = -2.54$ ppm [$J_1 = 3$ Hz, $J_2 = 7$ Hz, (1H)]; singlets at $\delta = -1.24$ ppm (3H), $\delta = -1.03$ ppm (9H), $\delta = -1.15$ ppm (3H); doublet at $\delta = -0.88$ ppm [$J_2 = 7$ Hz, (3H)].

(7): Singlets at $\delta = -3.15$ ppm (2H), $\delta = -1.68$ ppm (3H), $\delta = -1.56$ ppm (6H), $\delta = -1.13$ ppm (9H).

(8): Multiplets at $\delta = -4.65$ ppm (2H), $\delta = -2.46$ ppm (3H), $\delta = -1.70$ ppm (3H); singlet at $\delta = -1.10$ ppm (9H); doublet at $\delta = -0.95$ ppm [$J = 7$ Hz, (3H)].

The ketone *(9)* [4] can be converted into the phenyl-substituted tetrafluoroborate *(10)* if subjected to the same treatment as that described for methods a) and b). The yellow crystals of *(10)*, which melt at 123 °C, are stable at room temperature. Dissolution in methylene chloride, trifluoroacetic acid, or SO_2 leads to an intensive blue fluorescence.



(9) *(10)*

The constitution of *(10)* is confirmed by elemental analysis and by its NMR spectrum. NMR (in trifluoroacetic acid): Multiplet at $\delta = -8.1$ to -7.15 ppm (5H); multiplet (AB part of an ABX spectrum) at $\delta = -3.75$ ppm (2H); multiplet at $\delta = -2.50$ ppm (1H); singlet at $\delta = -1.52$ ppm (3H); singlet at $\delta = -1.29$ ppm (3H); doublet at $\delta = -0.90$ ppm [$J = 7$ Hz, (3H)]. UV spectrum (in methanol): $\lambda_{max} = 390$ nm; $\varepsilon = 735$.

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[1] *H. Meerwein* in *Houben-Weyl*: Methoden der organischen Chemie. 4th Edit., Thieme, Stuttgart 1965, Vol. VI/3, p. 299, 329; *K. Dimroth* and *P. Heinrich*, Angew. Chem. *78*, 714 (1966); Angew. Chem. internat. Edit. *5*, 676 (1966).

[2] *S. Oae*, J. Amer. chem. Soc. *78*, 4030 (1956); *H. R. Ward* and *P. D. Sherman jr.*, *ibid. 89*, 4222 (1967).

[3] *K. Dimroth* and *W. Mach*, Angew. Chem. *80*, 489 (1968); Angew. Chem. internat. Edit. *7*, 460 (1968).

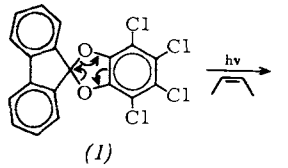
[4] *W. Michel*, Dissertation, Universität Marburg, 1961.

New Precursors for Arylcarbenes[1]

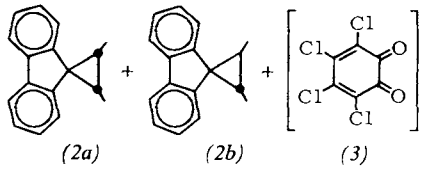
By *R. M. G. Nair*[*], *E. Meyer*[**], and *G. W. Griffin*[*]

We have found that photolysis [2] (24 h) of 4,5,6,7-tetrachlorospiro-[1,3-benzodioxole-2,9′-fluorene] *(1)* (10^{-3} mole)[3] in *cis*-2-butene (75 ml) leads to a mixture of *cis*- and *trans*-2,3-dimethylspiro[cyclopropane-1,9′-fluorene] *(2a)* and *(2b)*, respectively, in 23 % yield[4]. The formation of 3,4,5,6-tetrachloro-*o*-benzoquinone *(3)* was confirmed in rigid matrices by detection of typical oxidation processes by this compound. It was not isolated in *cis*-2-butene because of formation of adducts.

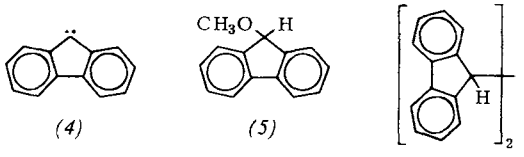
We propose that photolysis of *(1)* affords fluorenylidene *(4)*. Since *(2a)* and *(2b)* are interconverted when subjected to UV irradiation[4,5], no significance may be attached to the apparent nonspecificity of addition of *(4)* to *cis*-2-butene, which was used because of the lower solubility of *(1)* in the *trans*-isomer.



(1)



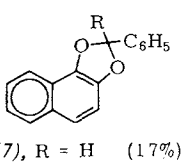
(2a) *(2b)* *(3)*



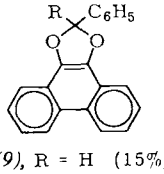
(4) *(5)* *(6)*

Our recent work with oxiranes leaves no doubt that carbenes are implicated in the photofragmentation of epoxides[5] and lends credence to our contention that fluorenylidene is the chemically significant species involved in the conversion of *(1)* to *(2a)* and *(2b)*. Corroborative evidence is provided by the photolysis (24 h) of *(1)* (10^{-3} mole) in methanol (90 ml), which yields fluorenyl methyl ether *(5)* in 30 % yield. *Kirmse* and *Horner*[6] have previously used alcohols to intercept arylcarbenes. 9-Diazofluorene, the accepted fluorenylidene precursor, also gives *(5)* under similar conditions. *(1)*, like diazofluorene[6], also gives 9,9′-bifluorenyl *(6)* in high yield (38 %) upon photolysis in cyclohexane (90 ml, 10^{-3} mole, 48 h).

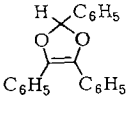
The following compounds also fragment to arylcarbenes which have been trapped with methanol (yields of methyl ethers in parentheses):



(7), R = H (17%)
(8), R = C_6H_5 (11%)



(9), R = H (15%)
(10), R = C_6H_5 (5%)



(11), (16%)

All products were separated by gas and elution chromatography and identified by comparison with authentic samples [7].

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[1] We gratefully acknowledge financial support from the Petroleum Research Fund of the American Chemical Society.

[2] The solutions were carefully degassed and irradiated in a sealed quartz vessel at 40–70 °C. The radiation source was an air-cooled Rayonet RPR-100 Chamber Reactor (from The Southern New England Ultraviolet Co., Middletown, Conn. U.S.A.) containing sixteen 8-watt low-pressure mercury lamps, or the larger preparative RPR-208 model. The yields reported are based on reactions performed in the latter unit.

[3] This compound (m.p. 281 °C) was obtained in 81 % yield by addition of diazofluorene to 3,4,5,6-tetrachloro-*o*-benzoquinone in ether under a nitrogen atmosphere. The solution was then heated under reflux until nitrogen evolution ceased whereupon the solvent was removed and the residue recrystallized from ethanol/acetonitrile.

[4] [a] *W. von E. Doering* and *M. Jones jr.*, Tetrahedron Letters *1963*, 791; [b] *M. Jones jr.* and *K. R. Rettig*, J. Amer. chem. Soc. *87*, 4013 (1965).

[5] *H. Dietrich, G. W. Griffin*, and *R. C. Petterson*, Tetrahedron Letters *1968*, 153.

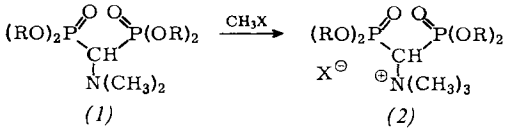
[6] *W. Kirmse, L. Horner*, and *H. Hoffmann*, Liebigs Ann. Chem. *614*, 19 (1958); *W. Kirmse, ibid. 666*, 9 (1963).

[7] We thank Dr. *M. Jones jr.*, Princeton University, for copies of the infrared spectra of *(2a)* and *(2b)*.

Bis(diethoxyphosphinyl)(trimethylammonio)-methylide, a Stable *N*-Ylide

By *H. Gross* and *B. Costisella* [*]

[Bis(diethoxyphosphinyl)methyl]dimethylamine *(1)* [1], which is readily accessible from formamide dimethyl acetal and diethyl phosphite is smoothly converted by reaction with dimethyl sulfate or methyl iodide in dioxane at room temperature into the quarternary salts *(2a)* and *(2b)*, respectively, which are obtained pure when washed several times



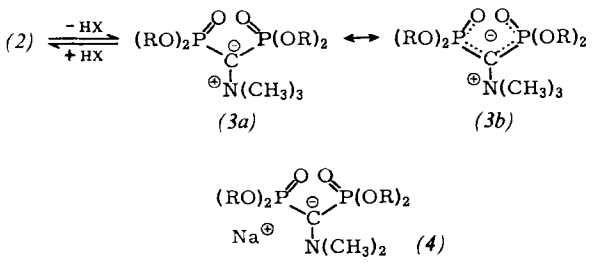
(1) *(2)*

R = C_2H_5

(a), $X^{\ominus}$ = $CH_3OSO_3^{\ominus}$
(b), $X^{\ominus}$ = $I^{\ominus}$
(c), $X^{\ominus}$ = $ClO_4^{\ominus}$

with ether [*(2a)*: yield 76 %, m.p. 105–106 °C; *(2b)*: yield 85 %, m.p. 116–118 °C, NMR spectrum $\tau_{CH_3-CH_2-}$ = 8.58 triplet (J = 7 Hz), 5.65 multiplet (J = 8 Hz, $\tau_{-N(CH_3)_3}$ = 6.10 singlet, $\tau_{>CH-}$ = 4.12 triplet (J = 20 Hz)]. When treated with silver perchlorate in an aqueous medium, *(2a)* gave the perchlorate *(2c)*, m.p. 134–135 °C, in 90 % yield.

The phosphonate proton of *(2)*, like that of *(1)* [1], is very strongly acidic. If *(2a)* is stirred for *ca.* 30 min with saturated aqueous potassium carbonate solution and then shaken with benzene, subsequent separation of the organic phase leads, after drying and evaporation in a vacuum, to a colorless crystalline compound of m.p. 38–40 °C, which according to its elemental analysis and spectral properties has the structure of an *N*-ylide *(3)*, namely, bis(diethoxyphosphinyl)(trimethylammonio)methylide. ^{1}H–NMR spectrum: $\tau_{CH_3-CH_2-}$ = 8.74 triplet (J = 7 Hz), 6.07 multiplet (J = 4 Hz), $\tau_{-N(CH_3)_3}$ = 6.47 singlet. The signal of the phosphonate proton that



(3a) *(3b)*

(4)

appeared as a triplet at τ = 6.80 or 4.12, respectively, for *(1)* [1] and *(2)* is not present in the spectrum of *(2c)*. The ^{31}P–NMR spectra [2] of the compounds *(1)–(3)* and of *(4)* [Na salt of *(1)*] [3] contain the following signals: *(1)* −18 ppm, *(2)* −11 ppm, *(3)* −28 ppm, *(4)* −33 ppm; the appreciably more negative shift of *(3)* compared with that of *(2)* indicates delocalization of the free electron pair of the carbanion as shown in *(3b)*; this presumably accounts for the stability of the ylide [4]. The same delocalization is shown on comparison of the chemical shifts of *(1)* and *(4)*.

The ylide *(3)* is readily soluble in water from which it can be recovered unchanged by evaporation or extraction. Addition of perchloric acid to a solution of *(3)* in dioxane followed by addition of ether leads to regeneration of the perchlorate *(2c)*.

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[1] *H. Gross* and *B. Costisella*, Angew. Chem. *80*, 364 (1968); Angew. Chem. internat. Edit. *7*, 391 (1968).

[2] We thank Dr. *E. Grundemann*, Dr. *W. Wiecker*, and Dipl.-Chem. *A. R. Grimmer* for measurement of the ^{1}H- and ^{31}P–NMR spectra.

[3] Compound *(4)* is obtained from *(1)* and NaH in dioxane.

[4] An analogous effect was assumed to explain the stability of the dicyano(trimethylammonio)methylide described by *Z. Arnold*, Chem. and Ind. *1960*, 1470; Coll. czech. chem. Commun. *26*, 1113 (1961).

Synthesis of Both Hexobarbital Enantiomers and of (+)-Thiohexobarbital from (+)-Methyl 2-Cyano-2-(1-cyclohexenyl)propionate [1]

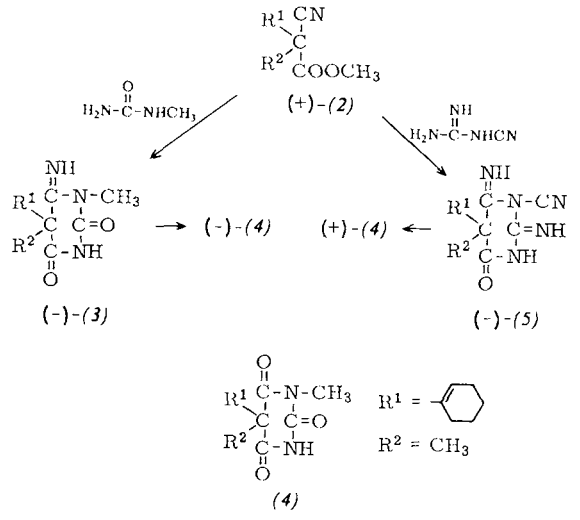
By *J. Knabe* and *D. Strauss* [*]

Since the enantiomers of hexobarbital [2] have different pharmacological properties [3] and resolution of the racemate is difficult on a large scale [2], we sought an alternative route for their synthesis.

We have found that the two hexobarbital enantiomers can be prepared in good yields from (+)-methyl 2-cyano-2-(1-cyclohexenyl)propionate [(+)-*(2)*]: (−)-hexobarbital [(−)-*(4)*] is obtained *via* (−)-iminohexobarbital [(−)-*(3)*] by condensing (+)-*(2)* with *N*-methylurea and (+)-hexobarbital [(+)-*(4)*] is obtained by condensing (+)-*(2)* with dicyanodiamide; in the last-mentioned reaction (−)-cyanodiiminobarbital [(−)-*(5)*], which is first formed, gives [(+)-*(4)*] on methylation with dimethyl sulfate and subsequent hydrolysis.

The formation of optically active hexobarbital from (+)-*(2)* and *N*-methylurea in about the same optical purity as is obtained by resolution of the racemate [2] confirms previous findings [4] that condensation of disubstituted cyanoacetic esters with *N*-methylurea is stereoselective [5]. We have found this also to be the case with *N*-methylthiourea, since we obtained (+)-thiohexobarbital from (−)-2-cyano-2-(1-cyclohexenyl)propionic acid [(−)-*(1)*] and *N*-methylthiourea.

The (+)-form of *(2)* is easily obtained from racemic *(1)* by resolution and subsequent esterification [6].



Experimental:

Synthesis of (−)-*(4)*: 5.7 g of (+)-*(1)*, $[\alpha]_D$ +32.76°, which was obtained from racemic *(1)* by way of the diastereoisomeric quinine salts, was esterified with diazomethane and the resulting ester was distilled. Yield 4.8 g of (+)-*(2)*, $[\alpha]_D$ = +45.27°, b.p. 114°C/2.3 torr. Condensation with *N*-methylurea in methanolic $NaOCH_3$ gave 3.0 g of (−)-*(3)*, which after recrystallization from ethanol had $[\alpha]_D$ = −12.29°, m.p. 160–161°C. (−)-*(3)* was hydrolyzed quantitatively by 25% H_2SO_4 to (−)-*(4)*, $[\alpha]_D$ = −11.64°, m.p. 153°C.

Synthesis of (+)-*(4)*: 3.5 g of (+)-*(1)*, $[\alpha]_D$ = +29°, was esterified with diazomethane to yield (+)-*(2)* which was condensed with dicyanodiamide in methanolic $NaOCH_3$ to give (−)-*(5)*, $[\alpha]_D$ = −58.67°, m.p. 252–254°C (decomp.) (yield 4 g). Methylation of 3.25 g of (−)-*(5)* with dimethyl sulfate and subsequent hydrolysis gave 2 g of (+)-*(4)*, $[\alpha]_D$ = +10.64°, m.p. 151–153°C.

Synthesis of (+)-Thiohexobarbital: 3.7 g of (−)-*(1)*, $[\alpha]_D$ = −31.44°, was esterified with diazomethane to give (−)-*(2)* and this was condensed with *N*-methylthiourea in ethanolic $NaOC_2H_5$, and the product was hydrolyzed with 10% H_2SO_4, yielding (+)-thiohexobarbital (0.9 g), m.p. 144 to 145°C (from ethanol), $[\alpha]_D$ = +38.28°.

Values of $[\alpha]$ refer to solutions in anhydrous ethanol at 20°C.

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[1] Part 5 of Barbituric Acid Derivatives. – Part 4: *J. Knabe* and *W. Geismar*, Arch. Pharmaz., in press.

[2] *J. Knabe* and *R. Kräuter*, Arch. Pharmaz. *298*, 1 (1965).

[3] *G. Wahlström*, Life Sci. *5*, 1781 (1966); *W. Rummel*, *U. Brandenburger*, and *H. Büch*, Med. Pharmacol. exp. (Basel) *16*, 496 (1967).

[4] *E. C. Kleiderer* and *H. A. Shonle*, J. Amer. chem. Soc. *56*, 1772 (1934); *W. J. Doran*, J. org. Chemistry *25*, 1737 (1960).

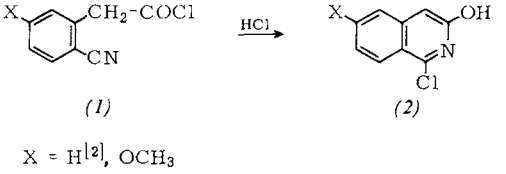
[5] *M. Conrad* and *A. Zart*, Liebigs Ann. Chem. *340*, 326 (1905).

[6] We thank Farbenfabriken Bayer A.G. for a gift of the racemic ester.

Synthesis of Derivatives of Isoquinoline, of 1,3-Benzoselenazin-4-one, and of 1*H*-2-Benzazepin-1-one

By *G. Simchen*[*]

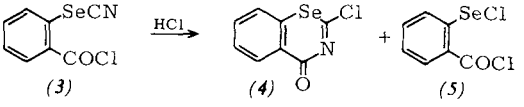
In continuation of our work on cyclizing acylation of imidoyl halides[1] we obtained nearly quantitative yields of 1-chloroisoquinolin-3-ols *(2)* from *o*-cyanophenylacetyl chlorides *(1)* and hydrogen chloride. UV spectroscopic studies show these products to exist in the lactim form independently of the solvent.



(1) *(2)*

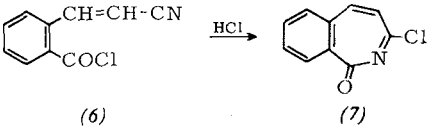
X = H[2], OCH_3

Although hydrogen halide adducts of selenocyanates are extremely unstable, we have succeeded in cyclizing *o*-selenocyanatobenzoyl chloride *(3)*[3] by hydrogen chloride at 60°C to 2-chloro-1,3-benzoselenazin-4-one *(4)*; *o*-(chloroformyl)-benzeneselenyl chloride *(5)*[5] is formed in a side reaction.



(3) *(4)* *(5)*

In analogous syntheses we obtained larger ring systems, namely, 3-chloro-1*H*-2-benzazepin-1-one *(7)* on treating 2-(chloroformyl)-*cis*-cinnamonitrile *(6)*[4] with hydrogen chloride. Further study is under way to show how far this ring system can be considered an azologous 2,3-benzotropone.



(6) *(7)*

1-Chloroisoquinolin-3-ols (2): 0.01 mole of (*o*-cyanophenyl)- or (2-cyano-5-methoxyphenyl)-acetyl chloride *(1)* [from the corresponding (*o*-cyanophenyl)acetic acid and PCl_5 in ether] is dissolved in 30–40 ml of di-*n*-butyl ether, HCl is passed in to saturation, and the mixture is warmed to 60°C for 4 h. Pure *(2)*, which precipitates on cooling, is filtered off, washed with benzene, and recrystallized from ethanol. X = H: yield 97%, m.p. 205°C[2]. X = OCH_3: yield 92%, m.p. 211°C.

2-Chloro-1,3-benzoselenazin-4-one (4): 2.2 g (0.009 mole) of *o*-selenocyanatobenzoyl chloride *(3)* [from *o*-selenocyanatobenzoic acid[5] and PCl_5 in ether at 0°C] was dissolved in 60 ml of dioxane pre-saturated with HCl and the mixture warmed at 60°C for 5 h. The dioxane was then distilled off in a vacuum, and the residue treated with hexane [to remove *(5)*] and subsequently sublimed at 80°C/10^{-2} torr. Yield 1.3 g (59%) of *(4)*, m.p. 125–126°C. The hexane solution was evaporated to dryness in a vacuum and the residue sublimed at 40°C/10^{-2} torr. Yield 0.6 g (26%) of *(5)*, m.p. 65–66°C.

3-Chloro-1H-2-benzazepin-1-one (7): 5.8 g (0.03 mole) of 2-(chloroformyl)-*cis*-cinnamonitrile *(6)*[4] (from 2-nitroso-1-naphthol and PCl_5 in hexane in 73% yield) was dissolved in 30 ml of dioxane. HCl was passed in at 70°C for 5 h. After removal of the dioxane in a vacuum the residue was treated with ether and then sublimed at 80–85°C/10^{-2} torr. Yield 2.6 g (45%) of *(7)*, m.p. 117°C.

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[2] *S. Gabriel*, Ber. dtsch. chem. Ges. *19*, 2354 (1886).

[3] *R. Lesser* and *A. Schoeller*, Ber. dtsch. chem. Ges. *47*, 2505 (1914).

[4] *J. A. Elvidge* and *D. E. H. Jones*, J. chem. Soc. (London) *C 1967*, 2059.

[5] *Houben-Weyl-Müller*: Methoden der organischen Chemie. Thieme, Stuttgart 1955, Vol. IX, p. 942.

Simplified Process for Preparation of Anhydrides of Aromatic Acids

By *P. Rambacher* and *S. Mäke* [*]

Anhydrides of aromatic carboxylic acids are prepared by reaction of an acid chloride with the sodium salt of the same or another acid [1], or by treating the acid chloride with pyridine and decomposing the reaction mixture with water [2]. The procedure becomes appreciably simpler if the acid chloride is allowed to react with a solution of sodium hydrogen carbonate to which a small amount of a weak tertiary base such as pyridine has been added. Use of a water-insoluble base or alkali hydroxide in place of the hydrogen carbonate leads to considerably lower yields [3]. The reaction is also suitable for preparation of large amounts of anhydride in very good yield and high purity.

o-Ethoxybenzoic anhydride: 16.8 g (0.2 mole) of sodium hydrogen carbonate is dissolved in 300 ml of water. 4 ml of pyridine is added, then 36.9 g (0.2 mole) of *o*-ethoxybenzoyl chloride is added dropwise during 30 min. The temperature is kept at 20 °C by cooling. 29.1 g (92.7%) of the anhydride (m.p. 74–75 °C) is isolated after 1 hour's stirring. Recrystallization from benzene/ethanol gives rod-shaped crystals of m.p. 77.5 °C.

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[2] *Houben-Weyl-Müller*: Methoden der organischen Chemie. 4 th. Edit., Thieme, Stuttgart 1952, Vol. VIII, p. 477.

[3] *L. Edeleanu* and *A. Zaharia*, Bull. Soc. Sciinte Fizice *3*, 80 (1894).

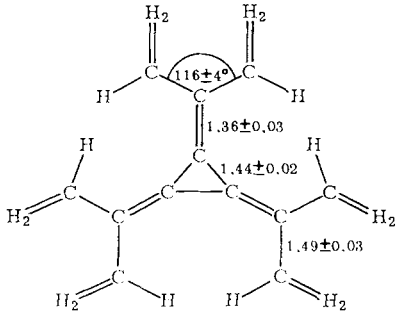
Crystal Structure of Triisopropylidenecyclopropane

By *H. Dietrich* and *H. Dierks* [*]

Triisopropylidenecyclopropane (prepared by *Köbrich et al.* [1]) crystallizes in the space group $P\,6_1$ (C_6^2) with $a = 9.39$ Å, $c = 21.36$ Å, $V = 1631$ Å^3, $n = 6$, and X-ray density 0.9912 g cm^{-3}. The space group and unit cell were determined previously by *Dunitz* and *Mugnoli* [2] who, however, found different cell dimensions and a much greater density.

We used three-dimensional X-ray diffraction data (filtered Cu–K_α radiation, multifilm technique), the intensities of reflections being estimated visually with the aid of comparison scales.

The molecules are arranged in flat sheets perpendicular to the *c*-axis, as concluded previously by *Dunitz* and *Mugnoli* from the high intensity of the (001) reflections. In crystals obtained by recrystallization from ethanol these layers are apparently stacked irregularly, as can be recognized in the diffraction diagrams from extension of the reflections along the length *c**. This disorder could be removed, as suggested by *Köbrich*, by tempering the crystals for 24 h at 120 °C.



The Figure shows the bond lengths and bond angles at the present stage of refinement ($R = 0.16$). The figures given are the mean values of chemically equivalent bonds and angles and their double standard error ($\pm 2\sigma$), calculated from the scatter of the individual values. The bonds in the cyclopropane ring are remarkably short, a fact which is probably due to the interaction between the three neighboring double bonds.

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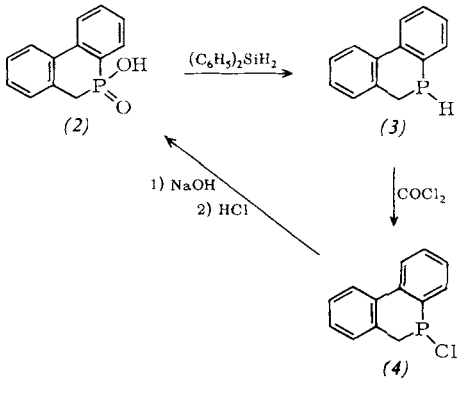
Dibenzo[*b,d*]phosphorin

By *P. de Koe*, *R. van Veen*, and *F. Bickelhaupt* [*]

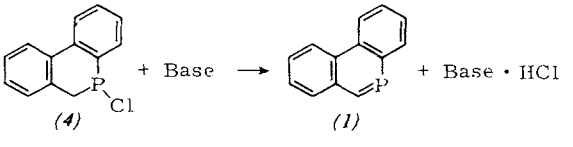
As part of our studies of aromatic compounds containing tervalent pπ-hybridized phosphorus as heteroatom we prepared the linearly annelated dibenzo[*b,e*]phosphorin [1]; we now report the preparation of dibenzo[*b,d*]phosphorin (= 9-phosphaphenanthrene) *(1)* in solution.

As starting material we used 5,6-dihydro-5-hydroxydibenzo[*b,d*]phosphorin-5-one *(2)* [2], which was reduced to 5,6-dihydrodibenzo[*b,d*]phosphorin *(3)* [4], b.p. 132 °C/0.01 torr, in 92% yield by diphenylsilane [3]. 20.15 g of *(3)* in 350 ml of methylene chloride was stirred under nitrogen with 7.3 ml of phosgene for 1/2 h at −30 °C and then for 1/2 h at room temperature [5]. The residue obtained on evaporation under vacuum gave, on molecular distillation (bath temperature 160 °C, 0.001 torr), 5-chloro-5,6-dihydrodibenzo[*b,d*]phosphorin *(4)* [4], m.p. 58–62 °C, as main fraction in a yield of 35%.



Removal of HCl was achieved by treating 490.6 mg of the product *(4)* in 90 ml of anhydrous, degassed ether at −196 °C with 394.6 mg of 1,5-diazabicyclo[5.4.0]undec-5-ene *(5)* [6] (23% excess) and, after the vessel had been sealed in a vacuum, warming the mixture to room temperature. A yellow precipitate was formed [after 3 h, 368.5 mg, of which 291.9 mg was hydrochloride of *(5)* (= 73% yield)]; for determination of the UV spectrum the colorless solution was filtered from the precipitate into a glass-to-glass sealed 0.1 cm cuvette.

The spectrum obtained (Fig. 1), which we ascribe to compound *(1)*, reached maximum intensity after 3 hours (extinction $E = 0.45$ at $\lambda = 372$ nm). When compared with the



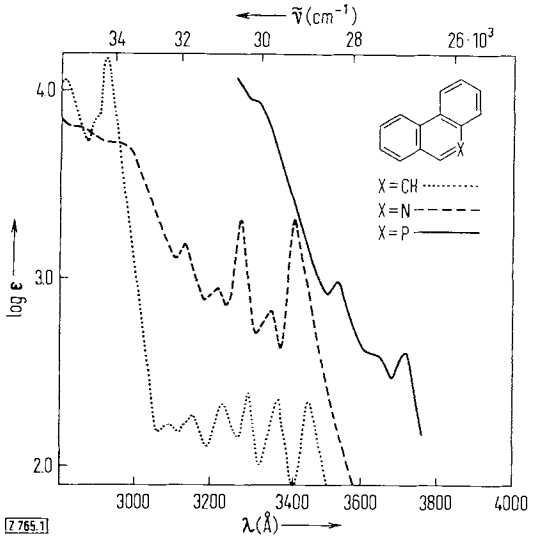


Fig. 1. UV spectra of phenanthrene (in cyclohexane), phenanthridine (in cyclohexane), and *(1)* (in ether). (The height of the curve for *(1)* is arbitrary.)

spectra of phenanthrene and phenanthridine it shows the known bathochromic shift ($\Delta\tilde{\nu}$ = 1950 cm^{-1} or 2350 cm^{-1}, resp.), which is less than for other heterocyclic aromatic phosphorus compounds[1,7]. In contrast to results in the anthracene series[1] the shape of the spectrum of *(1)* resembles that of the nitrogen analog more than that of the carbon analog. Dibenzo[*b,d*]phosphorin *(1)* could not so far be isolated in pure form. Its stability appears comparable with that of dibenzo[*b,e*]phosphorin: the intensity of the UV absorption of an ethereal solution of *(1)* decreases to about a half of its original value in three days and decreases irreversibly on cooling to −196 °C. *(1)* is unstable towards air.

In the mass spectrum of *(4)* the singly and doubly charged ions of *(1)* are prominent: *m/e* = 232, 28%, *(4)*$^+$; *m/e* = 196, 100%, *(1)*$^+$; *m/e* = 165, 37%, fluorenyl$^+$; *m/e* = 152, 7.5%, biphenylene$^+$; *m/e* = 98, 8.2%, *(1)*$^{2+}$[8].

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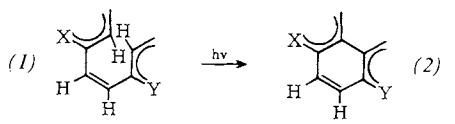
[8] We thank Prof. *Th. J. de Boer* and Drs. *N. M. M. Nibbering* of the Institute of Organic Chemistry, University of Amsterdam for measuring the mass spectrum and for help in its interpretation.

Photochemical Cyclodehydrogenations in the Indole Series[1]

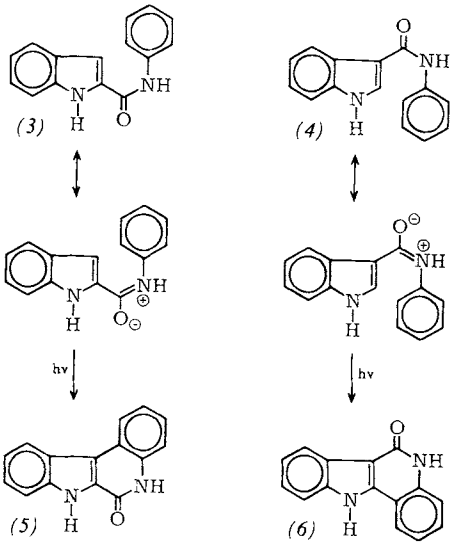
By *E. Winterfeldt* and *H. J. Altmann*[*]

Photocyclization of stilbene derivatives *(1)* affords highly condensed aromatic compounds *(2)* in a simple manner[2]. The benzene ring may be replaced by heterocycles[3].



As the amide group has a certain amount of double bond character (hindrance of rotation), this group can also be used to link the aromatic rings, as was demonstrated by means of benzanilide[4].

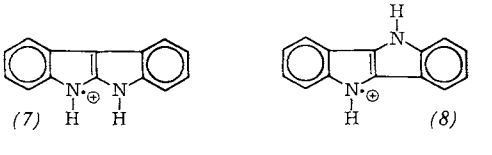
We have now irradiated the anilides *(3)* and *(4)* of α- and β-indolecarboxylic acid and have obtained the cyclization products *(5)* and *(6)* as the main products of a smooth reaction; they are readily recognized by means of their UV spectra. Further, absence of the signal of the α- or β-indole proton in the NMR spectrum proves completion of the cyclization.



(5): melts from 280 °C with sublimation	*(6)*: melts from 280 °C with sublimation
UV: λ_{max} (ε) 245 (36200), 268.5 (14900), 292 (4270), 305 (6400), 320 (5620), 333 (10200) 349 nm (11500).	UV: λ_{max} (ε) 222 (47500), 246 (49000), 293 (6590), 306 (7300), 322 (13900), 337 nm (19000).
IR: 1530, 1565, 1585, 1610, 1650 cm^{-1}.	IR: 1550, 1580, 1610, 1635 cm^{-1}.
NMR: τ = −2.4 (1), −1.9 (1), 1.5 (2), 2.5 (6).	NMR: τ = −2.6 (1), −1.5 (1), 1.75 (2), 2.5 (6).
MS: 234 *m/e* (100%) → 216 *m/e* (8%) M$^+$ 199.4 234 *m/e* (100%) → 205 *m/e* (19%) M$^+$ 180.5 117 *m/e* (8%) 103 *m/e* (12%)	MS: 234 *m/e* (100%) → 205 *m/e* (12%) M$^+$ 180 117 *m/e* (11%) → 103 *m/e* (15%) M$^+$ 90.5 102.5 *m/e* = 205/2 68.33 *m/e* = 205/3

The two products have been prepared previously by a more difficult route[4,5]; however, compound *(6)* could not be isolated in pure form. These compounds are conveniently accessible by the cyclodehydrogenation.

For both substances the molecular ion is the base peak in the mass spectrum, and conversion of this ion into the fragment *(7)* or *(8)* with loss of CO − proved by a metastable peak at 180 − is characteristic.



Experimental:

A solution of the anilide (100 mg) in dioxane (10 ml) and acetone (1 ml) is irradiated in a quartz vessel with a 500-watt medium-pressure mercury-quartz lamp for 60 hours. The cyclized products are eluted with methylene chloride acetone (1:1 v/v). Yield 15%.

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Separation and Properties of the *cis-trans*-Isomers of *N*-Alkylthioformamides

By *W. Walter, E. Schaumann*, and *K.-J. Reubke*[*]

Since the thioamide system is planar by mesomerism, two isomers *(a)* and *(b)* may occur when $R^1 \pm R^2$.

(a) *(b)*

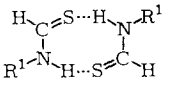
(1), R = R^2 = H, R^1 = $CH(CH_3)_2$
(2), R = R^2 = H, R^1 = CH_2-$CH(CH_3)_2$
(3), R = R^2 = H, R^1 = CH_2-C_6H_5

The rational isomers have proved separable so far only for *N,N*-dialkyl compounds[1] in the thioamide series and, among the secondary amides, for 2,4,6-tri-*tert*-butylacetanilide, in which rotation is sterically strongly hindered[2]. For *N*-alkylthioformamides (R = R^2 = H) there exist only ^{1}H–NMR investigations of the equilibrium position (pure liquid or solution in $CHCl_3$), but these show that, except for *N*-*tert*-butylthioformamide, the sterically unfavorable *trans*- or *Z* form[**] predominates over the *cis*- or *E* form[**][3,4].

By preparative thin-layer chromatography on silica gel (Merck PF 254) at –15 °C with acetic ester:hexane:diethylamine (4:10:1 v/v), applied five times successively, we have succeeded in isolating the forms *(a)* and *(b)* of the thioamides *(1)*, *(2)*, and *(3)*. After separation from the silica gel, the isomers of *(1)* and *(2)* were obtained as brownish liquids and those of *(3)* were obtained as brownish solids, each of these containing not more than 10% of the other isomer. Identification was effected by the ^{1}H–NMR spectrum[3] and by IR spectroscopy for the NH stretching modes (2×10^{-3} M solution CCl_4). The isomers had little stability at room temperature; the half-time for establishment of equilibrium at –15 °C is about four weeks. Thus the success of the separation is due less to a high activation energy than to a distinct difference in polarity of the isomers.

The IR spectra of *(a)* and *(b)* differ appreciably [film, *(3)* in KBr]. Noteworthy are the high intensities of the thioamide *B*-bands and their shift to higher wave numbers in the *E*-isomers *(a)* in comparison with the *Z*-isomers *(b)*: for *(a)* 1555 to 1565 cm^{-1} were found, and for *(b)* 1520 to 1530 cm^{-1}.

The changes in the IR spectrum of the *E*-isomers above 3000 cm^{-1} in comparison with the *Z*-forms and the equilibrium mixtures, and in particular the appearance of a new band at 3070 cm^{-1}, are ascribed by us to occurrence of cyclic dimers of type *(4)*.



(4)

In the UV spectrum the absorption maximum of the $\pi \rightarrow \pi^*$ transition is observed at longer wavelength for the *E*-isomer *(a)* than for the *Z*-isomer *(b)* (276 compared with 266 nm, in $CHCl_3$).

The isomers differ also in the rate of complex formation with cupric acetate; this should be possible only with the *E*-form *(a)*. In fact, 50% reaction (room temperature, $CHCl_3$) of *(a)* requires only a few minutes, but of *(b)* requires about 2 hours because of the need for conversion into the other form – the reactions can be followed by disappearance of the $\pi \rightarrow \pi^*$ bands.

The predominance of *Z*-isomers *(b)* in the equilibrium mixture can be understood on the basis of the dipoles: for form *Z (b)* there is considerable compensation *(6)*, but for form *E (a)* there is addition *(5)*, whereby *(a)* becomes electrostatically disfavored.

(5) *(6)*

Very marked electron delocalization within the thioamide system occurs in order to offset this disadvantage of the *E*-form *(a)*, and this may explain the short-wave shift of the thioamide *B*-bands (larger C–N double-bond character) and the bathochromic shift of the $\pi \rightarrow \pi^*$ transition.

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[**] For nomenclature see *J. E. Blackwood, C. L. Gladys, K. L. Loening, A. E. Petrarca*, and *J. E. Rush*, J. Amer. chem. Soc. *90*, 509 (1968).

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Acid-catalyzed Rearrangements of Hexamethylprismane and Hexamethyl-Dewar-benzene

By *R. Criegee* and *H. Grüner*[*]

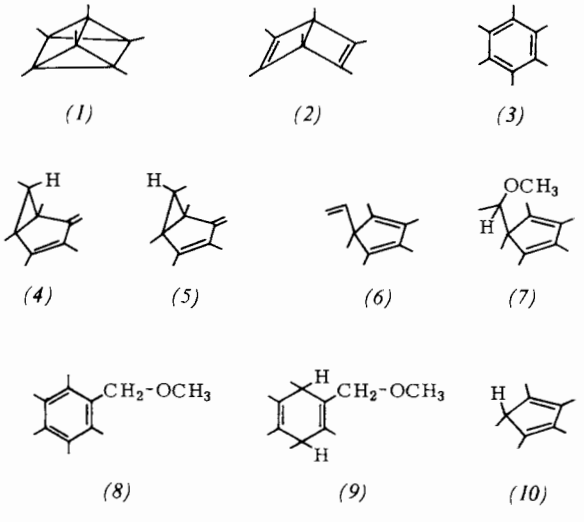
On thermal and metal-catalyzed decomposition, hexamethylprismane *(1)* gives variable amounts of hexamethyl-Dewarbenzene *(2)* and hexamethylbenzene *(3)*[1–3]. On the other hand, after reaction of *(1)* with 2% of *p*-toluenesulfonic acid (TsOH) in CCl_4 at 35–40 °C for 69 h the NMR spectrum shows that the sole product besides 10–20% of *(3)* is the 1,2,3,5,6-pentamethyl-4-methylenebicyclo[3.1.0]hex-2-ene *(4)* that was previously obtained by *Schäfer* and *Hellmann*[4] by another route. Product *(4)* was, however, isolated in only 37% yield because of its ready polymerization. The position of the methyl doublet (τ = 9.08) and of the quartet for the

single proton ($\tau = 9.40$) indicate the *exo*-position for the methyl group on the three-membered ring.

When *(4)* is warmed at 105 °C for 2 h with 2% of TsOH in benzene an equilibrium mixture – attainable from both sides – is formed containing approximately equal amounts of *(4)* and its *endo*-methyl isomer *(5)*, which was also obtained by *Schäfer* using a different method[5]. In the NMR spectrum of *(5)* the signals for the methyl group on the three-membered ring and for the single proton are at $\tau = 9.34$ and 9.25, respectively.

In the presence of 2% of TsOH in *o*-dichlorobenzene at 110 °C the compounds *(4)* and *(5)* rearrange almost quantitatively to 1,2,3,4,5-pentamethyl-5-vinylcyclopentadiene *(6)*[4], whose constitution follows from, *inter alia*, the UV spectrum (in hexane, $\lambda_{max} = 242$ nm, $\log \varepsilon = 3.82$) and the NMR spectrum [CCl_4; quart. methyl $\tau = 9.00$ (singlet), methyl on the double bonds $\tau = 8.33$ (singlet) and 8.23 (singlet), and vinyl protons recognizable only after addition of benzene as a multiplet at $\tau = 4.93$]. Compound *(6)* gives an adduct with maleic anhydride and when boiled with 1% methanolic sulfuric acid is partly converted into the ether *(7)*.

When compound *(2)* is boiled for 40 h with 0.03% sulfuric acid in methanol there is formed, as well as 13% of *(3)*, a mixture (separable by gas-chromatography or by distillation through a rotating-band column) containing 55% of 5-(1-methoxyethyl)-1,2,3,4,5-pentamethylcyclopentadiene *(7)*, 24% of 5-(methoxymethyl)-1,2,3,4,6-pentamethyl-1,4-cyclohexadiene *(9)*, and 4% of 1,2,3,4,5-pentamethylcyclopentadiene *(10)*. In hexane the ether *(7)* has $\lambda_{max} = 260$ nm ($\log \varepsilon = 3.58$) and in the NMR spectrum (CCl_4) gives signals at $\tau = 9.45$ (doublet, $J = 6$ Hz), 9.02 (singlet), 8.33 (multiplet), 6.93 (quartet, $J = 6$ Hz), and 6.73 (singlet) in the ratio 3:3:12:1:3 [6].



(1) *(2)* *(3)* *(4)* *(5)* *(6)* *(7)* *(8)* *(9)* *(10)*

With maleic anhydride compound *(2)* gives an adduct of m.p. 159–161 °C. The constitution of the isomeric ether *(9)* follows from absence of a UV maximum and from the NMR spectrum (CCl_4) which contains two doublets at $\tau = 9.02$ and 8.92 ($J = 7$ Hz) and the multiplet corresponding to the single proton at $\tau = 7.66$, also singlets for the methyl groups on the double bonds at $\tau = 8.38$ and 8.32, for the methoxy group at $\tau = 6.83$, and for the methylene group at $\tau = 6.15$ ppm with the expected intensity ratios. When heated for 27 h in a sealed ampoule at 270 °C compound *(9)* loses water and gives (methoxymethyl)pentamethylbenzene *(8)* of m.p. 63–65 °C, identical with a product synthesized from (chloromethyl)-pentamethylbenzene[7]. On catalytic hydrogenation it is converted into *(8)* and *(9)*.

Pentamethylcyclopentadiene *(10)*[8] [b.p. 39–40 °C/5 torr; λ_{max} (hexane) = 266, 250, 230 nm ($\log \varepsilon = 3.43$, 3.42, 3.37); NMR (CCl_4) $\tau = 9.04$ (doublet, $J = 7.5$ Hz), 8.25 (multiplet and 7.72 (multiplet) in proportions 3:12:1] gives a maleic anhydride adduct of m.p. 131–134 °C and is to be regarded as a fragmentation product of *(7)*, from which it is formed on 120-hours' heating with 0.1% methanolic sulfuric acid.

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[6] The corresponding chloro compound was mentioned by *H. Hellmann*, Chimia *22*, 50 (1968). According to a personal communication from *W. Schäfer* (March 13, 1968) he has obtained *(7)* by the same route as used by us.

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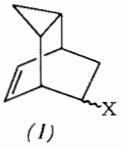
Valence Isomerizations of C_9H_{10} Hydrocarbons[1]

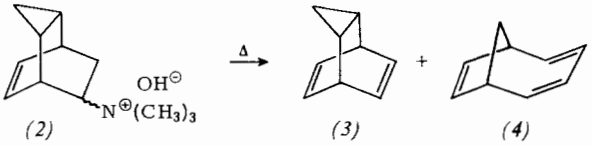
By *J. Daub* and *P. v. R. Schleyer*[*]

Quickening interest in the preparation, the interconversions, and other special properties of C_9H_{10} hydrocarbons and related systems[2–9] reflects the fascinating potential of these molecules. An hitherto unreported member of the C_9H_{10} family, tricyclo[3.2.2.0^{2,4}]nona-6,8-diene *(3)*, is the focus of attention of this communication.



(1)

(a), X = CN *(d)*, X = $NHCOOCH_3$
(b), X = COOH *(e)*, X = $NHCH_3$
(c), X = NCO *(f)*, X = $N^{\oplus}(CH_3)_3I^{\ominus}$

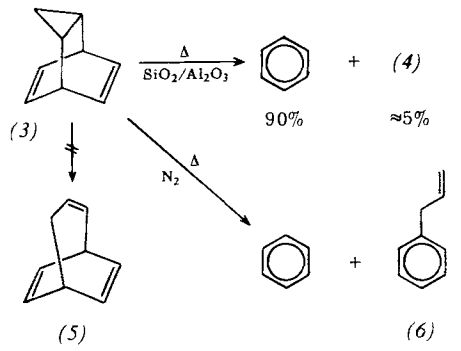


(2) *(3)* *(4)*

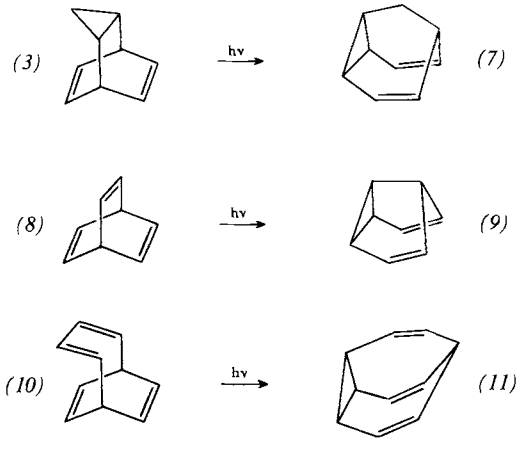
The Diels-Alder adduct of cycloheptatriene and acrylonitrile *(1a)*, a 60:40 mixture of *endo* and *exo* isomers, could be prepared in 44% yield at 170 °C. Conversion of *(1a)* to *(3)* followed a standard sequence involving intermediates *(1b)* through *(2)*[10]. The final step, the pyrolysis of quartenary salt *(2)*, gave a 55% yield of a C_9H_{10} fraction (b.p. 83–86 °C/40 torr) which proved to be a 4:1 mixture of *(3)* and an isomerized product *(4)*, bicyclo[4.2.1]nona-2,4,7-triene[4,6–8]. We think it likely that the latter arose by a cationic rearrangement route.

After purification by preparative gas chromatography[11], *(3)* was characterized spectroscopically: IR in CCl_4: 3050, 3005, 2955, 1630, 1580, 1435, 1355, 1250, 1215, 1095, 1040, 1020, 965, 900, 710, and 670 cm^{-1}; MNR in CCl_4: multiplets at $\tau = 9.4$ and 8.9 (secondary and tertiary cyclopropane hydrogens, respectively), $\tau = 6.4$ (bridgehead hydrogens), and quartets due to the two types of vinyl hydrogens at $\tau \approx 4.1$ and 3.55. When *(3)* was reduced with an uptake of 2 moles of hydrogen, tricyclo[3.2.2.0^{2,4}]nonane[12] was formed.

When *(3)* was pyrolyzed under nitrogen in the presence of silica-alumina catalyst at 240 °C, benzene was produced in

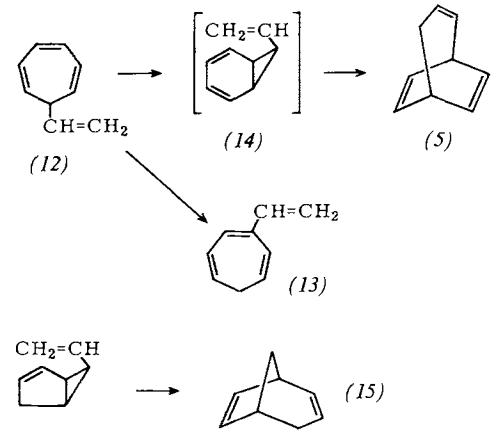


90 % yield. The desired ring-opening to give bicyclo[3.2.2]-nona-2,6,8-triene *(5)*[7] was not observed, but a small amount of by-product, tentatively identified as *(4)*, was formed. Pyrolysis of *(3)* in a nitrogen stream over Raschig rings at 310 °C gave benzene and allylbenzene *(6)* in a 2:1 ratio. Under these conditions neither *(4)* nor *(5)* was produced. The formation of benzene as the major product in these reactions suggests that cyclopropene was also formed, but we did not establish this possibility experimentally.



Photolysis of *(3)* (1 % solution in pentane/acetone (1:1 v/v); 450 W Hanovia Lamp, no filter) proceeded to give yet another product, tricyclo[3.3.1.$0^{2,8}$]nona-3,7-diene ("barbaralane") *(7)*, whose NMR spectrum agreed well with that reported[9]. Barbaralane *(7)* was not stable under these conditions; the yields were much higher at low conversions than at higher ones. This photolysis isomerization of *(3)* is reminiscent of the similar conversion of barrelene *(8)* to semibullvalene *(9)*[13] and of bicyclo[4.2.2]deca-2,4,8,9-tetraene *(10)* to bullvalene *(11)*[14]; perhaps the mechanisms of these transformations[13] also are analogous.

When 7-vinylcycloheptatriene *(12)*[15] was heated to 150 °C under a nitrogen atmosphere for 13.5 hours only a 13 % yield of a C_9H_{10} fraction (b.p. 55–57 °C/10 torr) was recovered by distillation from the higher boiling residue. Gas chromatography showed the volatile fraction to consist of 75 % bicyclo[3.2.2]nona-2,6,8-triene *(5)*[7] and 25 % 3-vinylcycloheptatriene *(13)*[15]. The IR spectrum of *(5)* was identical with that reported[7]; the NMR spectrum in CCl_4 showed absorptions at $\tau = 7.9$ (CH_2 group, complex quartet), $\tau = 7.05$ (bridgehead protons, multiplet), $\tau = 5.2$ and 4.2 (protons on the three carbon bridge, tripled AB spectrum with $J_{AB} = 11$ Hz), $\tau = 3.95$ and 3.55 (two olefinic protons each, complex triplet).



The formation of *(5)* evidently proceeded through the vinylnorcaradiene derivative *(14)* as intermediate. A similar reaction has recently been reported by *Goldstein* and *Odell*[16]; we have utilized an analogous vinylcyclopropane rearrangement for the synthesis of bicyclo[3.2.1]octa-2,6-diene *(15)*[17].

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[10] Cf. our recent use of a similar route for an analogous preparation [5].

[11] 15 % Carbowax, 60/80 mesh Chromosorb W, 125 °C.

[12] A reference sample of this compound was synthesized by cyclopropanation of bicyclo[2.2.2]octene. Tricyclo[3.2.2.$0^{2,4}$]-nonane has m.p. 125 °C; IR in CCl_4: 3075, 3005, and 1030 cm^{-1}; NMR in CCl_4: $\tau = 9.65$ and 9.15 (secondary and tertiary cyclopropane hydrogens), $\tau = 8.72$ and 8.44 (methylene hydrogens), and $\tau = 8.15$ (bridgehead hydrogens).

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Structure of Dimethylnitrosaminecopper(II) Chloride[1]

By *U. Klement* and *A. Schmidpeter*[*][2]

Nitrosamines form addition compounds with metal halides and non-metal halides. Potentially each of the three atoms of the nitrosamine skeleton possesses a donor function. In the case of halides having a prominent Lewis acid character coordination of the amino nitrogen was first assumed[3]; later, ^{1}H–NMR spectroscopic studies revealed coordination of the nitroso oxygen atom[4]. The IR spectra of nitrosamine complexes of the transition metal halides likewise indicate the presence of bonding to the oxygen atom[4, 5]; however, the nature of the bonding is unclear as yet since the stoichiometry of the 1:1 complexes with metal(II) halides suggests that they contain the nitrosamine not only as unidentate ligand.

We have examined X-ray spectrographically the well developed, but easily cleavable, red crystals of $(CH_3)_2N{-}NOCuCl_2$ *(1)*. The lattice constants (in Å) have the following values: $a = 6.376$, $b = 14.685$, $c = 7.265$; the space grouping is D_{2h}^{16}–*Pnam*. According to the density, 2.07 g/cm^3, the unit cell contains four formula units. 730 reflections were measured (counting tube) and corrected for absorption and the Lorentz polarization factor. Isotropic refinement of the values by the method of least squares led to an R value of 15%; further refinements are being carried out.

The structural skeleton is formed by slightly puckered $CuCl_2$ chains which run through the crystal parallel to the x-axis and in which the copper atoms are coupled by double chlorine bridges.

The distance between neighboring chains is 7.34 Å in the y-direction and 3.6 Å in the z-direction. In the x-direction the chains are shifted by about 0.5 Å with respect to one another. The nitrosamine molecules are perfectly planar and arranged alternately on both sides of a chain and with the copper atoms situated in the same plane paralled to (001). They direct thereby the nitroso group, which is approximately aligned with the axis of the chain, to the chain. The nitrosamine molecules of neighboring chains lie inverted above each other. The planarity was first proved independently of the space group symmetry, in that calculations were made for the noncentrosymmetric sub-group C_{2v}^9–*Pna*2$_1$. Further refinement and the reflection statistics showed a centrosymmetric space group and that all atoms except chlorine lie in the mirror plane. The layer structure appears also in the extreme cleavability parallel to (001).

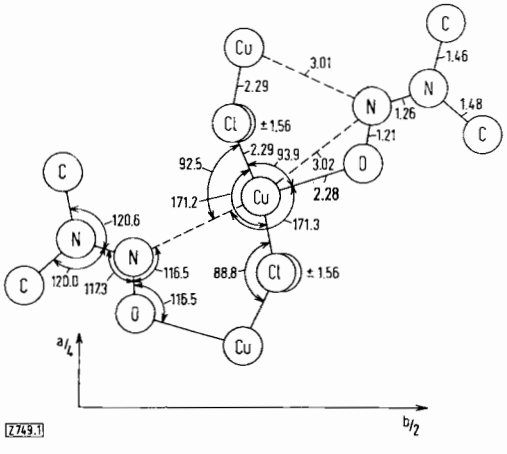
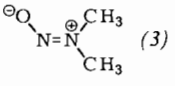


Fig. 1. (001)-Projection of two formula units of *(1)* with bond lengths (Å) and angles.

The structure found is reminiscent of that of the 1,2,4-triazolecopper(II) chloride *(2)*[6]. In both cases the copper atom is approximately octahedrally surrounded by four chlorine atoms and two donor functions of two molecule ligands situated *trans* to each other. In *(1)* the nitroso group appears in place of the neighboring nitrogen atoms of the ring in *(2)*. In both cases the $CuCl_2$ chain is folded as a result of the bridging of the copper atoms *via* the ligating molecules. In detail, however, the structures *(1)* and *(2)* are fundamentally different. In *(2)* and in the compound L_2CuCl_2 (L = H_2O[7], pyridine[8]) the chlorine atoms round a Cu atom form a rhombus with two short Cu–Cl distances of 2.28 to 2.34 Å and two long distances of 2.77 to 3.05 Å; in *(1)* on the other hand they form a square with uniformly short Cu–Cl distances. Whilst in *(2)* two chlorine atoms lie in the direction of the Jahn-Teller distortion, in *(1)* these positions are clearly occupied by the donor atoms of the ligands. Correspondingly the distances Cu–O and Cu–N are here considerably longer than in $(H_2O)_2CuCl_2$ (with 2.01 Å[7]) and in $(C_5H_5N)_2CuCl_2$ (with 2.02 Å[8]).

However, the distance Cu–O is shorter and the distance Cu–N much longer than one would expect to be the case along the axis of the Jahn-Teller distortion (both about 2.6 Å). The bonding of the copper to the nitrosamine is thus mainly *via* the oxygen. The nitroso nitrogen is equidistant from two neighboring copper atoms of a chain. The difference between the Cu–O and Cu–N distance is made possible by the fact that the Cu protrudes about 0.2 Å from the plane of surrounding chlorine atoms in the direction of the oxygen. A transition from octahedral to square pyramidal environment is therefore suggested.

The complexed nitrosamine is best described by the limiting formula *(3)*.



(3)

This formula also makes the weak bonding of the nitroso nitrogen understandable; the use of its lone pair leads to adjacent partial positive charges. The bond lengths of the free dimethylnitrosamine are not known. The best indication is provided by the values of methyl nitrite[9]; if one considers the spectroscopically verified stronger participation of the free lone pair of the amino nitrogen then for the nitrosamine N–O of 1.27 Å and N–N of 1.37 Å can be estimated. Compared with these values the N–N distance in *(1)* is, as expected, considerably shortened; remarkably, however, the N–O distance is also shortened.

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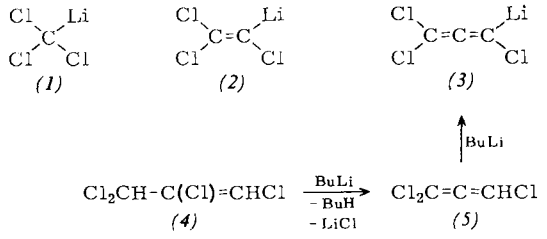
Cycloadducts from Trichloroallenyllithium[1]

By *G. Köbrich* and *E. Wagner*[*]

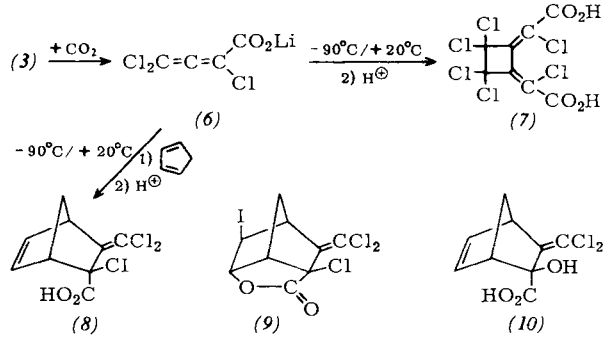
Trichloroallenyllithium *(3)* is interesting as a homolog of the known carbenoids *(1)* and *(2)*[2]; further, lithioallenes have hitherto been known only as intermediates[3].

We obtained stable solutions of *(3)* on treating trichloroallene *(5)*[4] or, better, 1,2,3,3-tetrachloro-1-propene *(4)* (*cis* and/

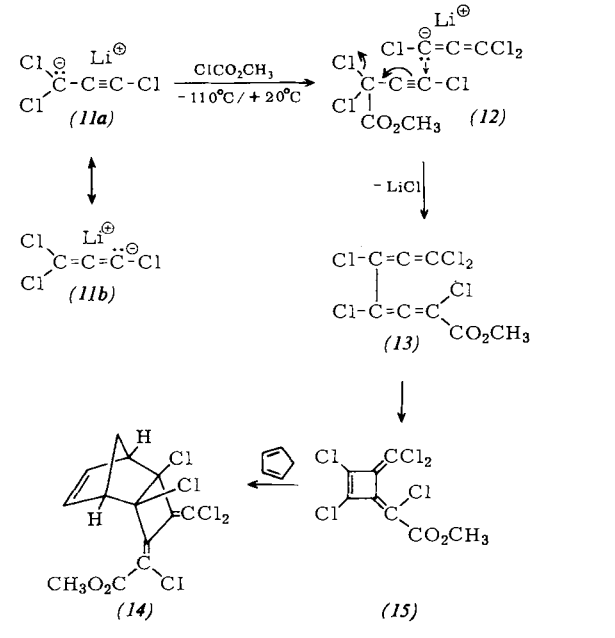


or *trans*)[5] with one or two molecular equivalents of *n*-butyllithium, respectively, in Trapp mixture[6] at −110 °C.

Trichloroallene *(5)* is metalated faster than it is formed from *(4)*, since only *(4)* is obtained alongside *(3)* if a sample of *(4)* is treated with less than 2 molecular equivalents of *n*-butyllithium. Carboxylation of *(3)* affords a mixture of dimeric carboxylic acids in 90% yield. About half of this mixture consists of *(7)*[4], which can be separated as the dimethyl ester (m.p. 161.5–163.5 °C)[7]. Proof that formation of monomeric trichloroallenyllithium from *(4)* is almost quantitative is provided by the diene reaction of the primary product *(6)* of carboxylation with cyclopentadiene (added at −90 °C), which gives a structurally homogeneous adduct $C_9H_7Cl_3O_2$ of m.p. 141–143 °C [yield 91% calculated on the amount of *(4)* used]. Of the four theoretically possible isomers the iodolactone reaction[8] decides in favor of *(8)* since it gives the tricyclic compound *(9)* (m.p. 157–158 °C; $\nu_{C=O}$ = 1800 cm^{-1}). In hot $NaHCO_3$ solution compound *(8)* forms *(10)* (m.p. 111–112 °C) instead of a tricyclene[8].



The deep violet color of trichloroallenyllithium indicates an ion-pair structure with the limiting forms *(11a)* and *(11b)*. The reasonable ambivalence is realized, at least formally, on treatment with methyl chloroformate which attacks at C-3 in contrast to carboxylation; surprisingly, the sole defined product is the unstable dimethylenecyclobutene *(15)* (m.p. 71–73 °C), which we consider to arise from the primary product *(12)* and an excess of *(3)* by way of the diallene *(13)* with subsequent cyclization.



Compound *(15)* and cyclopentadiene give the adduct *(14)* (m.p. 143-144.5 °C), whose NMR spectrum shows different τ values (6.44 and 6.66, each a quartet with J = 1.8–2.0 Hz) for the two bridgehead protons. This must be due to the influence of the ester group, which, therefore, is probably spatially close to a bridgehead and thus assumes in *(15)* a position remote from the second exocyclic double bond.

Thermolysis of *(3)*, which begins at −90 °C, gives neither tetrachlorohexapentaene nor the product of a dimerizing α-elimination, and no cyclopropane derivative if cyclohexene is added, but, instead, soot-like polymers are formed.

Experimental:

Preparation of *(3)*: A solution of 20 mmoles of *(4)* in 48 ml of Trapp mixture is treated dropwise under N_2 at −110 °C within 10–15 min with 40 mmoles of *n*-butyllithium in 20 ml of petroleum ether, and the mixture is stirred for a further 40–45 min at −110 °C.

Preparation of *(8)*: Compound *(3)* is carboxylated with an excess of pre-cooled powdered dry-ice[9], 24 ml of distilled cyclopentadiene is added and the mixture is allowed to come to room temperature within 24 h. On working-up by the usual technique[9], 4.61 g (91%) of *(8)*, m.p. 141–143 °C (after crystallization from CCl_4 and sublimation at 110 °C/1 torr), is obtained as acidic portion.

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[6] THF, ether, and petroleum ether (4:1:1) [9].

[7] Structures of new compounds are proved by analytical and spectroscopic data.

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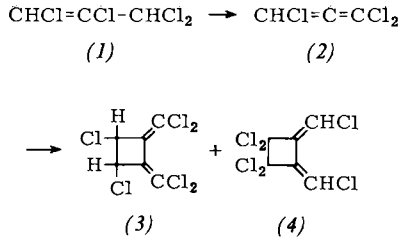
Preparation and Dimerization of Trichloroallene[1]

By *A. Roedig* and *N. Detzer*[*]

Treating 1,2,3,3-tetrachloro-1-propene *(1)* (*cis* and/or *trans*)[2] in a propane-ammonia mixture with sodamide gives trichloroallene *(2)* as an almost colorless liquid, which gradually solidifies (yield 76.5%). If recorded immediately after removal of a sample from the cooling bath, the IR spectrum (capillary layer) of this compound shows the bands at 1940 and 760 cm^{-1} typical of an allene, but warming causes these to change rapidly to the bands of the dimers *(3)* and *(4)*. Undiluted *(2)* decomposes explosively at room temperature. In petroleum ether, dimerization is complete in 3 days at 20 °C.



(1) (2) (3) (4)

The dimer mixture is not separable by distillation; its ^{1}H–NMR spectrum contains signals at $\tau = 5.08$ (very strong) and at 4.59, 3.03, and 2.97 (all weak). Calculation by the additivity scheme [3], which, however, does not permit differentiation of *cis*- from *trans*-isomers, gives $\tau = 5.10$ for *(3)* [4]. Since *trans* ring-protons usually have higher τ values than *cis* ring-protons [5], it is to be assumed that *(3)* exists mainly in the *trans*-form. The signals of the olefinic protons do not, however, permit a decision whether *cis-cis-* and *trans-trans-(3)* or only *cis-trans-(3)* is present in the mixture.

Experimental:

Trichloroallene *(2)*: 18 g of 1,2,3,3-tetrachloro-1-propene *(1)* is cooled to −75 °C in an N_2 atmosphere with rigid exclusion of moisture. 300 ml of propane and 50 ml of ammonia are condensed into this substance within $^1/_2$ h at the same temperature with stirring. Next, 5 g of water-free and benzene-free sodamide is added in small portions during 5 h and the mixture is stirred for a further 15 h at −75 °C. The resulting pale yellowish-green propane layer is then decanted from the dark ammonia layer and sucked through a fritted glass filter (externally cooled in dry ice), with exclusion of moisture, on to 50 g of a mixture (1:1) of active charcoal and silica gel that is placed in a flask cooled to −75 °C. The ammonia layer is washed again with three 50-ml portions of liquid propane. The united propane solutions are evaporated in a rotary evaporator at −70 °C at 12 torr and then at 0.1 torr, leaving the product *(2)* as a liquid that gradually solidifies to a white powder. Yield 11.0 g (76.5%).

Dimerization of *(2)*: 18.4 g of *(2)* in 45 ml of anhydrous petroleum ether (b.p. 30–50 °C) is kept at room temperature for 72 h with exclusion of moisture. After removal of the solvent in a vacuum the yellow oil is fractionated. 4.8 g of *(2)*, b.p. 42 °C/2 torr and a total of 13 g of mixed isomers *(3)* and *(4)*, b.p. 84 °C/0.01 torr, $n_D^{20} = 1.6051$ (after several distillations), are obtained.

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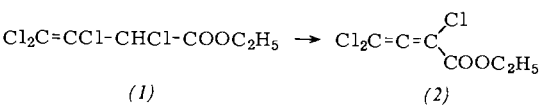
Preparation and Dimerization of Ethyl Trichloroallenecarboxylate [1]

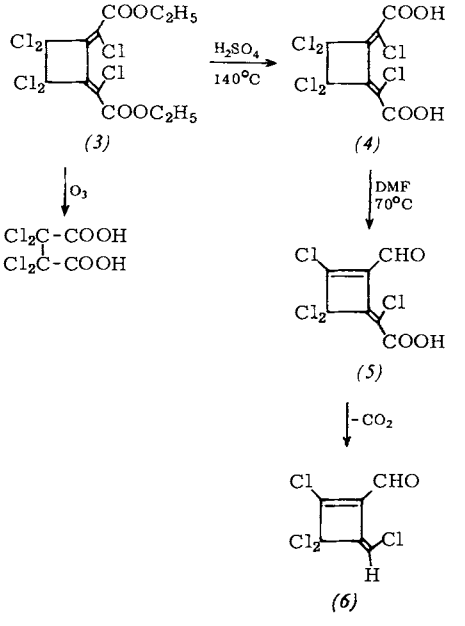
By *A. Roedig* and *N. Detzer* [*]

Reaction of ethyl 2,3,4,4-tetrachloro-3-butenoate *(1)* [2] and lithium *tert*-butoxide at −75 °C affords ethyl trichloroallenecarboxylate [trichloro-2,3-butadienoate] *(2)* as an almost colorless oil in 86% yield.



(1) (2)

The allenic ester *(2)* is less stable thermally than perchloroallene [3]. The intensity of the typical allene bands of the IR spectrum at 1953 cm^{-1} (capillary film) decreases very rapidly with increasing temperature. In contrast to that of trichloroallene [1], dimerization of *(2)* proceeds homogeneously in one direction; in light petroleum at room temperature it is complete in 20 h, affording a 100% yield of a crystalline dimer of m.p. 111–112 °C. Ozonization (0 °C, anhydrous methanol) of the dimer and oxidative hydrolysis (formic acid/perhydrol) give tetrachlorosuccinic acid, which was identified by IR-spectroscopical comparison with an authentic sample [4]. Thus the ethoxycarbonyl groups of the dimer are situated on the exocyclic methylene C atoms [5], but it has not been decided which stereoisomer is present: we assume that it is the *trans,trans*-form [6].



(3) (4) (5) (6)

The dicarboxylic acid *(4)* (decomp. 248 °C) corresponding to the diester *(3)* is decarboxylated in dimethylformamide at 70 °C, probably with allylic rearrangement by way of a kind of "Vilsmeier complex" that on hydrolysis yields the aldehydo acid *(5)* (decomp. 130 °C; yield 83%). The ^{1}H–NMR spectrum of *(5)* contains signals at $\tau = 1.94$ (aldehyde protons) and −0.70 (carboxyl protons). The acid *(5)* loses a further equivalent of CO_2 at about 100 °C with formation of the monoaldehyde *(6)*. Reaction of *(5)* with 2,4-dinitrophenylhydrazine solution at room temperature leads directly to the 2,4-dinitrophenylhydrazone (decomp. 238 °C) of *(6)*.

Experimental:

Ethyl trichloroallenecarboxylate *(2)*: The ester *(1)* (2.5 g, 10 mmoles) is cooled to −75 °C in a N_2 stream with rigid exclusion of moisture, propane (150 ml) is condensed in, and the whole is treated with lithium *tert*-butoxide (1.2 g, 15 mmoles) with stirring during 5 h. After a further 4 h at −75 °C the mixture is filtered rapidly into a vessel pre-cooled to −75 °C, and the propane is removed at −70 °C, first at 12 torr and then at 0.01 torr, leaving a colorless oil (yield 1.8 g, 86%). Diethyl 3,3,4,4,α,α′-hexachloro-$\Delta^{1,2}$-cyclobutanediacetate *(3)*: A solution of *(2)* (1.8 g) in 30 ml of dry light petroleum (b.p. 30–50 °C) is set aside for 20 h at room temperature with exclusion of moisture. Then, after removal of the solvent in a

vacuum there remains 1.8 g of *(3)* as almost pure, white crystals, m.p. 111–112 °C (from ethanol).

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Synthesis of Oligonucleotides on a Polymeric Carrier[1]

By *F. Cramer* and *H. Köster*[*]

For the synthesis of oligonucleotides on polymeric carriers, soluble[1,2] and cross-linked[3] polystyrenes have been used in which a mono- or a di-methoxytrityl group or a benzoyl group[4] acts as anchor for the growing chain.

The polymeric carriers used previously all swell to some extent, thereby giving rise to the following problems:

1. Reactions can be effected only in solvents that can swell. Only a limited number of solvents can be used to wash out by-products and excess of reagents.

2. Many substances are tenaciously retained by the gel, so that time-consuming washing with large quantities of solvent is necessary. In this respect, a soluble polystyrene is better than a polystyrene that is cross-linked with 1–2% of divinylbenzene (Merrifield type) since it can be purified by reprecipitation[1].

3. Use of aqueous systems for selective removal of protecting groups[5] is not always possible.

4. In syntheses by the diester method the growing chain has one charge per phosphodiester bond. The existence of an ionic species in a non-polar solvent cage may be one reason why, with increasing chain length, cleavage of the oligonucleotides from the polymeric carrier becomes increasingly difficult, as we found both with soluble polystyrene and with polystyrene cross-linked with 1–2% of divinylbenzene. Cleavage conditions had to be chosen that partially destroyed the labile *N*-glycosidic linkage of the purine nucleotides.

After systematic testing of various insoluble polymer types[6], we now use as polymeric carrier a highly cross-linked, rigid polystyrene-divinylbenzene copolymer whose porosity can be varied within wide limits. It can be obtained as beads that do not swell and has the following advantages:

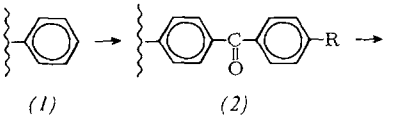
1. Aqueous solvents can be used; the carrier can be washed with all solvents without use of a gradient and can be freed from soluble impurities.

2. The condensation reactions occur as fast as in carrier-free systems.

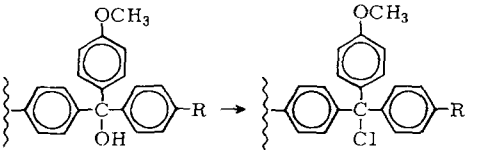
3. Removal of the oligonucleotide chains becomes easier rather than harder with increasing length.

4. On account of its bead form and rigidity the polymer is mechanically stable and easy to handle.

The copolymer *(1)* from styrene and divinylbenzene was subjected in nitrobenzene to a Friedel-Crafts reaction with benzoyl or *p*-methoxybenzoyl chloride and the polymeric ketone *(2)* thus obtained was then subjected to a quantitative Grignard reaction with *p*-bromoanisole. The resulting product, compound *(3)*, was then boiled with benzene/acetyl chloride under reflux or was treated with acetic anhydride/HCl at 0 °C, thereby giving the chloride *(4)*. In the statistical mean the polymer contains one trityl chloride group per 19 styrene units.



(1) *(2)*



(3) *(4)*

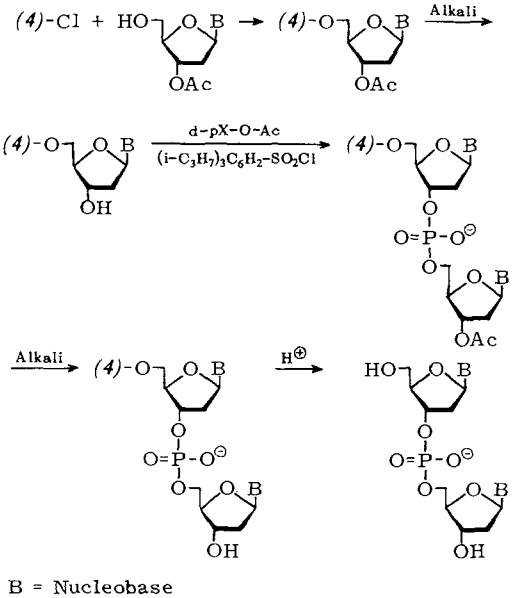
R = H, $-OCH_3$

A polymeric dimethoxytrityl alcohol of type *(3)* was also obtained by copolymerization of styrene, divinylbenzene, and bis-(*p*-methoxyphenyl)-(*p*-vinylphenyl)methanol, but we did not use it in the experiments now described.

The polymeric dimethoxytrityl chloride *(4)* R = OCH_3[7], could be loaded up to 50–60% with 3'-*O*-acetyldeoxythymidine (d-T–O–Ac) (0.2 mmole of d-T per g of polymeric carrier) and up to 5–10% with d-TpT–O–Ac (0.02 mmole of d-TpT per g of polymeric carrier) (pyridine, 48 h, 70 °C). Removal of the acetyl groups is effected with 0.1 N tetramethylammonium hydroxide in isopropyl alcohol (3 h, room temperature) or with a mixture of dimethylformamide, pyridine, and 1 M sodium ethoxide (5:4:1 v/v) (1 h, room temperature).

The synthesized oligonucleotide chains are removed from the carrier by treatment with 80% acetic acid for 1 h at 70 °C or for 6 h at room temperature; removal can also be effected by a pyridine-acetic acid buffer (pyridine:acetic acid:water = 3:10:3 v/v) in 48 h at room temperature. Since deoxyadenosine 5'-monophosphate is stable in 80% acetic acid for at least 24 hours and in the pyridine-acetate buffer for at least four weeks purine nucleotides can also be used.

The carrier can be loaded with pre-formed oligonucleotide and this can be lengthened by a single dinucleotide unit (block condensation). This process enables longer, biochemically interesting chains to be synthesized.



B = Nucleobase

	Nucleoside components	Phosphate components [a]	Yields (%) calculated on total amount of eluted nucleotide material [b]			
			d-TpT	d-TpTpX	d-TpTpTpT	d-TpTpTpTpTpT
I	*(4)*-d-T	d-pT—O—Ac	49.5			
II	*(4)*-d-TpT	d-pT—O—Ac	33.0	67.0		
III	*(4)*-d-TpT	d-pT—O—Ac	32.0	34.0	34.0 [c]	
IV	*(4)*-d-TpT	d-pTpT—O—Ac	36.2		33.3	30.6 [c]
V	*(4)*-d-TpT	d-pC(N^6—Ac)—O—Ac	58.7	41.3		
VI	*(4)*-d-TpT	d-pA(N^6—Ac)—O—Ac	70.1	29.9		
VII	*(4)*-d-TpT	d-pG(N^2—Ac)—O—Ac	74.1	20.9		

[a] A 50—100 fold excess of nucleotide was used. In experiment I a 10 fold excess gave the same yield.

[b] IR spectra indicate that all fissions occurred with at least 97% yield. For VI, λ_{max} of d-TpTpA = 262 nm (ε = 33400 was used). For VII, λ_{max} of d-TpTpG = 258 nm (ε = 30600 was used).

[c] After two condensations with the phosphate components.

Attachment of the nucleotide bond was effected by triisopropylbenzenesulfonyl chloride in pyridine (4 h or 6—8 h for block condensation).

Contrary to usual practice, water is not added after the condensation but the reaction is stopped by precipitation with anhydrous ether. Thorough washing with ether removes the excess of triisopropylbenzenesulfonyl chloride, and the excess of nucleotide is eluted with 20% aqueous pyridine. This method of working up saves time and regenerates the excess of nucleotide almost without loss and in such a form that, after removal of the water, it can be used directly for renewed condensation.

In this manner a condensation step can be carried out comfortably in one day, so that synthesis of d-TpTpTpTpTpT including loading and working up does not take more than a week.

The oligonucleotides synthesized can be degraded quantitatively with snake-venom phosphodiesterase to yield the required proportions of d-T and d-pT or d-T, d-pT and d-pX (X = A, C, G).

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[6] Experiments with a popcorn polystyrene cross-linked with 0.2% of divinylbenzene and carrying mono- or di-methoxytrityl chloride groups are not yet complete.

[7] Abbreviations: d = deoxy, T = thymidine, A = adenosine, C = cytidine, G = guanosine, X = A, C, T, or G, pT = thymidine 5'-phosphate, Tp = thymidine 3'-phosphate, T—O—Ac = 3'-*O*-acetylthymidine, N—Ac = acetylated amino group of the nucleobase.

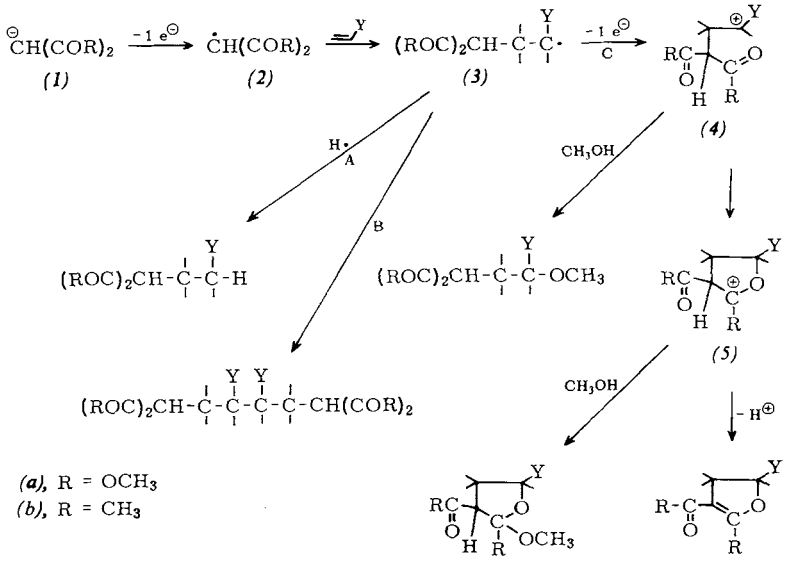
Oxidative Addition of Dimethyl Sodiomalonate and Sodioacetylacetone to Olefins[1]

By *H. Schäfer* and *A. Alazrak*[*]

We are engaged in a study of whether various organic anions can be added to non-activated olefins by way of radical intermediates.

When we oxidized dimethyl sodiomalonate *(1a)* or sodioacetylacetone *(1b)* anodically in the presence of cyclohexene, ethyl vinyl ether, styrene, or butadiene, we obtained the products named in the Table[2]. The anode voltage was controlled by a potentiostat and was always less than the polarographically determined half-wave potential of *(1a)* ($E_{1/2} \approx +0.89$ V against Ag/AgCl) or *(1b)* ($E_{1/2} \approx +0.8$ V). Usually, *ca.* 100 mmoles of *(1a)* or *(1b)* in an olefin/methanol mixture (1:2 to 1:1 v/v) were electrolyzed, in a cell without a diaphragm, at current densities of 0.01—0.05 A/cm².

The reactions probably begin with formation of a radical *(2)* at the anode; this radical then adds to the olefin, giving a new radical *(3)*. *(3)* can remove a hydrogen atom from the solvent or from the excess of malonic ester or acetylacetone (route A), or it can dimerize (route B), or it can be oxidized to the cation *(4)* at the anode, provided that the cation is stabilized by Y = phenyl or ethoxyl (route C). Two possibilities are open to the cation *(4)*: it may attack methanol electrophilically or it may attack the oxygen of the carbonyl



Anion	Olefin	Products	Yield (%) [a]
(1a)	Cyclohexene	Dimethyl 2-cyclohexenylmalonate	12
		Dimethyl cyclohexylmalonate	8
(1a)	Ethyl vinyl ether	Dimethyl (2-ethoxy-2-methoxyethyl)malonate	37
(1a)	Styrene	Methyl tetrahydro-2,2-dimethoxy-5-phenyl-3-furancarboxylate	43
		Tetramethyl 3,4-diphenyl-1,1,6,6-hexanetetracarboxylate	15
(1b)	Ethyl vinyl ether	4-Acetyl-2-ethoxy-2,3-dihydro-5-methylfuran [b]	36
(1b)	Styrene	4-Acetyl-2,3-dihydro-5-methyl-2-phenylfuran	30
		5-Phenyl-2-pentanone	6 [c]
		5,6-Diphenyl-2,9-decanedione	10 [c]
(1b)	Butadiene	*trans,trans*-5,9-Tetradecadiene-2,13-dione [d]	40 [c]

[a] Calculated on current consumption. — [b] IR: $\nu_{C=C}$ = 1598 cm^{-1}. [c] After ester fission of the crude product. — [d] IR: ν_{C-H} = 965 cm^{-1}.

group intramolecularly with formation of an alkoxymethyl cation *(5)*, which is then solvolyzed or deprotonated.

On the basis of this working hypothesis we attempt to influence the product distribution by variation of the anode potential and the current density.

Methyl tetrahydro-2,2-dimethoxy-5-phenyl-3-furancarboxylate:

A solution of dimethyl malonate (18 g, 136 mmoles) and sodium (1.1 g, 48 mmoles) in styrene (100 ml) and methanol (120 ml) was electrolyzed at 20 °C with an anode potential of +0.65 V (against Ag/AgCl) and a current density of 0.02 A/cm^2. After a current consumption of 16200 Cb most of the solvent was distilled off in a rotary evaporator at 60 °C, the residue was treated with saturated NaCl solution (30 ml), and the mixture was extracted with ether and worked up as usual. Distillation afforded 9.9 g (43%) of methyl tetrahydro-2,2-dimethoxy-5-phenyl-3-furancarboxylate (b.p. 114–115 °C/0.05 torr). This product gave the 2-oxo derivative (IR: $\nu_{C=O}$ = 1780, 1740 cm^{-1}) when treated with toluenesulfonic acid in 97% aqueous methanol. Chromatography of the distillation residue on silica gel with light petroleum (b.p. 40 to 60 °C):ether (3:1 v/v) yielded tetramethyl 3,4-diphenyl-1,1,6,6-hexanetetracarboxylate, m.p. (of one diastereoisomer) 131.5–132.5 °C (from benzene/light petroleum).

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[1] Part 1 of Anodic Oxidation of Organic Anions.

[2] Anodic dimerization of sodiomalonic ester: *R. Brettle* and *J. G. Parkin*, J. chem. Soc. (London) C *1967*, 1352 (where further references are given); coupling of sodioacetylacetone: *S. P. Mulliken*, J. Amer. chem. Soc. *15*, 529 (1893).

CONFERENCE REPORTS

Valence and Reactivity: an International Symposium of the Chemical Society (London) on d-Orbital Effects, January 9–11, 1968, in Oxford

Participation of "outer" d-orbitals (nd) in the bonding of non-metallic elements with principal quantum numbers n $\geqslant$3 is a central problem of inorganic chemistry[1]. As for the largely clarified participation of "inner" d-orbitals [(n-1)d] in transition-metal complexes, its solution would open numerous new aspects of the chemistry, spectroscopy, and quantum-chemical description of non-metal compounds.

In a general introduction to the symposium *C. A. Coulson* (Oxford) first formulated the essential questions: What is known about the energies and sizes of d-orbitals in isolated atoms? Can the "diffuse" d-orbitals in compounds be contracted by electronegative ligands, and what is the effect of such a contraction on the overlap with σ- and π-orbitals? What experimental data give valid information about d-orbital effects? Does participation of d-orbitals in π-systems lead to a conjugational barrier at the d-orbital center? Are transition states stabilized by d-orbital participation? The results of theoretical and experimental investigations of these questions were set out in 30 papers[2].

D. W. J. Cruickshank (Glasgow) reviewed the SCF calculations carried out in recent years for excited configurations of free atoms and ions. The results show that with optimal spin alignment (*e.g.* ^{7}F for S (sp^3d^2)) the radial parts of the d-orbitals shrink to the size necessary for participation in bonding. Energies of the "outer" d-orbitals of neutral atoms X are small and largely independent of the atomic number; but they are appreciably influenced by the state of ionization ($X \approx -2$ eV; $X^+ \approx -8$ eV; $X^{2+} \approx -18$ eV). By way of contrast, the energy of the "inner" d-orbitals of transition metals decreases with increasing nuclear charge ($Sc(d^1s^2) \approx -9$ eV; $Zn(d^{10}s^2) \approx -21$ eV). Calculations that take into account the "outer" d-orbitals, by means of an analytical two-term Slater function, lead – according to *T. Thirunamachandran* (London) – to the result that d-atomic orbitals are more diffuse for the d^1-configuration (*e.g.* P(sp^3d)) than for the d^2-configuration (*e.g.* S(sp^3d^2)).

C. Zauli (Bologna) summarized the bonding conditions in higher valence states where the octet rule is violated. He described the distortion of the valence orbitals by the ligand field, the energy gain on formation of the molecule, and the energy differences between excited covalent and ionic states. Since the promotion energies are generally comparable, 4s- and 4p-states must be considered as well as 3d-states. The d-orbital contraction in the ligand field can lead to participation of 3d-orbitals in the bonding, *e.g.* for sulfur compounds; the promotion energies could be compensated by electrostatic interactions. According to *K. A. R. Mitchell* (Vancouver) calculations with simple radical functions $R(r) = Nr^2e^{-\alpha r}$ with a distance of maximum probability at $r_{max} = 3/\alpha$ [a.u.] lead to exponentials $\alpha \approx 1.2$–1.5 for the orbitals of SF_6 and to $\alpha \approx 1.3$ for the d-orbitals of POF_3. Thus d-orbital participation should be considered in compounds of this type. However, for interhalogen compounds, polyhalides, and polyhalogen cations, according to *E. H. Wiebenga* (Groningen), a σ-HMO procedure without inclusion of d-orbitals suffices for prediction of the stable configurations, electronic transitions, bond distances, and non-existent compounds. The procedure uses only np-functions and, since the ionization energies, electron affinities, and bond distances are known, it requires only the resonance integrals $\beta_{\mu\nu}$ as a function of distance, these parameters being accessible spectroscopically. According to *R. J. Gillespie* (Hamilton) the qualitative model of electron-pair repulsion proves useful for predicting the geometry of simple molecules such as interhalogen or noble-gas compounds.

Molecular properties that should show the effect of d-orbital participation have been intensively investigated. *H. H. Jaffe* (Cincinnati) reported on d/π^* interactions in excited states which are particularly relevant because of the small

energy differences $E_d - E_\pi^*$. The electronic spectra of sulfones, sulfoxides, sulfonium salts, alkyl iodides, and anisoles that are *para*-substituted by acceptor groups X (X = halogen, SiR_3, GeR_3, SnR_3) were cited as examples. *D. S. Urch* (London) drew attention to the properties of inorganic compounds that can be explained by strong d/n interactions between unoccupied 3d-orbitals and free 3p-electron pairs.

According to *H. Bock* (München) simple models of d/π-, d/n-, and d/π* interactions are provided by R_3Si-substituted linear and cyclic, isoconjugated and heteroatomic π-electron systems such as polyenes, aromatic hydrocarbons, aryl ethers, ketones, and aldimines. These R_3Si-substituted π-electron systems differ significantly from R_3C- and R_3SiCH_2-substituted "standard" compounds in vertical ionization energies, charge-transfer maxima of suitable donor-acceptor complexes, half-wave reduction potentials, ESR coupling constants of the radical anions, and the electron transition energies. The energy differences can be interpreted on the basis of differing inductive polarizations ($+I_{SiR_3} > +I_{CH_2SiR_3} \gg +I_{CR_3}$) and additional back-donation of electrons $Si \leftarrow C_\pi$. The ionization energies in the photoelectron spectra of SF_6, SeF_6, and TeF_6 can be assigned, as was shown by *D. R. Lloyd* (Birmingham), on the basis of CNDO calculations only if d-terms are included.

E. A. C. Lucken (Geneva) reviewed the spectroscopic methods to measure the properties of ground states (NMR, ESR, NQR, and Mössbauer spectroscopy) and discussed the differences in determining energies (eigenvalues) and electron distributions (eigenfunctions). Unequivocal proof of d-orbital contributions that is possible by these methods is, however, limited by the assumptions required in evaluating the experimental results and by parameters introduced into the model calculations. Among other examples the (d← n)-electron back-donation in R_3SiCl (NQR), $(d/p)_\pi$-conjugation in R_3Si-substituted π-electron systems, and $(d/p)_\pi$-bonding in phosphorus compounds $R_3P{=}X$ (ESR, ^{13}C-, ^{29}Si-, and ^{31}P–NMR) were considered.

H. Zeil (Karlsruhe) discussed bond distances of acetylenes $(CH_3)_3X{-}C{\equiv}C{-}Cl$ (X = C, Si, Ge, or Sn) determined by microwave spectroscopy and electron diffraction, and the NQR, IR, and Raman spectra of such molecules. For instance, the C–Cl bond length is shorter, the force constant $f_{C\equiv C}$ smaller and f_{C-Cl} larger for the Si compound than for the *tert*-butyl derivative. This finding supports $(p \rightarrow d)_\pi$-bonding, as do also the ^{35}Cl–NQR coupling constants, which decrease in the series from C- to Sn-acetylenes. Further evidence for d-orbital effects in compounds of elements of the fourth main group may be deduced from the quadrupole splittings in the ^{119}Sn-Mössbauer spectra, as was shown by *J. J. Zuckerman* (Ithaca) and *J. D. Donaldson* (London). According to *B. Lindberg* (Uppsala) $(d/p)_\pi$-contributions for, *e.g.*, S=O bonds can be inferred from the spectra of inner electrons that result from X-ray excitation, and which may be correlated with the effective nuclear charge and the arrangement of electrons in the valence shell. In contrast to the interpretation of the preceding results, *M. P. Bogaard* (Bristol) found that the NQR spectra of polyhalide anions such as I_3^- and IBr_2^- can be interpreted on the basis of a three-center four-electron MO theory without assuming d-orbital contributions.

Mutually contradictory reports have been given about the d-orbital centers as conjugational barriers in π-electron systems, with PN rings as examples. In his review *N. L. Paddock* (Vancouver) reported thermochemical and structural studies of PX bonds in compounds of the type $R_3P{=}X$ (X = O or NR), where the effects of substituents on bond enthalpies or P=O stretching frequencies are evidence of $(d/p)_\pi$-bonds. Here two π-components at right angles to each other can be conceived, which are no longer degenerate in PN rings. Calculated HMO eigenvalue schemes for rings containing three to six P=N units show the same alternation as, *e.g.*, the measured photoionization energies. Predicted structures agree with X-ray structure analyses, as *A. J. Wagner* (Groningen) reported. However, *H. R. Allcock* (University Park/USA) reported experimental results that contradict π-delocalization in PN rings; in particular, the electron transitions ($\nu_m > 50000\ cm^{-1}$!), which are independent of the number of PN units ($n \rightarrow \infty$), and the half-wave reduction potentials of certain derivatives, which are in accord only with the Dewar PNP island model.

Transition states in reactions of Si and P compounds can be stabilized by d-orbitals with increase in the coordination number, in contradistinction from those of C compounds. The previously known material was summarized by *R. F. Hudson* (Canterbury): for Si and P derivatives inversions as well as retentions of configuration are known, depending on the reaction conditions and on the nature of the leaving group. Retention occurs particularly in cyclic transition states such as occur in the Wittig reaction. $X_3P{=}^{18}O$ compounds are hydrolyzed without exchange of ^{18}O, in contrast to carboxylic esters; however, trialkylfluorosilanes racemize in methanol without detectable hydrolysis. Numerous further examples help toward the conclusion that the transition state can be stabilized by unoccupied higher orbitals but that these need not necessarily be of 3d type. *G. Schiemenz* (Kiel) showed that Hammett constants of phosphorus substituents can be determined from ^1H–NMR data and that the σ-values obtained show a –M effect of phosphorus. *B. G. Gowenlock* (Edinburgh) reported on gas-phase reactions of silanes. Other papers on the properties and reactions of metal complexes were contributed by *C. W. Fryer* (Coventry), *J. A. McGinnety* (Evanstown), and *P. Uguagliati* (Padua), and on special methods of calculation by *R. Wratten* (Sheffield) and *W. T. Dixon* (London).

Finally *C. A. Coulson* reviewed the answers that had been given during the symposium to the questions that he put forward at its opening. d-Orbitals clearly play a larger part in π-bonding than in σ-compounds (such as the interhalogens). Ground and excited states must be considered separately. Except for compounds such as $R_3P{=}X$, the chemical evidence for d-orbital contributions is not compelling because, generally, only acceptor functions of substituents are determined and these could be due to other orbitals that have π-symmetry. The intensive attempts to clarify the "d-orbital effects", which can be reproduced in quantum-mechanical calculations, including d-orbital contraction, are, however, likely to yield decisive results in the foreseeable future.

[VB 145 IE]

German version: Angew. Chem. *80*, 491 (1968)

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[1] Cf., *e.g.*, *F. G. A. Stone* and *D. Seyferth*, J. inorg. nuclear Chem. *1*, 112 (1955); *C. Eaborn*: Organosilicon Compounds. Butterworth, London 1960; *H. H. Jaffe* and *M. Orchin*: Theory and Applications of Ultraviolet Spectroscopy. Wiley, London 1962; *R. F. Hudson*, Pure appl. Chem. *9*, 371 (1964); *N. L. Paddock*, Quart. Rev. (chem. Soc., London) *1964*, 168; *H. Bürger*, Fortschr. chem. Forsch. *9*, 1 (1967); Abstracts of the 1st Int. Conference on Silicon Chemistry, Pure appl. Chem. *13* (1967).

[2] Cf. Abstracts of the Int. Symposium "Valence and Reactivity", Oxford 1968. The Chemical Society (London); and literature cited therein.

Investigation of the Ionic Mobility of Some Copper(I) Compounds by Nuclear Magnetic Resonance

By *H. Richtering* and *G. W. Herzog* [*]

Cationic mobility of CuBr and CuI is greater in the high-temperature phases than in aqueous solutions at room temperature. The shape and width of the NMR signals of ^{63}Cu, ^{65}Cu, ^{79}Br, ^{81}Br, and ^{127}I were studied between –100 and +500 °C; for ^{63}Cu the spin-lattice relaxation time T_1 was also determined at temperatures up to 330 °C.

For the cubic low-temperature phases the width of all the signals is constant at low temperatures (1.5 to 2.5 G) and they can be used to provide the second moments, the values

derived agreeing fairly well with those obtained from the lattice structure. Between 20 and 150 °C the width of the Cu signals decreases for both compounds (to < 0.4 G), which is to be ascribed to increasing mobility of the Cu^+ ions with rising temperature; by using *Bloembergen, Purcell,* and *Pound*'s theory[1] the mean residence time of a Cu^+ ion in its lattice position is found to be $\tau_{Cu^+} \approx 5\times10^{-5}$ sec at 100 °C. In the same region the halogen signals become first narrower and then appreciably broader (>5 G). For Br the width passes through a maximum at 240 °C; this maximum occurs at the same temperature for samples of various degrees of purity but is the more pronounced the larger the number of bivalent cations (Cu^{2+}, Cd^{2+}) that are present. The maximum in signal width corresponds to a minimum in T_1, caused by quadrupole interaction[2]. Thus at 240 °C the mean frequency of interchange of defect sites in the Cu lattice (which contribute to the quadrupole interaction) is of the order 10^8 Hz, the Larmor frequency of Br nuclei in the external magnetic field (14000 G). The Cu signals become somewhat broader below the transition temperature for the change cubic → hexagonal. Here the width of the signal is already appreciably influenced by T_1; for ^{63}Cu T_1 decreases from 5–10 msec at 25 °C to *ca.* 500 μsec at 330 °C. Shortly before the transition point τ_{Cu^+} thus approaches the reciprocal Larmor frequency of the Cu nucleus (1.0×10^8 Hz).

For the hexagonal β-phases (CuBr 390–470 °C; CuI 373 to 410 °C) the Cu signals are first broader, unsymmetrical, and shifted downfield by 0.5 G (CuBr) or 2 G (CuI). The shift decreases with rising temperature, and the signals become symmetrical and narrower.

For the cubic α-phases of CuI above 440 °C the width of the signals decreases further: $\tau_{Cu^+} < 10^{-8}$ sec. Halogen signals cannot be observed for either the β-phases or the α-phases of CuI.

Lecture at Göttingen (Germany) on December 14, 1967 [VB 139 IE]
German version: Angew. Chem. *80*, 449 (1968)

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[1] *N. Bloembergen, E. M. Purcell,* and *R. v. Pound,* Physic. Rev. *73*, 679 (1948).

[2] *F. Reif,* Physic. Rev. *100*, 1597 (1965).

Oxygen Radicals and Chemiluminescence

By *J. Stauff*[*]

Weak chemiluminescence (10^3–10^8 $h\nu\cdot cm^{-3}\cdot sec^{-1}$) is observed in very many oxidations by hydrogen peroxide, hypohalite, or ozone and also by molecular oxygen. This can be traced to oxygen radicals of the type O_2H, O_3H, and O_2R (R = an organic group) arising as intermediates which on recombination afford oxygen in the singlet state ($^1\Delta$ or $^1\Sigma$), *e.g.*, $2\ O_2H \rightarrow H_2O_2 + O_2^*$ ($\Delta H = -58$ kcal/mole). The excited oxygen can pass to the ground state with emission of red light.

However, emission in the wavelength region 360–580 nm is also found spectroscopically; so processes must also occur that are resolved by collision of two excited singlet oxygen molecules, their energies then being added together. This view is supported by a quadratic dependence of the emission on the O_2 concentration in the Cu^{2+}-catalyzed oxidation of sulfites by molecular oxygen. The rate of onset of chemiluminescence produced by recombination of two O_2H radicals (from $Ce^{4+} + H_2O_2$) is very much greater than the rate of recombination of the radicals, whence it is concluded that light is emitted only on collision of two individual O_2 species, and that this does not necessarily require formation of an O_2–O_2 complex *in statu nascendi* although this may happen in other cases (*e.g.*, $O_3 + H_2O_2 \rightarrow O_4^* + H_2O$).

O_2H radicals can be determined by ESR spectroscopy in a flow apparatus; their reaction kinetics are thus known. For OH radicals and for O_3H radicals arising therefrom (*e.g.*, from Ti^{3+} and H_2O_2) complex formation with the cations produced makes quantitative interpretation of the ESR signals difficult; nevertheless, connections between radical reactions and chemiluminescence can be recognized.

The bluish-yellow chemiluminescence is an indicator for appearance of O_2H radicals and, at pH $>$ 5 or in solvents with low dielectric constants, of O_2^- radicals; furthermore, it can be used as indicator when following autoxidations and one-electron transfers to O_2, as well as in the action of O_2 on semiquinones and many other electron-donors (including biological ones). In particular, complexes of heavy-metal ions with amino acids, proteins, nucleotides, and nucleic acids in the presence of cysteine and other donors or of natural oxidases give measurable light emission when treated with oxygen, and this can be used as a means of studying their reaction mechanisms.

Lecture at Giessen (Germany) on January 30, 1968 [VB 141 IE]
German version: Angew. Chem. *80*, 449 (1968)

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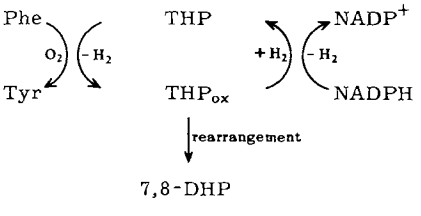
Tetrahydropterins as Coenzymes of Enzymatic Hydroxylation

By *M. Viscontini*[*]

S. Kaufman[1] has shown that the coenzyme of an enzymatic hydroxylation system is a tetrahydropterin. This system operates in a fairly complicated manner with formation of an oxidized tetrahydropterin (THP_{ox}) as well as of a 7,8-dihydropterin (7,8-DHP) in the presence of the redox coenzyme

$$NADP^+ \underset{-H_2}{\overset{+H_2}{\rightleftharpoons}} NADPH$$

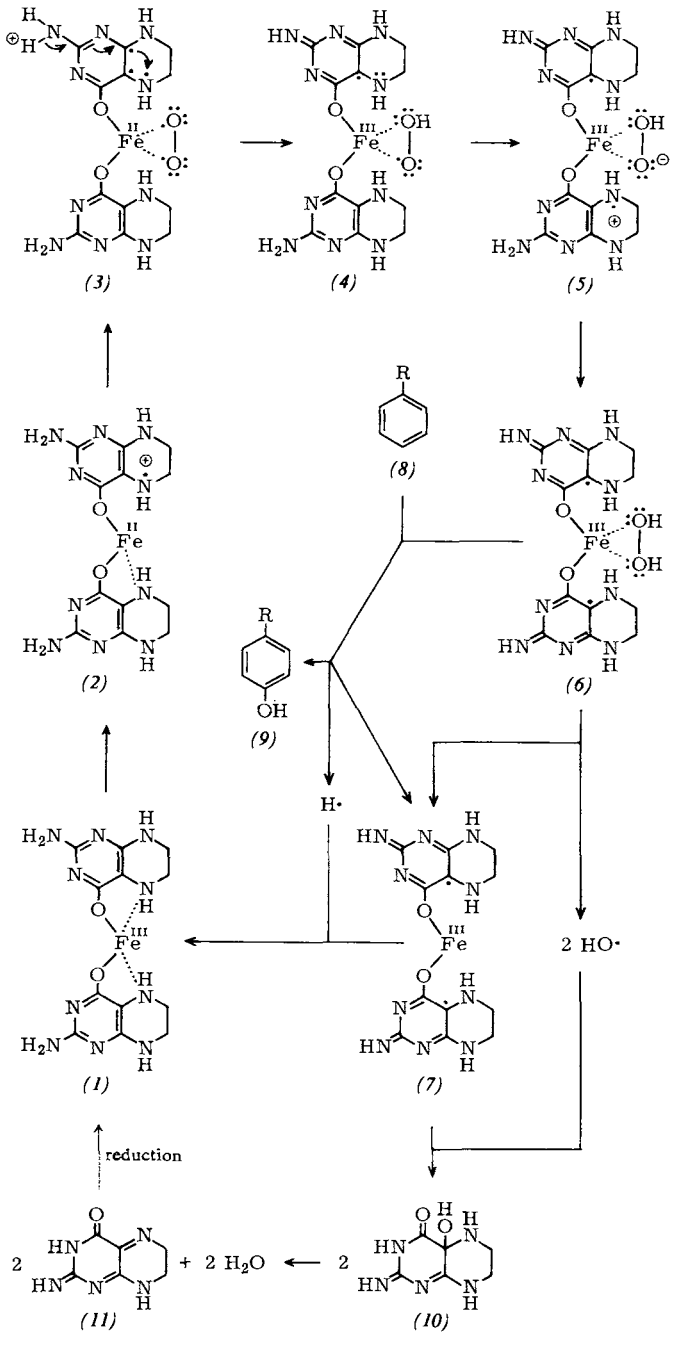
The mechanism of enzymatic hydroxylation of phenylalanine to tyrosine can be represented as in Scheme 1.



In order to study the course of the hydroxylation we first prepared pure tetrahydropterins and investigated the chemical properties of these particularly unstable substances. We have been able to show that the tetrahydropterins are oxidized to 7,8-dihydropterins under physiological conditions (pH 6.8, atmospheric oxygen). A very unstable quinonoid dihydropterin *(11)* is formed as intermediate, its UV spectrum being the same as that of *Kaufman*'s "oxidized tetrahydropterin".

Phenylalanine and tryptophan can be hydroxylated under physiological conditions in the presence of tetrahydropterins and Fe^{III} (yield 3–5 %). The Fe^{III} takes up an electron from the tetrahydropterin which is converted into a radical cation. Then the Fe^{II} thus formed adds an O_2 molecule and passes the electron on to it; a proton finally migrates from the radical cation to the negatively charged oxygen. An analogous transfer of an electron and a proton from a second tetrahydropterin molecule leads to a complex *(6)* consisting of THP radicals, Fe^{III}, and hydrogen peroxide, which can hydroxylate aromatic compounds.

On the basis of these results we propose Scheme 2 as a model for enzymatic hydroxylation [2]:



Lecture at Konstanz (Germany) on February 1, 1968 [VB 143 IE]
German version: Angew. Chem. *80*, 492 (1968)

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[1] *S. Kaufman*, J. biol. Chemistry *239*, 332 (1964).

[2] *M. Viscontini*, Fortschr. chem. Forsch. *9*, 605 (1968)

Cooperative Conformational Changes of the Helix Structures of Biopolymers and Analogous Model Substances in Solution

By *Th. Ackermann* [*]

Under suitable experimental conditions (temperature, solvent composition, pH value), and even in the dissolved state, polypeptides and polynucleotides adopt a secondary structure that corresponds largely to the model of the Pauling α-helix and to the Watson-Crick model of the DNS double helix. Alteration of the experimental conditions can convert the molecules of the dissolved biopolymer from the ordered helix state into the statistically disordered state of a bundle; this conversion is often referred to as the helix-random coil transition.

Experiments with a series of model systems (*e.g.*, poly-γ-benzyl L-glutamate dissolved in a mixture of dichloroacetic acid and 1,2-dichloroethane or an equimolar mixture of salts of polyribouridylic acid and polyriboadenylic acid in aqueous buffer solutions) have shown the helix-coil transition to be a reversible cooperative process that proceeds almost completely within a relatively narrow temperature range. The transition is clearly detectable by characteristic changes in physical properties of the solutions; these may be studied by, *e.g.*, measurement of optical rotation, viscosity, UV absorption, IR absorption, and the chemical shift of the nuclear resonance signals of α-CH protons of polypeptides in relation to temperature or solvent composition.

The stability of the helix structures in the dissolved state is influenced, not only by the intramolecular hydrogen bonds, but also by solvation effects and by the energetic interaction of the ring systems of the heterocyclic bases present in the polynucleotides. Thermodynamic parameters of such systems can be determined by exact measurement of the temperature relation of the heat capacity by means of recording adiabatic calorimeters.

Not only the transition enthalpies but also the characteristic cooperative parameters can be found by such measurements. Comparative measurements on DNS samples with various base compositions permit statements about the influence of the base pairs adenine-thymine, adenine-uracil, and guanine-cytosine on the thermal stability of the helix structures [1–3].

Lecture at Köln (Germany) on January 19, 1968 [VB 142 IE]
German version: Angew. Chem. *80*, 450 (1968)

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[1] *Th. Ackermann* and *H. Rüterjans*, Ber. Bunsenges. physik. Chem. *68*, 850 (1964).

[2] *Th. Ackermann* and *E. Neumann*, Biopolymers *5*, 649 (1967).

[3] *E. Neumann* and *Th. Ackermann*, J. physic. Chem. *71*, 2377 (1967).

Investigations of Roman Wall Paintings

By *R. Giovanoli* [*]

According to *W. Klinkert* [1], Roman wall painting differs from modern frescoes in the way in which it was made. Since we can expect little appreciably new as addition to our knowledge of the "fresco buono" technique of wall painting, our investigations were directed mainly to testing the more recent methods of study that have not yet found wide application in archaeometry. The first comprehensive application was that by *U. Hofmann* [2] to Attic ceramics.

In our study of fragments of wall painting (from the frigidaria of two Roman villas in Switzerland), we used X-ray diffraction, X-ray fluorescence spectrometry, electron diffraction, and electron microprobe techniques, and we recognized the various color tones as resulting from blue, wine red, pale green, and yellow pigments, and from the white of the plaster.

X-Ray fluorescence analysis disclosed the following element contents:

- In the plaster Ca (secondary element Sr) and Si
- In blue pigment layers Cu, Ca, and Si
- In red pigment layers Fe, Si, Ca, and some Cu
- In green and in yellow layers traces of Fe, otherwise as for the plaster.

Use of X-ray and electron diffraction led to recognition of the crystal species α-Fe_2O_3 (hematite) and $CaCuSi_4O_{10}$ (the ancient synthetic pigment "Egyptian blue"), as well as calcium carbonate, but other colored material lay below the limits of detection. However, the fine structure of the electron diffraction of extracts from surface prints of green fragments and yellow fragments gave indications of the presence of clay mineral structures.

Ground sections showed their layer structure in the electron microprobe. Element concentration profiles confirmed the X-ray findings and led to the additional conclusions that the colored bodies in the green pigment layers were glauconite and that those in the yellow pigment layers were an ocher (kaolinite with α-FeOOH).

From the thickness of the pigment layers of the various fragments it was further concluded that the blue layers were purposely applied more thickly, so that the full color tone of the coarsely crystalline Egyptian blue became clearly evident; our imitation of Egyptian blue, when powdered in a mortar, is pale blue and does not possess the deep color tone of the crude product. Such fragments thus cannot be deemed "fresco buono" in the strictest sense.

The instrumentation used has proved useful for characterization of the composition and intimate structure of such fragments of paintings and similar objects.

Lecture at Bern, on February 2, 1968 [VB 146 IE]
German version: Angew. Chem. *80*, 494 (1968)

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[1] *W. Klinkert*, Mitt. dtsch. arch. Inst., Röm. Abt. *64*, 111 (1957).

[2] *U. Hofmann*, Angew. Chem. *74*, 397 (1962); Angew. Chem. internat. Edit. *1*, 341 (1962).

Porphin Derivatives as Experimental Models for Mass-spectroscopic Fragmentation Reactions

By *H. Budzikiewicz* [*]

As a result of the concept that decomposition of a molecule during mass-spectroscopy is induced by a localized positive charge, such study of organic compounds has in recent years concerned mainly the influence of various functional groups and structural units on the fragmentation pattern. To obtain a more general picture it is necessary to test the available results for applicability to complex systems and for their limitations. Porphin derivatives are suitable as experimental models because in all their decomposition reactions the positive charge is localized preferentially in the π-system of the macrocycle whilst fragmentation occurs in the side chain.

In the case of 1,2,3,4,5,6,7,8-octaethyl-1,2,5,6-tetrahydroporphin the preferential formation of even-numbered electron systems in the singly and doubly charged regions can be demonstrated by comparing the relative intensities of the daughter ions formed by successive loss of ethyl radicals; this is also indicated by the preferred course of the McLafferty rearrangement which affords ions with even numbers of electrons. The mass spectra of porphyrins and chlorins that are not substituted in the *meso*-position confirm the principle of benzyl cleavage observed with simple aromatic compounds whilst the mutual steric hindrance of the side chains in 6,7-substituted compounds causes fission of the bonds leading directly to the aromatic ring and also leads to simultaneous loss of two substituents with formation of a metastable peak. The last-mentioned observation is of particular importance for the theory of metastable transitions. Comparison of the mass spectra of 10-methoxy- and 10-isopropoxy-methylpheophorbide indicates the limits within which analogies may be drawn on purely empirical application of mass spectroscopy: the differing behavior of the two types of compound can be explained by the fact that the energetics of cleavage of various bonds proceeding from the same center (C-10) may be more or less favorable according to the nature of the substituents.

Lecture at Braunschweig (Germany) on February 5, 1968 [VB 147 IE]
German version: Angew. Chem. *80*, 495 (1968)

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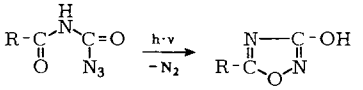
New Investigations of Heterocumulenes[**] and their Derivatives

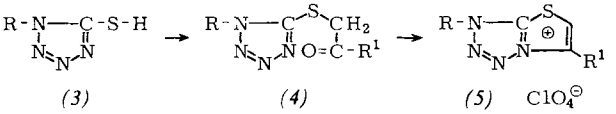
By *R. Neidlein* [*]

N-Acylcarbamoyl azides *(1)* are converted by loss of nitrogen



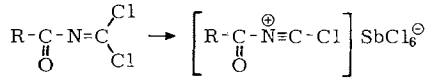
(1) *(2)*

into 1,2,4-oxadiazol-3-ols *(2)*, whose structure is proved by degradative reactions and by IR and ^{1}H–NMR spectroscopy, as well as by synthesis of their methyl ethers by another route. The tetrazole-5-thiols *(3)*, that can be obtained



(3) *(4)* *(5)* $ClO_4^{\ominus}$

from isothiocyanates and hydrazoic acid with subsequent rearrangement, are converted by way of the intermediate *(4)* into the quasiaromatic thiazolo[3,2-*d*]tetrazolylium salts [isolated as perchlorate *(5)*], whose properties and reactions have been intensively studied.



(6) *(7)*

Whereas reaction of *N*-(dichloromethylene)carboxyamides *(6)* with electrophilic metal chlorides such as $SbCl_5$ gives *N*-acylchloroformonitrilium salts *(7)*, only addition products can be obtained from *N*-(dichloromethylene)sulfonamides and electrophilic metal chlorides. Also, *N*-[(alkylthio)chloromethylene]sulfonamides cannot be converted into the corresponding nitrilium salts but decomposition reactions occur in which are formed sulfonyl chlorides and adducts of the electrophilic metal chlorides to the alkyl thiocyanates that are split off. Further syntheses with *N*-(dichloromethylene)-sulfonamides lead to substituted 1,3,4-oxadiazoles, 1,3,4-thiadiazoles, tetrazoles, 1,2,4-oxadiazoles, 1,2,4-triazoles, *etc.*

Lecture at Bonn (Germany) on February 6, 1968 [VB 149 IE]
German version: Angew. Chem. *80*, 496 (1968)

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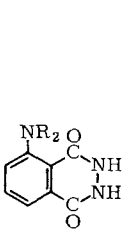
[**] By heterocumulenes are meant compounds having cumulated double bonds, and whose C atoms are replaced by heteroatoms, *e.g.* isocyanates, carbodiimides, thionylimines, *etc.*; cf. *H. Ulrich*: Cycloaddition Reactions of Heterocumulenes. Academic Press, New York-London 1967.

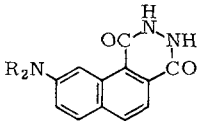
Chemiluminescence of Cyclic Diacylhydrazides and Diazaquinones

By *K.-D. Gundermann* [*]

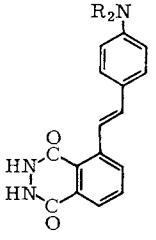
Dialkylamino groups in the 3-position of the phthalhydrazide system are sterically resonance-hindered, and thus compounds of type *(1)* show only very weak chemiluminescence on hemin-catalyzed oxidation in aqueous-alkaline H_2O_2.



(1)

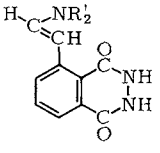


(2)

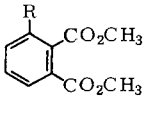


(3)

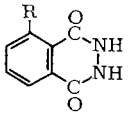
Compounds of type *(2)* [1] [vinylogs of *(1)* in the wider sense] are more effective than luminol (3-aminophthalhydrazide) in purely aqueous systems. However, in mixtures of DMSO and water, hydrazides of type *(3)* [1] and *(4)* [vinylogs of *(1)* in, respectively, the wider and the narrower sense] are much superior to luminol and hydrazides of type *(2)*. Compound *(4)* with R′ = cyclohexyl and *n*-pentyl was synthesized from dimethyl 3-methylphthalate *(5)* by way of the steps *(6)*–*(11)*.

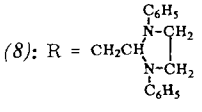


(4)

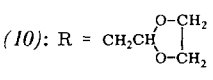


(5): R = CH_3
(6): R = CH_2Br
(7): R = CH_2CN

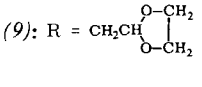




(8): R =



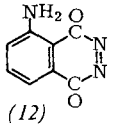
(10): R =



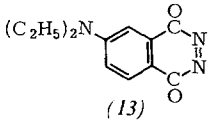
(9): R =

(11): R = CH_2CHO

Dehydrogenation of the monosodium salts of the corresponding hydrazides with *tert*-butyl hypochlorite in dimethyl ether leads to the azaquinones *(12)*–*(14)*.



(12)



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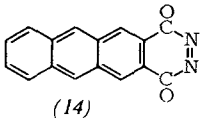
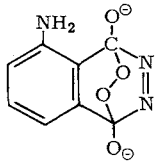


(14)

Compounds *(13)* and *(14)* are deep violet in the crystalline state and chemiluminesce when their acetone solutions are mixed with aqueous sodium hydroxide. The light yield is a function of the amount of H_2O_2 present, which, however, can also be replaced by oxygen [2]. The quantitative findings support the mechanism proposed by *Rauhut* [3] for the chemiluminescence of luminol and related compounds, which postulated decomposition of a peroxide of type *(15)* as energy-releasing step.



(15)

Lecture at Göttingen (Germany) on February 1, 1968 [VB 150 IE]
German version: Angew. Chem. *80*, 494 (1968)

[*] Prof. Dr. K.-D. Gundermann
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[1] *K.-D. Gundermann*, Angew. Chem. *77*, 572 (1965); Angew. Chem. internat. Edit. *4*, 566 (1965).

[2] *K.-D. Gundermann*, Lecture at GDCh-Hauptversammlung Berlin, September 1967.

[3] *M. M. Rauhut, A. M. Semsel,* and *B. G. Roberts*, J. org. Chemistry *31*, 2431 (1966).

The Behavior of Modifications of Arsenic Sesquioxide

By *I. N. Stranski* [*]

The behavior of arsenolite (cubic) and claudetite (monoclinic) offends against some of the rules for polymorphic substances, *e.g.*, against the rule that crystals cannot be heated above their transition point (or melting point) and also against Ostwald's stepwise rule. The fundamental assumption [1–5], which has been confirmed by structural analysis of claudetite, is that the two forms differ basically in the nature of the lattice components and in their mode of union: claudetite has a layer lattice with cross-linkage by primary valences within the layers and by van der Waals bonding between the layers; arsenolite, however, contains a molecular lattice of diamond type formed from saturated, isolated As_4O_6 molecules.

All the anomalies in the phase transitions (evaporation, condensation, dissolution, crystallization, melting, and solidification) are caused by the fact that the units of the initial phase must be rearranged to units of the product phase. Appreciable activation energies are required in practice for this process, and particularly so when primary valences have to be cleaved.

The condensation as arsenolite instead of as the stable claudetite that is observed above and below the transition point (*ca.* −30 °C) results because up to *ca.* 800 °C arsenic oxide vapor consists almost exclusively of saturated As_4O_6 particles, whose bonding must be at least partly destroyed before incorporation into the claudetite lattice. Correspondingly, the evaporation of claudetite is hindered in comparison with that of arsenolite, and its rate of evaporation at comparable vapor pressure is lower by many powers of ten, because only secondary valences need to be broken during destruction of the claudetite lattice.

For dissolution and for crystallization from solutions the decisive factor is whether the solvent can (*e.g.*, H_2O) or cannot (*e.g.*, $AsBr_3$) set up an equilibrium between the units composing the various phases. In the negative case measurements of solubility can lead to totally false conclusions about the transition point. That arsenolite can be heated unchanged, not merely above its transition point, but even above its melting point, arises because the melt has a claudetite-like structure, so that cleavage of the lattice is necessary also for conversion into the molten state. Whereas in many cases the activation energy can be lowered catalytically (*e.g.*, by entry of H_2O into the action), it is often added as thermal energy or ion impact in enforced condensations. However, in such cases amorphous, glassy condensates usually result, and

crystalline claudetite is formed only under special experimental conditions.

The modifications of arsenic oxide provide a clear model system for the study of phase transitions that are influenced by structure.

Lecture at Hamburg (Germany) on February 2, 1968 [VB 148 IE]
German version: Angew. Chem. *80*, 495 (1968)

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[1] *K. A. Becker, K. Plieth,* and *I. N. Stranski,* Progr. inorg. Chem. *4*, 1 (1962).

[2] *K. A. Becker, W. Kollmitt,* and *I. N. Stranski,* Z. physik. Chem. N.F. *37*, 314 (1963).

[3] *K. A. Becker, H. Karge,* and *I. N. Stranski,* Z. physik. Chem. N.F. *44*, 1 (1965).

[4] *K. A. Becker, H. Karge,* and *I. N. Stranski,* Z. physik. Chem. N.F. *44*, 7 (1965).

[5] *I. Klipping,* Z. physik. Chem. N.F. *54*, 68 (1967).

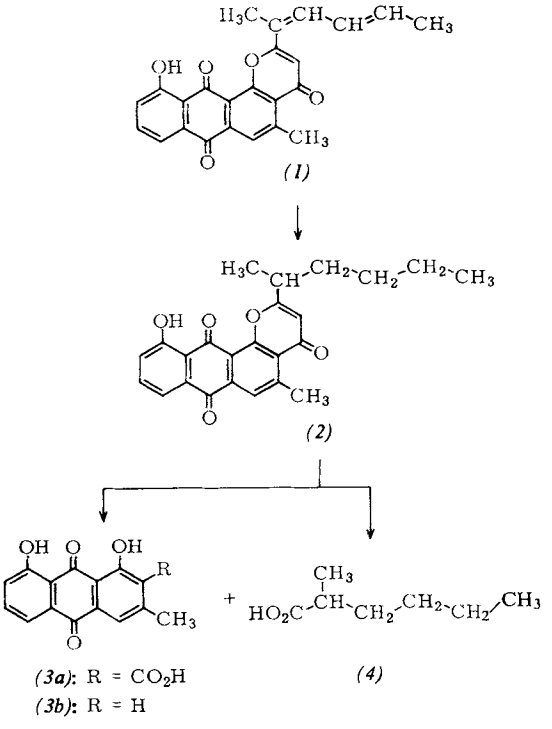
Indomycins and Indomycinones

By *H. Brockmann* [*]

From the mycelium of *Streptomyces* sp. *Ind.* 927, *J. Schnell* [1] has isolated: indomycin A, yellowish-red, provisional molecular formula $C_{40}H_{52}N_2O_{10}$ [6 C–CH_3, NH–CH_3, $N(CH_3)_2$, 5 active H atoms], $[\alpha]_D^{20} = +345°$ ($CHCl_3$), bacteriostatic against *B. subtilis* to a dilution of $1:2.5 \times 10^5$, carcinostatic against Ehrlich ascites tumor at 2 mg/kg mouse; indomycin B, brownish-yellow, provisional formula $C_{38}H_{48}N_2O_{10}$ [5 C–CH_3, NH–CH_3, $N(CH_3)_2$, 5 active H atoms], $[\alpha]_D^{20} = +319°$ ($CHCl_3$), bacteriostatic against *B. subtilis* to $1:2.5 \times 10^6$, carcinostatic against Ehrlich ascites tumor at 2 mg/kg mouse; and indomycin C, brownish-red crystals, provisional formula $C_{41}H_{52}N_2O_{11}$ [6 C–CH_3, NH–CH_3, $N(CH_3)_2$, 7 active H atoms], $[\alpha]_D^{20} = +254°$ ($CHCl_3$), carcinostatic against Ehrlich ascites tumor at 30 mg/kg mouse.

The indomycins have a bitter taste, are yellowish-red in organic solvents, violet in methanolic alkali hydroxide, and red in concentrated sulfuric acid, give a red vat with dithionite, and contain a quinone group with a chelated hydroxyl group. Further, biologically inactive, yellow indomycinones were also isolated from the mycellium; these are either the indomycin chromophores or compounds resembling them very greatly in structure.

The constitution of the yellow crystalline, optically inactive α-indomycinone *(1)* was proved by *K. H. Dahm* [2], by ozone degradation of dihydro- and tetrahydro-α-indomycinone *(2)* to 9,10-dihydro-1,8-dihydroxy-3-methyl-9,10-dioxo-2-anthracenecarboxylic acid, chrysophanic acid *(3b)*, and



(1)

(2)

(3a): R = CO_2H
(3b): R = H

(4)

2-methylhexanoic *(4)* or butyric acid respectively, supplemented by ^1H–NMR and mass spectra of *(2)*, of dihydro-α-indomycinone, and of their acetates. The configuration of the side chain has not yet been established.

Lecture at Clausthal-Zellerfeld (Germany) on January 26, 1968 [VB 156 IE]
German version: Angew. Chem. *80*, 493 (1968)

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[1] *J. Schnell,* Dissertation, Universität Göttingen, 1963; in the present report, the indomycins are designated A, B, C and not α-, β-, γ-, as they are in *Schnell*'s work.

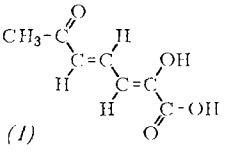
[2] *K. H. Dahm,* unpublished.

SELECTED ABSTRACTS

Olefins were converted into aldehydes by *H. C. Brown, R. A. Coleman,* and *M. W. Rathke* by hydroboronation of the olefins, treatment of the trialkylboranes with CO and $LiAlH(OCH_3)_3$ at atmospheric pressure and room temperature, and subsequent careful oxidation. Examples: 1-hexene → heptanal (yield 98 %); isobutene → 3-methylbutyraldehyde (91 %); norbornene → 2-norbornanecarbaldehyde (87 %). / J. Amer. chem. Soc. *90*, 499 (1968) / –Kr.

[Rd 840 IE]

Microbiological conversion of 3-methylpyrocatechol into 2-hydroxy-6-oxo-*trans*-2-*trans*-4-heptadienoic acid *(1)* is described by *D. Catelani, A. Fiecchi,* and *E. Galli.* After incubation of 3-methylpyrocatechol with a *Pseudomonas desmolyticum* culture in phosphate buffer of pH = 7, a yellow



(1)

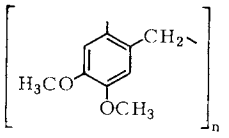
compound of m.p. 122–124 °C (decomp.) could be isolated from the culture liquid; this product was identified as *(1)*. / Experientia *24*, 113 (1968) / –Ma.

[Rd 850 IE]

Exchange of oxygen and hydrogen atoms of *o*-nitrotoluene was observed by *E. K. Fields* and *S. Meyerson.* On pyrolysis of a solution of *o*-nitrotoluene in methanol at 600 °C (11 sec contact time) methyl anthranilate was formed as principal

product (48 mole-% yield). Intramolecular oxidation and reduction yields anthranilic acid which in absence of methanol loses the COOH group and gives aniline. Nuclear-substituted *o*-nitrotoluenes such as 4-fluoro-2-nitrotoluene, 4-chloro-2-nitrotoluene, 3-nitro-*o*-xylene, and nitro-*p*-xylene give 4-fluoro-, 4-chloro-, and 3-methyl- and 4-methyl-anthranilate, respectively, in *ca.* 35 mole-% yield. / Tetrahedron Letters *1968*, 1201 / –Ma. [Rd 851 IE]

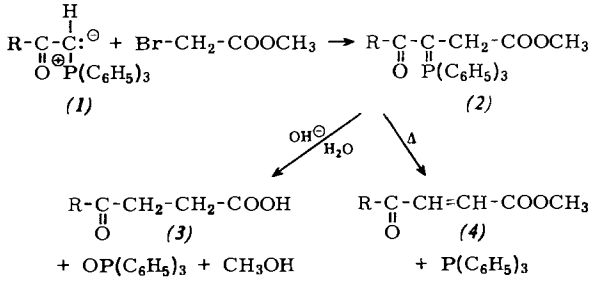
Cyclotetraveratrylene *(1)*, the first derivative of the symmetrical cyclododecatetraene system, was obtained alongside the known cyclotriveratrylene *(2)*, by *J. D. White* and *B. D. Gesner*, when they warmed a solution of 2,4-dimethoxybenzyl alcohol in glacial acetic acid with a few drops of concentrated H_2SO_4 at 90 °C [68 % of *(2)*, 16 % of *(1)*] or treated veratrole in 70 % H_2SO_4 with aqueous formaldehyde at 0 °C.



(1), n = 4
(2), n = 3

In contrast to the rigid crown conformation of *(2)*, the product *(1)* is flexible and provides the possibility of pseudorotation around the methylene-C atoms. At low temperatures the mobile molecule can be frozen in a single conformation (chair or saddle form). / Tetrahedron Letters *1968*, 1591 / –Ma. [Rd 855 IE]

A new synthesis of esters of γ-keto acids and of β-acylacrylates has been described by *H.-J. Bestmann, G. Graf*, and *H. Hartung*. Triphenylphosphineacylmethylenes (β-oxoalkylidenetriphenylphosphoranes) *(1)* react with ethyl bromoacetate in a molar ratio of 2:1 to give triphenylphosphineacylmethoxycarbonylmethylmethylenes (β-oxoalkylidenemethoxycarbonylmethyltriphenylphosphoranes) *(2)* in a yield of about 70 %.



Alkaline hydrolysis of *(2)* in aqueous methanol leads to removal of triphenylphosphine oxide and methanol, with smooth formation of γ-keto acids *(3)* (R = CH_3, 69 %; R = C_3H_7, 45 %; R = C_6H_5, 94 %). The methylene H atoms in the ylides *(2)* are activated by the adjacent ester group. Consequently when the compound is heated to 150–180 °C, it decomposes into triphenylphosphine and the β-acylacrylate *(4)* (R = CH_3, 30 %; R = C_3H_7, 62 %; R = C_6H_5, 85 %). / Liebigs Ann. Chem. *706*, 68 (1967) / –DK. [Rd 798 IE]

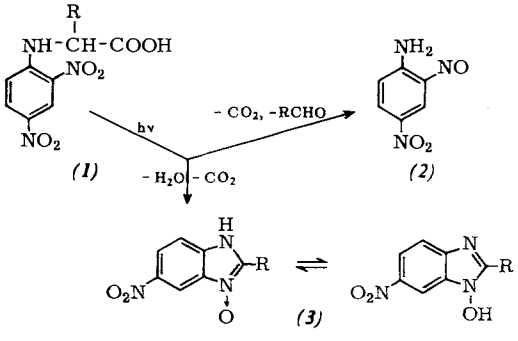
Dimethylaminotrimethylstannane *(1)* **is an efficient dehydrochlorinating agent,** as was found by *D. J. Cardin* and *M. F. Lappert*:

$(CH_3)_3Sn{-}N(CH_3)_2 + Cl{-}A{-}H \longrightarrow (CH_3)_3SnCl{\cdot}HN(CH_3)_2 + A$
(1) *(2)*

The reaction proceeds under mild conditions and almost quantitatively. Compound *(2)* is easily separated because of its low solubility. The efficiency of the reagent is thought to be partly due to the weak, strongly polar Sn–N bond, the high basicity of *(1)*, the high heat of formation of crystalline *(2)*, and in inorganic reactions, the intermediate formation of metal-Sn bonds. Other amido compounds, such as $[(CH_3)_3Sn]_3N$ and derivatives of the more strongly electropositive elements, should behave in a similar manner. Examples: $IrHCl_2(PPh_3)_3$ and $IrH_2Cl(PPh_3)_3$ are dehydrochlorinated in xylene at 80–100 °C within 2 hours and 1.5 hours respectively, with formation of $IrCl(PPh_3)_3$ and $IrH(PPh_3)_3$. At 40 °C *n*-C_4H_9Cl gives 5.2 % *cis*- and 88.5 % *trans*-$CH_3{-}CH{=}CH{-}CH_3$, together with 6.3 % $CH_3{-}CH_2{-}CH{=}CH_2$. / Chem. Commun. *1967*, 1034 / –Ma. [Rd 819 IE]

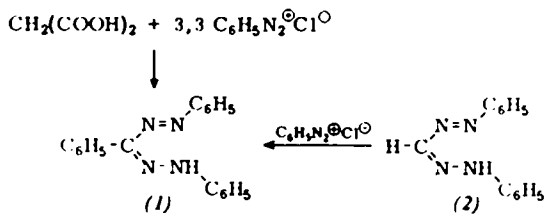
New technetium compounds have been prepared by *J. H. Holloway* and *H. Selig*. When an excess of NO, NOF, or NO_2F was condensed at –195 °C on TcF_6 they obtained the nonvolatile compounds $NOTcF_6$ *(1)* (yellow), $(NO)_2TcF_8$ *(2)* (off-white), and NO_2TcF_7 *(3)* (yellow), respectively. $(NO)_2TcF_8$ has the same structure as $(NO)_2WF_8$ and $(NO)_2ReF_8$, which can be prepared analogously. The magnetic moment of *(2)* (1.72 BM.) is in accord with octacoordinated Tc(VI), but that of *(1)* (2.82 BM.) is too high for this. *(3)* has a magnetic moment of 1.62 BM. / J. inorg. nuclear Chem. *30*, 473 (1968) / –Kr. [Rd 842 IE]

The photolysis of *N*-(2,4-dinitrophenyl)-α-amino acids *(1)* (DNP-amino acids) yields 4-nitro-2-nitrosoaniline *(2)* and/or 2-substituted 6-nitrobenzimidazole 1-oxides *(3)*. *D. J. Neadle* and *R. J. Pollit* studied the well known light-sensitivity of DNP-amino acids and found that *(2)* is generally formed from DNP-amino acids having an α-hydrogen atom. Photolysis of DNP-α-alanine leads to *(3)*, R = CH_3, in a yield that varies in a complex manner with the pH value of the solution.



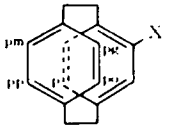
The photolysis of DNP-threonine leads, as expected, to *(3)* with R = $CHOH{-}CH_3$, and also to *(3)* with R = H; the authors attribute the formation of the latter product to a retroaldol-like reaction. / J. chem. Soc. (London) *C 1967*, 1764 / –DK. [Rd 797 IE]

Triarylformazanes have been obtained by *F. A. Neugebauer* and *B. Küchler*. For example, 1,3,5-triphenylformazane *(1)* was obtained in 44 % yield from 1 mole of malonic acid and 3.3 moles of benzenediazonium chloride in DMF/pyridine (dec. p. 176–177 °C). 1,5-Diphenylformazane *(2)* is converted into *(1)* under the same conditions, so that *(2)* may be assumed to be an intermediate in the formation of *(1)*. The new method is useful for the preparation of substituted triarylformazanes. For example, only 4-fluoroaniline is required for the preparation of 1,3,5-tris(4-fluorophenyl)formazanes,



whereas 4-fluorobenzaldehyde and 4-fluorophenylhydrazine were also required in the old method. Liebigs Ann. Chem. *706*, 104 (1967) DK. [Rd 795 IE]

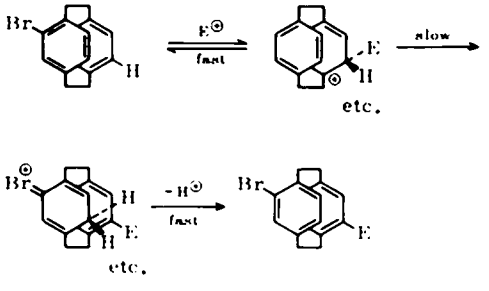
On electrophilic substitution of monosubstituted [2.2]paracyclophanes *(1)* *H. J. Reich* and *D. J. Cram* found the values given in the table. Compounds *(1a)*-*(1f)* were treated with



(1)

	X	% *para* (p)	% of *pseudo* *ortho* (po)	*para* (pp)	*meta* (pm)	*gem* (pg)
a	CO_2CH_3					89
b	$COCH_3$					56
c	CO_2H					63
d	NO_2		2	6	8	70
e	CN		16	25	26	
f	Br	5	16	26	6	
g	Br	17	5.6	41		

Br_2 + Fe, and *(1g)* with CH_3COCl + $AlCl_3$. The annexed reaction mechanism is proposed. J. Amer. chem. Soc. *90*, 1365 (1968) / -Kr.

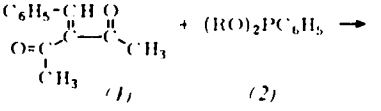


[Rd 845 IE]

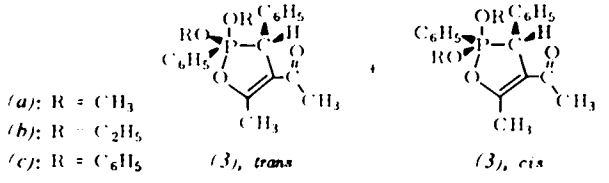
Adsorption of alkali salts onto silica gel from acetone solution was studied by *R. Maatman et al.* for the cases of LiCl, $LiNO_3$, and NaI. Cations and anions are reversibly adsorbed to equal extents (without ion exchange); on addition of small amounts of water (< 2 vol-%) the extent of adsorption increases, but with larger amounts of water decreases again. Langmuir isotherms were used for finding the equilibrium constants for formation of surface species of LiCl ($2-6 \cdot 10^2$ l mole^{-1}) and for $LiNO_3$ and NaI (both ≈ 10 l mole^{-1}). The concentration of the adsorption centers of silica gel varies according to the water content between 0.2 and 0.6 mmole g^{-1} (8×10^{13} cm^{-2}; distance between the centers on regular distribution over the surface ≈ *ca.* 35 Å). No adsorption of salt was found when *n*-propyl, *n*-butyl, or isopentyl alcohol was used as solvent. / J. physic. Chem. *72*, 97 (1968) / -Hz. [Rd 856 IE]

The cause of superconductivity is suggested by *H. Krebs* as being that orbitals of the solid overlap in such a way that electrons are able to move in at least one direction without having to pass through a planar or conical atomic nodal plane. This is verified for the simplest case when the s orbitals form a band that is energetically separated from others in a lattice. This hypothesis is discussed with reference to the bonding in many metallic-conducting inorganic compounds for which superconductivity has been observed. Z. Naturforsch. *23a*, 332 (1968) Hz. [Rd 857 IE]

Stereoisomerism at the P atom of cyclic oxyphosphoranes has been observed by *F. Ramirez, J. F. Pilot, O. P. Madan,* and *C. P. Smith.* From 3-benzylidene-2,4-pentanedione *(1)* and the phosphonite esters *(2a)* *(2c)* they obtained the 1,2-oxa-P^V-phospholenes *(3a)* *(3c)*, which according to the ^{31}P NMR spectra in CH_2Cl_2 at 25 °C exist in two diastereoisomeric forms.



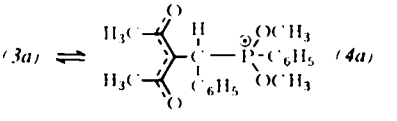
(1) *(2)*



(a): R = CH_3
(b): R = C_2H_5
(c): R = C_6H_5

(3), *trans* *(3)*, *cis*

The phospholene ring of *(3)* occupies an apex and a corner of the basal plane of a trigonal bipyramid, and the P-phenyl ring and an alkoxy group occupy the other two equatorial positions. The other alkoxy group forms the second apex of the pyramid. Interchange between CH_3O and C_6H_5 begins at about 52 °C, and at still higher temperature *(3a)* passes reversibly into the open-chain dipolar form *(4a)*.



(3a) *(4a)*

On reaction of the phosphinite esters $ROP(C_6H_5)_2$ (R = CH_3, C_2H_5, C_6H_5) with *(1)* there is formed only a single compound analogous to *(3)* (containing two equivalent phenyl groups) which also decomposes to a dipolar ion at elevated temperatures. / J. Amer. chem. Soc. *90*, 1275 (1968) / -Kr. [Rd 843 IE]

An eight-membered gold-oxygen ring (with four μ-hydroxo groups) is present, according to *G. E. Glass, J. H. Konnert, M. G. Miles, D. Britton,* and *R. S. Tobias,* in dimethylgold(III) hydroxide, which is tetrameric in the crystalline state and in all the solvents studied. The orthorhombic unit cell contains 32 (monomeric) formula units (space group Pbca, *a* = 19.35, *b* = 9.65, *c* = 19.59 Å). The rings are stacked one above the other and are held together by strong intramolecular hydrogen bonds. The close packing of this stack leads to a very dense structure. Even in solution, $[(CH_3)_2AuOH]_4$ is clearly very rigid; two kinds of methyl protons can be distinguished by NMR spectroscopy up to at least 94 °C. There may be several crystalline modifications of this substance. / J. Amer. chem. Soc. *90*, 1131 (1968) / -Kr. [Rd 844 IE]

Handbuch der theoretischen Chemie (Handbook of Theoretical Chemistry). By *Leopold Gmelin*. Facsimile reprint of the 1st edition of 1817. Verlag Chemie, Weinheim/Bergstr. Vol. 1: 382 pages, Vol. 2: 588 pages, Vol. 3: 664 pages. All three volumes in a cassette, DM 260.–.

At the time when *Leopold Gmelin* first wrote his "Handbuch der theoretischen Chemie" 48 elements had been discovered. Nevertheless, his preface opens with words which could well be read in books published in our own day: "The great advances made in chemistry in recent times, which have rendered worthless otherwise excellent handbooks of chemistry . . . , justify the present author in writing this work." 150 years have passed, and "Gmelin" has grown steadily, both in volume and in stature.

To celebrate this jubilee the Gmelin Institut has issued a facsimile reprint of the long unobtainable first edition of this handbook. The three modest volumes (their binding also follows the style of the original) will impress everyone possessing a sense of history. Few people no doubt are aware that Gmelin's handbook originally embraced inorganic, organic, and, to a lesser extent, physical chemistry. *Berzelius* wrote to *Gmelin* in 1830: "Now that we have your handbook it is no longer any achievement to become a learned chemist, because everyone who acquires and uses a copy is up-to-date with his science." It is fascinating to learn what it was to be up-to-date 150 years ago. The chapter on electricity in *Gmelin* begins "Electricity is sometimes taken to denote 2 unweighable fluids with very many analogous properties but directly opposed in their behavior toward each other, and sometimes only one, the relative excess or deficiency of which produces the manifestations of positive or negative electricity." These words are typical of the outstanding characteristics of this work: its strict, systematic approach, and the efforts of the author to embrace the state of knowledge objectively and exhaustively.

What in 1817 seemed a virtue was no longer so less than 30 years later. *Gmelin* himself, in 1844, wrote in his "Textbook of 'unorganic' chemistry": "The greater my efforts to make my handbook of chemistry more complete with each new edition, the less suitable it becomes for teaching the rudiments owing to the excess of detail. This state of affairs has troubled me so much with the fourth edition, on which I am at present engaged, that I have felt obliged to compile the present textbook for my lectures . . . The essence has been to include only the precepts and facts that are of general theoretical or practical importance". The problem of comprehensiveness *versus* critical selection is thus practically as old as the handbook itself.

The Gmelin Institut deserves our gratitude for the idea of the facsimile reprint, not only because it grants us access to a piece of history, but also, and especially, because the three modest volumes, which represent the entire state of knowledge of their time, encourage us to reflect on the present state of chemistry and on chemical literature from its inception.

H. Grünewald [NB 688 IE]

Gelchromatographie (Gel chromatography). By *H. Determann*, Springer-Verlag, Berlin-Heidelberg-New York 1967, 1st Edit., xii, 204 pages, 40 figures, DM 32.–.

The method of gel chromatography has within a short space of time become a valuable technique used in many chemical and medical laboratories. Its wide scope explains why most reviews describe only parts of the field, or fail to give a comprehensive account of experimental details. The present book closes this gap.

Five chapters describe the present state of gel chromatography. The practical section which describes the gels, the apparatus, and the experimental techniques will be most useful to the novice. Little is as yet known about the fundamentals of gel chromatographic separation, not least because our knowledge concerning the state and properties of cross-linked systems is still very limited. In the theoretical section, the attempt by the author to compare critically the different postulates about gel chromatography will stimulate the reader to reflect our ideas concerning the method and to carry out further experiments.

The sections on principles of application and results show how difficult it is to follow work published in periodicals devoted to different subjects. The detailed descriptions and the numerous literature references make this book a valuable guide for all faced by fresh problems in this field.

It is to be hoped that this book will receive the attention it deserves by workers engaged in the study of those disciplines in which this technique can be used. *W. Heitz* [NB 709 IE]

Acryl- und Methacrylverbindungen (Acrylic and Methacrylic Compounds). By *H. Rauch-Puntigam* and *T. Völker*. Springer-Verlag, Berlin-Heidelberg-New York 1967. 1st Edit., xx, 429 pages, 24 figures, DM 89.–.

The technical development of acrylic and methacrylic compounds began in Germany at the end of the nineteen-twenties and beginning of the thirties. The result was not only Plexiglas and the important polymer dispersions, but also acrylonitrile fibers and polyvinyl chloride *via* the acrylate copolymers. A presentation of this field was therefore urgently indicated, though more difficult than that of individual compounds such as vinyl chloride or styrene.

The large number of possible functional derivatives of the carboxyl group, *e.g.* acids, salts, esters, amides, nitriles, chlorides, and aldehydes, and the manufacture, properties, and uses of the polymers are manifold; furthermore, acrylic compounds readily polymerize and have the ability to copolymerize with one another and with all other vinyl compounds – a host of possibilities which provided a strong stimulus to the development of the field from the very beginning, but which renders the task of making a clear overall survey somewhat difficult.

The authors, evidently themselves active in this field, have accomplished this task successfully.

They begin with a detailed description of the monomers, their preparation, chemical reactions, physical properties, and analysis. α-Substitution products other than the α-methyl derivatives have not been forgotten.

Subsequent chapters deal with polymerization and, in a clear and comprehensive manner, bring the reader up-to-date with the state of affairs in this field.

The sections on the preparation, properties, and application of the polymers, Plexiglas and the methacrylate polymers in general, have been given particular attention. In addition to water-soluble polymers, nitrile polymers, and above all polyacrylonitrile fibers, bead polymerization, and emulsion polymers, the latest developments such as reactive polymers and reactions on polymers are presented in detail.

This excellently produced book concludes with a compilation of the analytical procedures used for characterizing polymers. It will be highly useful to all plastics chemists as an introduction, an all-embracing means of orientation, and a reference work. *H. Fikentscher* [NB 715 IE]

Praktische Chemie für Mediziner (Practical Chemistry for Doctors and Medical Students). By *H.-G. Henning*, *W. Jugelt*, and *G. Sauer*. Verlag Volk und Gesundheit, Berlin 1966, 364 pp., numerous figures, DM 22.40.

In contrast to most textbooks in current use the present work is built up deductively, *i.e.* special cases are treated secondarily and are derived from the general laws. For instance, the

authors assume atoms and chemical bonds to be axiomatic and subsequently derive the laws of stoichiometry and compound formation as a logical consequence.

In place of a senseless enumeration of countless substances, the book concentrates on reactions and compounds important to an understanding of theoretical chemistry. The theory of electronegativity is used to discuss the most important main and subgroup elements. In view of the fact that the book is intended for medical students, it is surprising that theoretical problems are dealt with in such detail. More difficult subjects such as orbital models, energy problems in chemical reactions, kinetics, *etc.* are represented without mathematical ballast but are nonetheless plausible and clear. Selected subjects from the fields of kinetics, electrolytic dissociation (pH, p*K*, titration, buffers, *etc.*), and catalysis are discussed in particular detail, since a knowledge of such topics is indispensable to the biochemist and doctor. The preferential treatment of theoretical problems is particularly welcome.

In the section dealing with organic chemistry the clear presentation and the strict classification of the principal types of compounds and functional groups are a characteristic feature. The modern way of writing organic reaction mechanisms is demonstrated clearly.

The chapter on analytical chemistry is likewise praiseworthy. There is no accumulation of widely varying and rarely occurring ions to overwhelm, plague, and bore the reader, and he is not asked to analyze a blown-up pharmacy. He is, on the other hand, made familiar with modern methods such as photometry, polarimetry, ion exchange, paper chromatography, thin-layer chromatography, *etc.*

W. Littke [NB 694 IE]

Handbuch der Kolorimetrie; Band III: Kolorimetrie in der Biologie, Biochemie und Medizin (Handbook of Colorimetry; Vol III: Colorimetry in Biology, Biochemistry, and Medicine) Part B: Inorganic Part. By *B. Kakáč* and *Z. J. Vejdelék*. Translated by *E. Hachová*. Gustav-Fischer Verlag, Jena. 1966. 1st Edit., xiii, 510 pp., 44 figures, DM 49.60.

The inorganic part of Volume III of this handbook [*] deals with the quantitative analysis of inorganic components in biological substances by means of their light absorption in the visible region. The arrangement of the book follows that of the periodic table. In addition to normal salt-like constituents of vegetable and animal tissues or liquids, it is necessary to determine chemically bound metals such as iron, magnesium, cobalt, zinc, and also the toxicologically important elements arsenic, lead, mercury, chromium, *etc.* The preparation of the material to be analyzed is described in detail, especially the "mineralization" necessary in many instances. As in previous volumes, detailed instructions and critical comments regarding sensitivity, reproducibility, and sources of error constitute a most valuable aid to the user. The now complete work unquestionably fills a gap, and is likely to prove indispensable in biological, medicinal, and pharmaceutical laboratories, where photometric determinations are frequently carried out. It provides an effortless and yet reliable guide to the available methods.

H. Böhme [NB 723 IE]

The Organic Chemistry of Nitrogen. By *N. V. Sidgwick*. Edited by *I.T. Millar* and *H. D. Springall*. Oxford University Press, London 1966, 3rd Edit., xii, 909 pages, numerous illustrations, bound, 168 s.

The well known book by *N. V. Sidgwick* (1873–1952) published in 1910, the 2nd edition of which was rewritten in 1937 by *T. W. J. Taylor* and *W. Baker*, has been completely revised for the 3rd edition by *I. T. Millar* and *H. D. Springall* of Keele University. Its size has been increased by about 50 % in comparison to the 1937 edition. In 1910 *Sidgwick* (the reviewer is happy to record the presence of a detailed biography) may have found it attractive to classify the organic chemistry of nitrogen separately from the rest of the material. In 1937 such an arrangement was already problematic, not only because of the interim growth of the material, but above all because by then the "nitrogen part" of organic chemistry had become so interwoven in the general subject that its isolation in the form of a textbook must have been recognized as a risky undertaking.

The introduction to the third edition, appearing a whole generation later, indicates that the new authors have been conscious of this problem. The arrangement of the book leads one to conclude that the last chapter, Nucleic acids (44 pages), is intended to be the great climax for which the other chapters prepare the way; it is surely for this reason too, that Diazines (40 pages) have been restored. Unhappily, it is in the field of nucleic acids more than in any other that progress is so rapid that to talk of the state of knowledge in 1964 – representing the scope of the book – is rather like discussing olden days. In fact, descriptions such as those given on pages 834, 849 and 864 were already out-of-date at the time of publication.

In the 28 preceding chapters it is in many instances precisely the highlights of organic nitrogen chemistry since 1937 which have fallen victim to mere reference to other monographs. What remains is pure textbook chemistry on subjects about which good reviews have long existed in most languages, albeit not, as here, in the straitjacket of the nitrogen aspect. Is there any point in describing acid amides, nitriles, and amines in textbook form without mentioning carboxylic acids and alcohols?

The present book suggests an unequivocal negative.

The chapter on Amides (pp. 223–250) makes no reference to *Meerwein*'s work on acid amide acetals, which set a new landmark in this field. The Vilsmeier-Haack method is no more mentioned than is its elegant extension by *C. Jutz*. The names *B. N. Menschutkin, T. Zincke, W. König, N. J. Leonard* and many others are conspicuous by their absence. For a mention of the great champion of nitrogen chemistry, *Theodor Curtius*, one might have been prepared to sacrifice the somewhat less important and unsupported historical references, such as (p. 796) "*Baeyer* named the product after a girl called Barbara, with whom he was in love at the time". In the discussion of azo compounds there is no mention of *S. Hünig*'s method of oxidative azo coupling, a surprising omission in an allegedly exhaustively investigated subject. The immonium-carbonium mesomerism which illuminates so many reactions of organic nitrogen compounds is not dealt with. In addition, it hardly seems proper to scorn all mention of spectroscopic data and discussion.

Other important subjects are dismissed too summarily, *e.g.* the enamines (pp. 132–134) whose essential character is not elucidated. The esters of cyanic acid, like the pentazoles, receive only a few lines, though these chapters do not yet appear in conventional textbooks.

These are just a few examples. The expert knowledge in the chapter by *R. McWeeny*, Quantum Theory of Valence, has not rubbed off on any of the remaining chapters.

Most important of all, in view of the book's basic construction, the fundamental question to be asked about any book – to what circle of readers should the book be recommended – is unanswerable.

F. Kröhnke [NB 702 IE]

Synthetic Methods of Organic Chemistry, Vol. 21. By *W. Theilheimer*. S. Karger, Basel-New York 1967. 1st Edit., xx, 540 pp., numerous figures and tables, SFr 195.–/DM 195.–/ $ 46.80.

Volume 21 continues the well-known and proven series in the accustomed manner [1]. Classification and selection therefore

[*] Cf. Angew. Chem. *79*, 328 (1967); Angew. Chem. internat. Edit. *6*, 380 (1967).

[1] Cf. Angew. Chem. *79*, 283 (1967); Angew. Chem. internat. Edit. *6*, 277 (1967).

need no explanation. There are 462 pages, containing almost 1000 examples selected from the literature between 1964 and 1966. The value as specifications for synthesis goes beyond that of individual cases, and can thus serve as a welcome stimulus for original work. Embraced are starting materials, products, and methods spanning the whole of organic chemistry. It is evident that the synthesis of carbocyclic and heterocyclic compounds is progressively gaining in importance. Reading the "Trends in Synthetic Organic Chemistry" (7 pages, 86 refs.) is particularly stimulating; this contains well-defined novel syntheses. A well arranged and very detailed subject index (112 pages) considerably assists orientation, especially if the classification system used is not to the readers's liking.

It is necessary once again to consider whether the mass of information compiled between the covers of the 21 volumes would not be even more accessible with the aid of a cumulative index in the form of a punched card register.

S. Hünig [NB 722 IE]

Hyperfine Interactions. Edited by *A. J. Freeman* and *R. B. Frankel*. Academic Press, New York-London 1967, 1st Edit., xvi, 758 pages, $ 16.00.

The present book is part of a report of a NATO Advanced Study Institute meeting held between the 8 and 26 August, 1966, in Aix-en-Provence, France. The reader is spared a word-for-word rendering in that each lecture has been rewritten in the form of a readily understandable report after the meeting. Thus, even the layman can obtain an insight into the complex material presented.

The book consists of 25 contributions by specialists on aspects of hyperfine interactions such as nuclear spin resonance, paramagnetic resonance, atomic radiation resonance, perturbed angle correlations, dynamic polarization and relaxation, optical hyperfine structure determinations, specific heats of nuclear spin systems, and the Mössbauer effect. Individual, more theoretical articles concern the Hartree-Fock theory of the hyperfine interaction in atoms and magnetic compounds, the calculation of the magnetic hyperfine structure constants of the ground state of light atoms and also the conductivity electron density and spin density effects of dislocations and localized moments in metals.

The discussion concentrates on hyperfine interactions in inorganic solids and in individual atoms. No description is given, however, of hyperfine interactions in organic molecules and radicals, which are important for chemists interested in analytical aspects. *Bleaney* presents a didactic introduction to paramagnetic resonance, *Narath* to nuclear spin resonance in solids, *Abragam* and *Kirsch* dynamic polarization and relaxation, *Mössbauer* and *Cläuser* the Mössbauer effect, and *Cohen* the perturbed angle correlations of nuclear gamma rays.

Gschwind contributes a more detailed account of the paramagnetic resonance of ions in the excited state, and of electron spin-nuclear spin double resonance (ENDOR), *Steudel* deals with optical hyperfine interaction measurements using a double Fabry-Pérot interferometer, *Budnik, Skalski,* and *Shaltiel* nuclear resonance in metals, *Dekker, de Waard, Housley, Gonser,* and *Walker* the Mössbauer effect and *Matthias, Karlsson,* and *Murnik* perturbed angle correlations.

Lounasmaa, Stone, and *Lubbers* discuss the specific heat, cooling effects, and orientation of nuclear spin systems.

This conference report provides a wide survey of the current position and problems of hyperfine interactions in solids, atoms, and ions and can therefore be confidently recommended to the solid state physicist, the physical chemist, and the inorganic spectroscopist.

The analyst working with organic materials will find it of little interest because, as mentioned above, the hyperfine interactions of organic compounds have been omitted.

F. Kneubühl [NB 707 IE]

Introduction to the Principles of Heterogeneous Catalysis. By *J. M. Thomas* and *W. J. Thomas*. Academic Press. London-New York 1967. 1st Edit., x, 544 pp., numerous illustrations and tables, 120 s.

The scientifically very stimulating and technically very important field of heterogeneous catalysis has been the subject of several large collective works and a number of periodical publications (Congress Reports, Advances) during past decades. For some time, however, no modern monograph has been published that embraces the overall field. This is all the more surprising in that research in this sector, both in academic and in industrial laboratories, has assumed very large proportions and is still growing. In addition, universally applicable results have been obtained in many of the subsidiary fields.

In view of the accumulated literature it is not merely remarkable but also in a sense praiseworthy that the two Welsh authors, both students of *K. W. Sykes*, should have undertaken to fill the gap. *J. M. Thomas* is responsible largely for the scientific, and *W. J. Thomas* for the technical chapters. The authors have succeeded in covering all the important aspects while still adhering to their avowed principle that brevity is the key to understanding: Introduction; Adsorption; Experimental Aspects; Pore Structure and Surface; Lattice Dislocations; Geometric, Electronic and Related Factors; Selective and Polyfunctional Catalysts; Mechanism of Typical Reactions; Reactor Design. In all chapters extensive reference is made to the original literature, so that the work, though intended as a textbook for undergraduates and young researchers, can also be used as a work of reference. Naturally, it is possible to disagree on the relative prominence given to various subjects, *e.g.* the overemphasis placed on adsorption at the expense of mixed catalysts, or the electronic factor; however, the book presents the most important things consisely but understandably throughout. The stimulating effect of such books has been proven by experience, and Thomas-Thomas will be of incalculable value to all who work in, or who wish to take up, this field. Printing and presentation are commensurate with the price and up to the publisher's usual standard. *G.-M. Schwab* [NB 706 IE]

Infrared Spectra of Adsorbed Species. By *L. H. Little*, supplementary chapters by *A. V. Kiselev* and *V. I. Lygin*, Academic Press. London-New York 1966. xii, 428 pages, numerous illustrations, 100 s.

Infrared Spectroscopy in Surface Chemistry. By *M. L. Hair*, Marcel Dekker Inc., New York 1967. xiii, 315 pages, several illustrations, $ 15.75.

The chemistry of solid surfaces has attracted increasing attention in recent years, owing largely to the investigation of heterogeneous catalysis reaction mechanisms and of intermediate products. Quite apart from pure scientific interest a knowledge of the state of the surface and its reactions is becoming increasingly important for other investigations, *e.g.* the study of pigments and the incorporation of fillers in polymers. IR spectroscopy furnishes a great deal of information about functional groups on surfaces, their interaction with adsorbed molecules, and about the groups formed. The same technique can be applied to the study of thin metal films and finely divided metals deposited on carriers.

Almost simultaneously, two books have appeared which aim at describing the method, its potentialities, and its limitations, as well as that which has already been achieved. Comparison of the two works reveals that *Little*'s book contains a good deal more text than is suggested by its extra hundred pages. Closer line spacing and fuller pages are responsible, but the penalty is that reading becomes much more tiring. *Little* gives a more comprehensive selection of literature references and includes many papers which contribute to the study of surface chemistry without IR measurements. Furthermore, his book reproduces many more spectra. By way of contrast,

Hair attempts to provide a coherent account at the expense of detail, and evaluates the literature according to his own concepts. This latter book is thus easier to read. Certain formulations, *e.g.* covalent −Al=O double bonds (*Hair*, p. 166) should be overlooked.

Unhappily, as so often in the past, neither author does anything like justice to literature that has appeared in languages other than English. All the more welcome, then, that *Little* has been able to get the Soviet researchers *A. V. Kiselev* and *V. I. Lygin* to contribute their own wide-ranging experience and the abundant Russian literature. The use of IR spectroscopy in the study of surfaces can be traced back to work by *Terenin* in the early nineteen-forties.

As an introduction *Hair* provides several chapters on adsorption and IR spectroscopy which *Little* assumes to be already familiar. *Little* describes the experimental technique in greater detail and more thoroughly. Both authors give special treatments of the OH groups on oxide surfaces, above all on silica, and the surface acidity of silica-alumina adsorption on zeolites, and the chemisorption of carbon monoxide on metals and metal oxides. *Little* deals in detail with the adsorption of hydrogen and hydrocarbons. The literature up to about 1966 has been taken into account, and *Little* appends a list of the most important articles published after his book had gone to print.

Both books can be recommended. *Hair* provides a good survey of, and the results obtained with, the technique, while *Little* gives more information about special problems and is, moreover, less expensive. *H. P. Boehm* [NB 719 IE]

The Palladium-Hydrogen System. By *F. A. Lewis*, Academic Press, London-New York 1967, 1st Edit., xii, 178 pp., numerous illustrations, 45 s.

The well-known monographs on hydrogen in metals by *Smith* and by *Gibb* have, to some extent, been superseded by recent developments. The present book, by *Lewis*, reviews the present state of research specifically in regard to the system palladium-hydrogen. This system is of particular theoretical interest as the prototype of a simple alloy, but it is also of practical interest as a membrane material for fuel cells and for the purification and isotopic separation of hydrogen.

The results of both old and recent work on the thermodynamic, chemical, mechanical, electrical, and magnetic properties are presented in a thoroughly comprehensive manner; separate chapters are devoted to the absorption of hydrogen in palladium alloys, to diffusion, and to isotopic separation. A short chapter deals with attempts to provide a theoretical insight into hydrogen absorption by means of model representations.

No final picture can be expected of a field which is in a state of such intensive development, with active research being conducted in numerous laboratories. It is precisely in such laboratories that this book will be of great help because of its complete literature survey, a factor which should also ensure it a wide distribution.

H. Brodowsky [NB 699 IE]

Fractional Solidification. Vol. 1. Edited by *M. Zief* and *W. R. Wilcox*. Marcel Dekker, Inc., New York 1967, 1st Edit., xvi, 714 pages, numerous illustrations and tables, $ 28.75.

Research and production processes involving solvent-free recrystallization from the melt are becoming progressively more important. The editors, well known from their own work in this field, and twenty specialists chosen by them have succeeded in unifying the individual methods of separation in an all-embracing work, thus finally closing the gap between detailed individual works (*e.g.* about zone melting) and review articles.

Part I lays down the thermodynamic basis of fractionating crystallization from the melt, Part II deals with laboratory apparatus (normal solidification, discontinuous and continuous zone melting with modifications, column crystallization, zone reprecipitation as a transition from recrystallization from solution), and Part III outlines industrial techniques (particularly multiple crystallization by means of cooled drums and the Phillips process). Industrial desalination of sea water brings us to the applications section (Part IV), which deals especially with electronics (semiconductors *etc.*), ultrapure pharmaceutical preparations, analysis, and special techniques. Part V deals briefly with economic aspects. About 1500 literature references, 40 tables, and 266 illustrations in the form of photographs, technical drawings, or diagrams ensure comprehensive evaluation of the material. Part VI consists of a tabular appendix of about 130 inorganic elements, compounds, and systems (298 references), about 110 organic compounds, individual data for 250 organic substances (126 references), and 71 patents to aid the chemist or metallurgist in his investigation. *K. Maas* [NB 701 IE]

Soil Biochemistry. Edited by *A. D. McLaren* and *G. H. Peterson*. Marcel Dekker Inc.. New York 1967. 1st Edit., xiii, 509 pp., numerous figures, $ 22.75.

This monograph represents a collective effort by 25 English-speaking authors. The book is in three parts: I. Isolation and characterization of biochemical components of the soil, *i.e.* nitrogen compounds, nucleic acids and derivatives, organic phosphates, carbohydrates, organic acids, and free radicals. Part II deals with metabolisms, energetic relationships such as photosynthesis, respiration, enzymatic and chemoautotropic reactions, nitrogen-, phosphate-, and sulfur cycles, lignin degradation and humic acid formation, microbial decomposition of phenol, decomposition of herbicides and surface-active agents, and enzyme reactions in the soil. Part III presents microbiological and biochemical aspects of the rhizosphere, and, finally the discussion even extends to the exploration of the surface of planets.

The number of publications, experimental results, and interpretations in the complex field of soil biochemistry has become so vast that no individual can now embrace them all. The authors deserve our gratitude for going to the trouble of sifting the literature of the past 70 years (in some parts of the book up to 1966) and for summarizing and interpreting 2147 publications. The inclusion of not only the English-language literature but also of important references in other languages is particularly welcome. The book, which is entirely up-to-date, introduces the reader to the problems involved in a succint and pregnant manner.

Despite the number of contributors involved, the book is written in a remarkably uniform style. Its content is very well balanced and the work can claim considerable scientific and didactic merit. The first chapter "Introduction to the Biochemistry of Terrestrial Soils" could, it is true, have been omitted without loss, as it contains an arbitrary and not always skilful enumeration of a number of processes and facts which are dealt with again much more soundly in later chapters. A number of misprints will have to be eliminated from subsequent editions.

The two editors are to be warmly congratulated for a book which is recommended to all interested in the chemistry and biology of soil. *F. Scheffer* [NB 725 IE]

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Richard Kuhn in Memoriam [*]

BY O. WESTPHAL [**]

"You may call me an 'experimental philosopher' who endeavors to get at the root of things not only by cogitation but also by experimenting." (*R. Kuhn* [1])

Richard Kuhn was born on December 3, 1900, in Vienna-Döbling (Fig. 1). His father, Councillor *Richard Clemens Kuhn*, was a hydraulic engineer in the Austrian Government Service. It is reported that he

Fig. 1. Birthplace of *Richard Kuhn*, where he also spent his youth.

was held in general esteem and had carried out important projects such as the reconstruction and modernization of Trieste harbor and the planning of the Oder-Danube Canal. He liked music and was an accomplished pianist. His mother, *Angelika* née *Rodler*, was a primary school teacher and retained her profession after the birth of the two children, *Angelika*, and a year later *Richard* (Fig. 2).

Richard Kuhn received an unusual schooling. His mother taught him at home for several years, covering the entire primary school curriculum. He only had to

Fig. 2. The parents, with daughter *Angelika* and son *Richard* in 1907.

report once a year for examinations and was told: "Good, carry on." He started his first regular schooling in 1909 when he entered the Döbling Gymnasium. There he spent eight years together with his friend *Wolfgang Pauli*, who later became a renowned physicist. *Pauli* and *Kuhn* remained lifelong friends, and would often recollect exciting hours spent with their physics and mathematics teacher *Kottenbach*, who, many years later, at the age of 85 was still being visited by *Kuhn* in Austria.

When only 12 years of age *Richard Kuhn* was greatly influenced by a friend of the family, Professor *Ernst Ludwig*, who was Director of the Institute of Medical Chemistry of Vienna University. *Ludwig* took his teaching duties very seriously, especially the demonstration of experiments, and when he was preparing his lectures over the weekend the young *Richard Kuhn* was allowed to accompany him and to take part in preparing the experiments. "There were many wondrous things indeed: mercury solidifying in liquid air,

[*] Address read at the Academic Memorial Service on November 15, 1967 in Heidelberg.

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[1] *R. Kuhn*, From the address delivered on the occasion of the conferring of the honorary degree of Doctor of Philosophy by Vienna University, December 13, 1960.

metals precipitated from solutions by electric current, and vast quantities of rowan berries which were used in those days for extracting malic acid" [1]. *Ernst Ludwig* made him a present of his "Lehrbuch der Chemie für Aspiranten der Pharmazie", which *Kuhn* studied avidly every evening. *Kuhn*'s graduation was also unusual. It was the end of 1917, the war was approaching its climax, and young men were being mobilized. *Kuhn* was also called up and found fit. "At the Gymnasium they thrust my graduation certificate into my hand without any written or even oral examination ... and next day I was reporting to the Signals Regiment in St. Pölten." At St. Pölten he had to take part in security duties during those troubled days, particularly towards the end of the war, and lived through some rather difficult times. On November 18, 1918, he was discharged "until further notice" and, as he once remarked later, remained in that status all his life.

A few days later, on November 22, 1918, he was already eagerly seeking admission to Vienna University. There is a photograph of him, which he had taken for his parents for Christmas of that year (Fig. 3).

Fig. 3. *Richard Kuhn* in Vienna, end of 1918.

It was very difficult to obtain working space in a laboratory in Vienna in those days but, with the help of his godfather, Professor *Richard Paltauf*, Director of the Institute of Pathology, *Kuhn* obtained a laboratory position at the Institute of Medical Chemistry under Professor *Hans Fischer*, who had in the meantime succeeded *Ernst Ludwig*. His actual teachers, however, were *Wilhelm Schlenk* and *Rudolf Wegscheider*. *Kuhn* recalled that *Wegscheider* always used to lecture around 3 P.M. and that this may have been the reason for poor attendance by students; *Kuhn* regretted this very much because he was deeply influenced by *Wegscheider*'s lectures on physical chemistry. He also studied analytical chemistry very seriously under *A. Franke*.

After three semesters and two excellent intermediate examinations under *Schlenk*, *Kuhn* moved from Vienna to Munich. He was aware of the world renown of *Richard Willstätter* (Fig. 4) and had heard of his famous lectures.

Fig. 4. A lecture by *Richard Willstätter*, Munich, 1921.

Kuhn was attracted by *Willstätter*'s virtuosity in organic synthesis and especially by his mastery of research into plant dyestuffs. *Kuhn* found great aesthetic joy in beautiful colors, and, with an early developed appreciation of formulas, he soon admired and was attracted by *Willstätter*'s work. He worked in Munich at an accelerated pace. He was frequently tested, and was progressively given more and more laboratory exercises and assignments. He carried out analyses under Professor *Lecher* so quickly and accurately that it was often thought that something must be amiss; ever more difficult analyses were presented to him, but he mastered them all. Thus, after only six semesters, he was allowed to begin his doctor's thesis under *Willstätter* on the "specificity of enzymes in carbohydrate metabolism". On November 22, 1922, four years to the day after he entered Vienna University, *Kuhn* obtained his Doctorate with the highest marks that could be given.

In the course of the work on the doctorate thesis, *Willstätter* suggested to the young *Kuhn* that he should study seriously the most advanced methods of analytical chemistry. In those days, microanalysis had been developed in Austria to a high level of perfection and accuracy. *Kuhn* interrupted work on his doctorate and returned temporarily to Vienna to study organic analysis under Professor *E. Philippi*. He later wrote that he owed *Philippi* particular gratitude because "most of the work which I undertook later would have been impossible, owing to the very small quantities of substances available, without the techniques which I learned from him. The extent of his influence on me may be assessed from the fact that later, not only as a lecturer in Munich but even for some time as Professor in Zurich, I carried out with my own hands innumerable microanalyses for my doctorate students and assistants" [1].

The remarkable photograph (Fig. 5), dated 1922, symbolizes the exceptional esteem of the great teacher *Willstätter* for his student *Richard Kuhn*. In turn, *Kuhn* was obviously deeply influenced by *Willstätter*. Among other things, *Kuhn*'s later brilliant lectures had many features in common with *Willstätter*'s fascinating art of lecturing.

Kuhn's early life in Munich was very primitive. He was several times evicted by the City Fathers as an "undesirable alien" from the central part of the city where there was an acute shortage of accommodation, so that he had to live a considerable distance from the Institute, which he covered on foot.

Fig. 5. *Richard Willstätter* and *Richard Kuhn* in Munich in 1922.

Once he forgot to shut the skylight in his attic, and on his return found snow covering his habilitation thesis which, in those days, was still written by hand. Many pages were completely disfigured. After the first shock, *Kuhn* accepted the mishap with good grace and rewrote the spoiled pages in his fine hand. There are still in existence some yellowed manuscripts, never handed in, on investigations which he obviously thought unsuitable for publication, which show how very clearly, with only a few alterations and minor corrections, the entire concept was already formed in his mind.

A few months before *Kuhn*'s doctorate, in August 1922, *Willstätter* requested for his 50th birthday that the festive address at the Munich Arts Gallery be read by his favorite student. *Willstätter*'s esteem for *Kuhn* was enormous; he recognized a promising talent and did all he could to foster it. We know of how, in the difficult days of inflation, he provided funds for *Kuhn* to attend a Congress in Edinburgh by casually slipping dollars into his pocket, and of other such instances of help to the young student. *Willstätter*'s Memoirs[2] contain vivid descriptions of life in Munich in the early 1920's, with its political and economic chaos.

Even in those early days *Kuhn* was distinguished by rapid comprehension, enormous powers of insight and imagination, and very high precision and discipline in his work. *Kuhn* came to Munich at a time when *Willstätter* was switching over from classical organic chemistry to the chemistry of enzymes (see[2], pp. 331–332). One of the first, and particularly significant, accomplishments of the young *Richard Kuhn* was that he convinced *Willstätter* of the importance of quantitative physicochemical methods of identification and of accurate kinetic measurements in enzyme chemistry. He introduced such methods for accurate measurement of reaction rates, for determining activities, and for following quantitatively enzyme enrichment and purification processes. *Willstätter* was very impressed and mentioned this to many leading chemists of the day. Thus, he suggested to his friend *Fritz Haber* that there should be more properly organized physical chemistry departments in Germany.

These early enzyme studies also involved absorption and elution methods with carrier substances, which were to become so important later. As substrates for enzyme studies, *Richard Kuhn* used glucosides, oligosaccharides, and polysaccharides, *i.e.* sugar derivatives. Specificity studies led him inevitably into stereochemistry where he found his first great field of independent work. Together with *Friedrich Ebel*, his first doctorate student, he studied the optical activity of substances obtained by addition to ethylenic double bonds, *e.g.* by addition of hypochlorous acid to fumaric and maleic acids; the chloromalic acids and their ring closure to ethylene oxide dicarboxylic acids[3]. *Ebel* obtained his doctorate with "*summa cum laude*", and this greatly increased the influx of doctorate students to the 23-year old *Kuhn*. Using the classical example of the Walden inversion, *Kuhn* and *Theodor Wagner-Jauregg* determined the stage of the reaction at which the steric rearrangement of the substituents takes place[4].

For his habilitation, which took place on March 3, 1925, in Munich, *Kuhn* presented a paper on the "Mechanism of Action of Amylases"[5] and gave a lecture on "The Role of Theory in Organic Chemistry" In addition, he put forward twelve theses (Fig. 6).

Habilitations-Schrift:

Der Wirkungsmechanismus der Amylasen; ein Beitrag zum Konfigurations-Problem der Stärke.

Probe-Vorlesung:

Die Stellung der Theorie in der organischen Chemie.

Thesen:

1. Bei den Phosphor-molybdänsäuren wird die Vereinigung von mehr als 12 MoO_3 mit 1 P durch gleichzeitigen Einbau von Schwefelsäure-, Selensäure- und Tellursäure-Resten in das Kristallgitter ermöglicht.
2. Es ist zu erwarten, daß Chlordioxyd paramagnetisch ist.
3. In den Grundgleichungen der chemischen Kinetik ist, soweit sie sich auf die Reaktion zwischen ungeladenen Molekülen und Jonen in wässriger Lösung beziehen, die Annahme der Proportionalität zwischen Reaktionsgeschwindigkeit und Konzentration der reaktionsvermittelnden Molekülgattungen aufzugeben.
4. Die Abhängigkeit katalytischer Hydrierungen vom Sauerstoffgehalt des Platins bezw. Wasserstoffs steht mit dem Einfluß des Sauerstoffs auf die Intensität der Balmer-Serie in Einklang.
5. Bei Alkyl-halogeniden findet der Ersatz von Halogen durch die SH-Gruppe ohne intermediäre Bildung des entsprechenden Olefins statt.
6. Die Spannungstheorie A. v. Baeyers hat die Entwicklung unserer Kenntnisse von den höheren Polymethylenen und ihrer Derivate entscheidend gehemmt.
7. *Es liegt kein Beweis für die Richtigkeit der Zuckerformeln E. Fischers in der nach B. Tollens* üblichen Modifikation vor.
8. Das Gaultherin stellt das einfachste bisher bekannte natürliche Derivat des Traubenzuckers dar, das keinen butylenoxydischen Sauerstoffring besitzt.
9. Aus der Affinität einer Malzamylase zur Stärke läßt sich auf die Lage der Verzuckerungsgrenze schließen.
10. Die meist weitgehende Dissoziation der Enzym-Co-enzymbindung (Zymase-Cozymase, Trypsin-Enterokinase, Amylasen-Neutralsalze) bedeutet für die Organismen eine wichtige doppelseitige Regulierungsmöglichkeit ihrer fermentativen Funktionen.
11. In der Erholungsphase des Muskels findet neben der Verbrennung von Milchsäure ein Wiederaufbau von Kohlehydraten aus Milchsäure statt.
12. Der Insulintod, in vielen äußeren Symptomen dem Hungertode gleichend, stellt einen Erschöpfungstod in Bezug auf die Zucker-Reserven dar.

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Fig. 6. The twelve theses defended by *Richard Kuhn* before the Philosophical Faculty at his habilitation in Munich on March 3, 1925 [*].

[2] *R. Willstätter*: Aus meinem Leben. Verlag Chemie, Weinheim 1949.

[3] *R. Kuhn* and *F. Ebel*, Ber. dtsch. chem. Ges. *58*, 919, 2088 (1925).

[4] *R. Kuhn* and *Th. Wagner-Jauregg*, Ber. dtsch. chem. Ges. *61*, 504 (1928).

[5] *R. Kuhn*, Liebigs Ann. Chem. *425*, 1 (1925).

[*] The author is indebted for a copy of the printed invitation to Dr. *Leonhard Schuler*, Heidelberg, who was at that time a chemist in Munich.

Some of the theses were rather provocative for Munich, especially Thesis No. 6 (Fig. 6) which criticized Baeyer's strain theory. *Adolf von Baeyer*, *Willstätter*'s predecessor at the Department of Organic Chemistry, was for many years regarded in Munich as the high priest of organic chemistry. *Kuhn* claimed that the hydroaromatic rings should not be considered planar, as assumed by *von Baeyer*, but puckered, thus making it possible to explain in a simple way the stability of rings with seven or more methylene groups. In this, *Kuhn* considered himself a disciple of *van't Hoff* and of his concept of a tetrahedral carbon atom with its four valences.

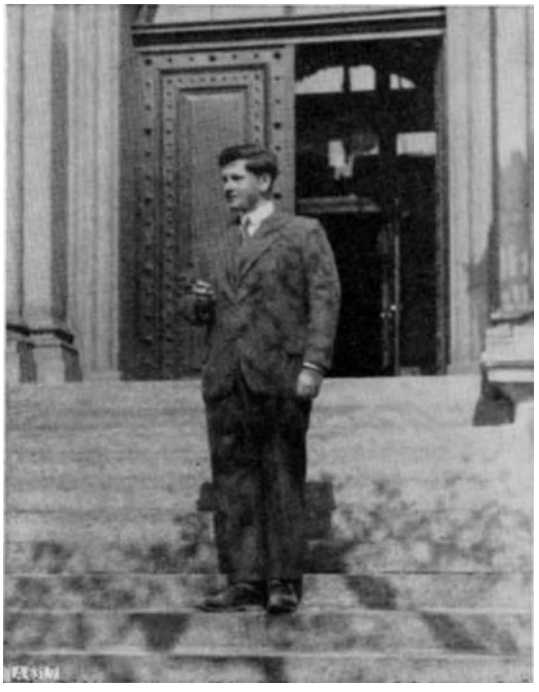


Fig. 7. *Richard Kuhn*, as a 27-year old ordinary Professor of Organic and Analytical Chemistry, at the gate of the Chemical Institute of the ETH in Zurich.

Only eighteen months after his habilitation, following a special recommendation by *Willstätter* [6] (who had himself declined the invitation), *Kuhn* was invited to take over the Department of General and Analytical Chemistry at the Federal Technical University of Zurich. In his inaugural lecture [7] on June 18, 1927, *Kuhn* developed a kind of program for the chemistry of those days, and said that it follows three paths. One path leads to *theoretical research*, governed by numbers and measurements. A second path leads to *technology* and here *Kuhn*, an Austrian by birth, was singing to his Swiss audience in the year 1927 a hymn to German chemical technology, of which he remained a lifelong admirer. A third path leads to *biology*. In a remarkable train of thought, he added that, in the final analysis, the triad which he was endeavoring to express might well be rooted in the very psyche of man and might correspond to an age-old nostalgia: dreams on the nature and the origin of things, the dream of gold, and the dream of eternal youth.

One of his enthralled listeners in Zurich was *Daisy Hartmann*, a student of pharmacy. They were married in 1928 and had two sons and four daughters.

The three years from October 1926 to October 1929 saw the beginning of many investigations of particular importance in his life's work. Among the problems which *Richard Kuhn* tackled in Zurich, and which originated in his stereochemical investigations was the restricted rotation around carbon-carbon bonds in biphenyl derivatives. He was especially interested in the *ortho*-substituted biphenyls showing restricted rotation. In those days, however, the formulas [8] of the two enantiomorphs shown in Fig. 8 were by no means proved.

Fig. 8. Mirror image forms of *ortho*-substituted biphenyl derivatives [8].

For a long time, the folded form *(1)* (see Fig. 9) was also considered as a possible conformation for biphenyl derivatives and was based on the concepts of *Kaufler* [9]. Together with *Zumstein* [10], *Kuhn* was the first to show clearly that the distance between the two amino groups of benzidine cannot be of the order of 1.5 Å as in formula *(1)* but must be of the order of 10 Å as in the stretched formula *(2)* shown in Fig. 9. Only the stretched shape can explain the restricted rotation observed in so many *ortho*-substituted biphenyls.

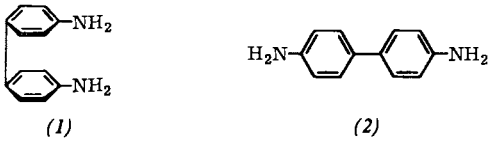


Fig. 9. The two space formulas of benzidine [8].

A short time earlier, *Bjerrum* [11] had shown that the distance between charged groups can be established by determining the ratio of the respective dissociation constants. *Kuhn* applied *Bjerrum*'s quantitative theory to his problem and found unambiguously [10] that form *(2)* and not form *(1)* corresponds to reality.

One of the first quantitative determinations of the activation energy for the rotation of *ortho*-substituted diphenic acids was published by *Kuhn* and *Albrecht* as early as 1927 [12, 13].

[6] See [2], p. 351.

[7] *R. Kuhn*, Die Chemie der Gegenwart und die Biologie der Zukunft. Inaugural lecture (1927), E.T.H. Zürich, Rascher u. Co. 1927.

[8] *R. Kuhn* in *K. Freudenberg*: Stereochemie. Verlag Deuticke, Wien 1933, p. 804.

[9] *F. Kaufler*, Liebigs Ann. Chem. *351*, 151 (1906); Ber. dtsch. chem. Ges. *40*, 3250 (1907).

[10] *R. Kuhn* and *F. Zumstein*, Ber. dtsch. chem. Ges. *59*, 488 (1926).

[11] *N. Bjerrum*, Z. physik. Chem. *106*, 220 (1923).

[12] *R. Kuhn* and *O. Albrecht*, Liebigs Ann. Chem. *455*, 272 (1927).

[13] *R. Kuhn* and *O. Albrecht*, Liebigs Ann. Chem. *458*, 221 (1927).

While the *o,o'*-dinitrodiphenic acid antipodes cannot be racemized, even under vigorous conditions, the *o,p'*-dinitrodiphenic acid is racemized with an activation energy of 26 kcal/mole. This work was followed by several similar investigations by other authors, especially *Roger Adams* in the USA, in which the space requirements of substituents were determined quantitatively for the first time. In *Karl Freudenberg*'s "Stereochemie", under the title "Molecular Asymmetry", *Kuhn* introduced the concept of atropisomerism (Atropisomerie)[8]: "Compounds that have an isomerism which is based on restricted rotation of single bonds are called atropisomers for short" (atropos = incapable of rotation).

In further studies of the atropisomerism of biphenyls, to which the quite different atropisomerism of *Ansa* compounds was added in 1940 (*A. Lüttringhaus*), the concept of atropisomerism was at first used in a much narrower sense and was applied only to systems in which intramolecular rotation was hindered by atoms or by bulkier substituents. It had been forgotten that *Kuhn*'s original definition includes cases without any substituents. For example, the cycloalkene ring in simple *trans*-cyclooctene (Fig. 10) is so rigid that a few years ago *Cope*[14] succeeded in separating it into two enantiomorphs, both with a relatively high optical stability. In a paper dedicated to *Richard Kuhn* for his last birthday[15], *Lüttringhaus* wrote: "*Richard Kuhn* coined the concept of atropisomerism in 1933, *i.e.* several years before the concepts of conformation or constellation had acquired a definite meaning. It is often overlooked that *Kuhn* had far-sightedly defined atropisomerism in such a manner that it coincides fully with what we now call conformation isomerism, and especially rotational isomerism ...".

Fig. 10. The enantiomorphs of *trans*-cyclooctene [14].

All these studies of the spatial location of atoms in molecules go back to *van't Hoff*'s concept of the tetrahedral nature of carbon compounds. We know of many examples of *Kuhn's* veneration of this earlier genius. For example, *Kuhn* published in 1961 a biographical study[16] of *van't Hoff* on the occasion of the 50th anniversary of his death. Similarly to *van't Hoff*, *Kuhn* had an extraordinary grasp of stereochemical problems. He could clearly visualize the most complex spatial formulas, and he played with them in his imagination.

Further work, started in Zurich, concerned –C=C bonding. Investigations carried out with *F. Ebel* and others gave *Kuhn* the idea of synthesizing polyenes, *i.e.* compounds with several conjugated double bonds. In his first paper with *Alfred Winterstein*[17], *Kuhn* wrote: "It is a delightful task of organic chemistry to make use of the bonding capacity of carbon for the artificial construction of compounds in which a given structural group is repeated uninterruptedly". *Richard Kuhn* enjoyed this mixture of playing with atoms and molecules and of the urge for theoretical understanding. He synthesized the diphenylpolyenes shown in Fig. 11, first only as far as 1,16-diphenylhexadecaoctaene [18], and found to his surprise that even the lower members of the series are colored. These were the first hydrocarbons proved with certainty to be colored, and it was just this property that inspired *Kuhn* to prepare increasingly higher polyenes. In 1938, jointly with *Kurt Wallenfels*[19], *Kuhn* succeeded in synthesizing the violet-black 1,22-diphenyldocosaundecaene, and finally the virtually insoluble green-black 1,30-diphenyltriacontapentadecaene, *i.e.* a compound with 15 conjugated double bonds. According to *Kuhn*[20], it is hardly possible to make still higher polyenes in the pure state because of their extreme insolubility.

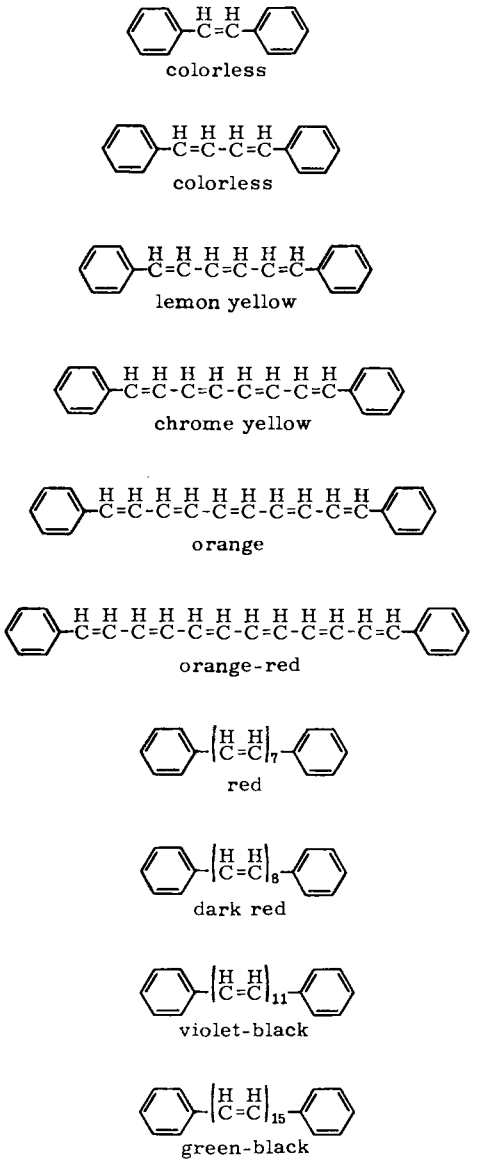


Fig. 11. Diphenylpolyenes.

[14] *A. C. Cope et al.*, J. Amer. chem. Soc. *84*, 3191 (1962); *85*, 3276 (1963); see *E. L. Eliel*: Stereochemistry of Carbon Compounds. Academic Press Inc., New York 1962.

[15] *A. Lüttringhaus, U. Hess*, and *J. Rosenbaum*, Z. Naturforsch. *22b*, 1296 (1967).

[16] *R. Kuhn*, Naturwiss. Rdsch. *15*, 1 (1962).

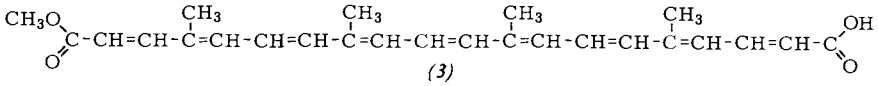
[17] *R. Kuhn* and *A. Winterstein*, Helv. chim. Acta *11*, 87 (1927).

[18] *R. Kuhn*: Synthesis of Polyenes. 6th Pedler lecture (Royal Society, London); J. chem. Soc. (London) *1938*, 604.

[19] *R. Kuhn* and *A. Wallenfels*, Ber. dtsch. chem. Ges. *70*, 1331 (1937); *71*, 1889 (1938).

[20] *R. Kuhn*, Angew. Chem. *50*, 703 (1938).

His work with *Winterstein* led logically to new fields, notably to the study of carotenoids and to physicochemical investigations of constitution and color. In February 1928 at the Zurich Chemical Society, *Paul Karrer* read a paper on crocetin, a C_{20} dyestuff pigment extracted from saffron, but could give no plausible explanation of the colored nature of this dicarboxylic acid. At the same time, *Kuhn* and *Winterstein* had seen the analogy between natural pigments such as crocetin (C_{20}) or bixin (C_{24}) and the synthetic diphenylpolyenes, and supposed that in the natural pigments the two phenyls were replaced by carboxyl groups. For bixin, the red pigment of bixa seeds, which is well known because of its use in coloring Edam cheese, *Kuhn* and *Winterstein* [21] proposed a polyene structure



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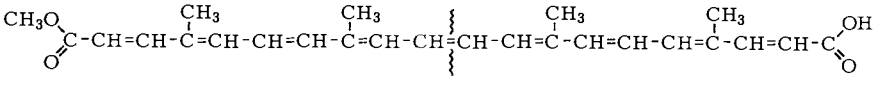

(4)

Fig. 12. Proposed structures for bixin, November 1927 *(3)* and 1932 *(4)* [21,22].

(3) (Fig. 12), which they corrected a few years later [22] to the now fully accepted symmetrical structure *(4)*.

The gap between theoretically interesting synthetic compounds and natural substances had now been bridged, thus opening the way for a major advance in the field of vitamins – in the same year *H. von Euler* [23] reported from Stockholm that vitamin A is a polyene and that carotene exerts vitamin A action in vitamin A-deficient animals. It was thus demonstrated that *Kuhn*'s polyenes also occur in nature. The fact that a vitamin had entered this field of study considerably strengthened *Kuhn*'s interest in this line of research. He had always been particularly interested in the biological aspects of chemistry, and upon hearing *Adolf Windaus* read a paper on vitamin D and on its formation from ergosterol by irradiation that same year (1929) in Zurich, Kuhn decided that he too wanted to devote himself increasingly to the study of vitamins.

Toward the end of 1929, on the initiative of *Ludolf von Krehl*, *Kuhn* was invited to Heidelberg as Director of the Chemistry Division of the newly founded Kaiser Wilhelm Institute for Medical Research. Later, *Kuhn* wrote a memorial article for the birthday centenary of *Ludolf von Krehl* [24]; the draft, in *Kuhn*'s characteristic hand, was found among his papers (Fig. 13).

The new Institute was built on the Neckar. It had four wings, which housed the four divisions for chemistry,

Das Kaiser-Wilhelm-Institut für Medizinische Forschung, das 1930 in Heidelberg gegründet wurde, verdankt seine Entstehung vor allem Gedanken von L. von Krehl: Seine Überzeugung war es, daß die theoretischen Grundlagen der Medizin auf den Gebieten der Physik, Chemie, Physiologie und Pathologie besonderer Förderung bedürften.

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Fig. 13. *Kuhn*'s note for the 100th birthday anniversary of *L. von Krehl* (1961).

physics, physiology, and pathology. These wings are connected by a centrally located library (Fig. 14); it was an ideal conception, a place where one could work at one's best and virtually undisturbed.

Fig. 14. The Kaiser Wilhelm Institute for Medical Research, Heidelberg, in the thirties.

There were two great creative periods in the life of *Richard Kuhn*, one starting in the thirties, the other in the middle fifties. These periods of greatest productivity can also be recognized by arranging in chronolog-

[21] *R. Kuhn* and *A. Winterstein*, Helv. chim. Acta *11*, 427 (1928).

[22] *R. Kuhn* and *A. Winterstein*, Ber. dtsch. chem. Ges. *65*, 648 (1932), Formulas III and IV.

[23] *B. v. Euler*, *H. v. Euler*, and *H. Hellström*, Biochem. Z. *203*, 370 (1928); see also *R. Kuhn* and *H. Brockmann*, Ber. dtsch. chem. Ges. *64*, 1859 (1931); *R. Kuhn*, Forsch. and Fortschr. *9*, 426 (1933).

[24] *R. Kuhn*, Münchener med. Wschr. *103*, 2493 (1961); Geschichte des Max-Planck-Instituts für Medizinische Forschung. Jahrb. d. MPG (1961), Part 2.

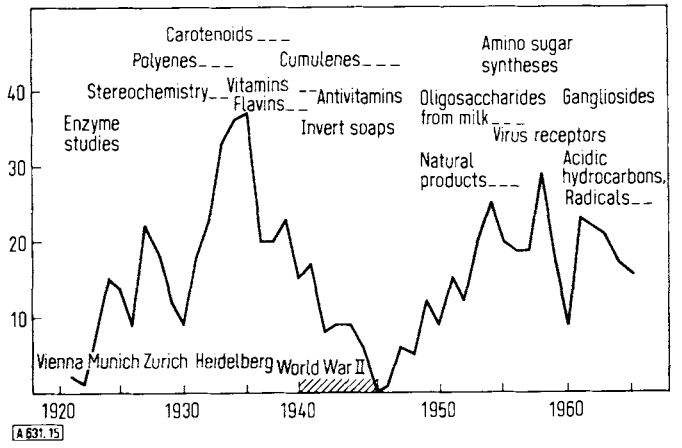


Fig. 15. The creative activity of *Richard Kuhn* and his collaborators. Subjects and numbers of annual publications.

ical order the approximately 700 papers which *Kuhn* published together with about 150 co-workers (Fig.15). The diagrams in Fig. 15 also show the main subjects on which *Kuhn* and his students have worked.

Many young co-workers joined *Kuhn* in Heidelberg. Some, *e.g. I. Löw*, *H. Trischmann*, and *E. F. Möller*, remained with the master until his death. A photograph from that period (Fig.16) shows *Kuhn* and his wife, *Brockmann* and his wife, *Hoffer* and *Wassermann*, farther to the left *Grundmann*, *Wagner-Jauregg*, and *Trischmann*, and, in the background, *E. Lederer*, *Roth*, *Möller*, and others.

Fig. 16. *Kuhn*, his wife, and his associates in Heidelberg (1932).

This was a circle of people who worked with great intensity of purpose and enthusiasm, initially on polyenes and carotenoids.

There were also many discussions, especially during the daily coffee-break around 5 P.M. *Kuhn* not only took part in these discussions but also unobtrusively examined his students. It was his habit to take all journals on the day of their appearance and to read them the same evening. He not only immediately incorporated the essential contents into his mental armoury but also, as a kind of hobby, picked out with a very sure eye any misprints in the papers; the next day he frequently checked whether his coworkers had also noticed these misprints. In this and similar ways all his students acquired with almost no effort an extensive knowledge of the literature. *Kuhn* used to say: "What I read in the evening I know by heart next morning, it sediments by itself". *Kuhn*'s phenomenal memory for formulas, numbers, and data, and for people and their histories, was one of his outstanding characteristics, which was also reflected in his dealings with students. He advised them: "Take the Zentralblatt für Chemie, it should always be on your bedside table".

Kuhn was an outstanding chess player with great combinatorial talent and he enjoyed playing chess, not only with his co-workers (Fig. 17).

Fig. 17. *Kuhn* and *Winterstein* playing chess, with *Ursula Ehrenberg* lookin on (1932).

Bogoljubov, former Russian world champion, lived in Heidelberg at the time; *Kuhn* liked playing with him and often won. Another frequent opponent was Herr *Schmauss*, landlord of the "Goldene Rose" in Heidelberg. *Kuhn* was also a keen follower of sports, particularly of soccer. At the beginning of each week he would know the results of many games, particularly of the Vienna teams. He enjoyed playing tennis, both in Zurich and later in Heidelberg. For many years, together with sports-inclined associates, he played volley-ball at the University sports grounds located near the Institute.

Together with *Edgar Lederer* and *Hans Brockmann*, *Kuhn* now turned his attention to chromatography, which he had already used as a method of separation during his time with *Willstätter*. New improved media were found for the absorption and elution of pigments, and several pigment mixtures were separated on columns. The first result was the separation of carotene into α- and β-carotene. Both purified substances were obtained as beautiful crystals[25] (Fig. 18), which satisfied *Kuhn*'s aesthetic sense. This was followed by

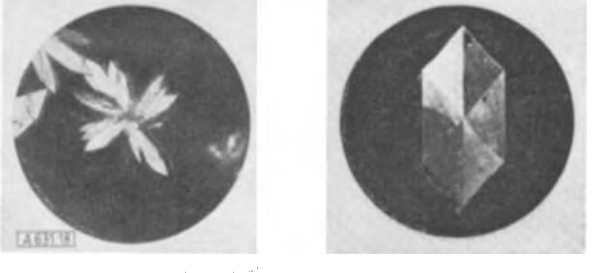


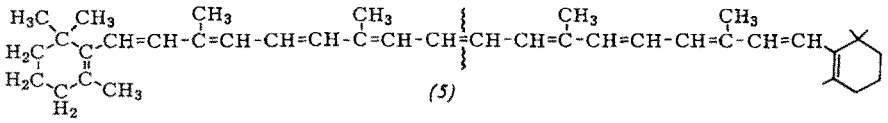
Fig. 18. Crystals of α- (left) and β-carotene (right) (both from solution in benzene-methanol mixture) between crossed nicols. Magnification × 225 in the original publication [25], about × 90 in this reproduction.

identification of γ-carotene[26], which occurs in small quantities in many plants together with the other carotenes. Structural studies then clarified the relationship of carotene to vitamin A[27]. Vitamin A,

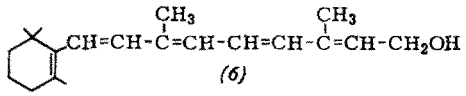
[25] *R. Kuhn* and *E. Lederer*, Ber. dtsch. chem. Ges. *64*, 1349 (1931).

[26] *R. Kuhn* and *H. Brockmann*, Ber. dtsch. chem. Ges. *68*, 407 (1933).

[27] See *e.g. R. Kuhn* and *H. Brockmann*, Hoppe-Seylers Z. physiol. Chem. *213*, 1 (1932); Ber. dtsch. chem. Ges. *64*. 1959 (1931).



(5)



(6)

In vivo: $C_{40}H_{56} + 2\,H_2O \longrightarrow 2\,C_{20}H_{30}O$

Fig. 19. The structural relationship of β-carotene (provitamin A) *(5)* to vitamin A *(6)*.

$C_{20}H_{30}O$, was shown to be a hemi-derivative of β-carotene, $C_{40}H_{56}$, and *Kuhn* suggested that the cleavage occurs *in vivo* by a type of hydrolysis (Fig. 19). β-Carotene was thus recognized as provitamin A, after English researchers had already expressed the same idea.

In 1933 *Kuhn* reported to the Royal Society in London [28] the concept that carotenoids in plants may undergo cleavage of the C_{40} arrangement and be transformed into diverse polyenes, *e.g.* into lower pigments such as bixin (C_{24}), crocetin (C_{20}), or azafrin (C_{27}), into odoriferous substances such as methylheptenone or ionone, or into bitter substances such as saffronal which is formed from picrocrocin (Fig. 20).

Important work on constitution and color [29] was carried out by *Kuhn* jointly with Professor *Karl Wilhelm Hausser*, the physical chemist who was the first Director of the Physics Division of the Kaiser Wilhelm Institute. Shortly before his premature death (June 4, 1933), *Hausser* showed at a colloquium at the Institute in November 1932, that these studies had resulted in the formulation of the first quantitative relationship between light absorption and the number n of double bonds in vinylogous series, *e.g.* in diphenylpolyenes (see Fig. 11). An important finding was the relationship between the location of the longest-wave absorption maximum λ_1 and the square root of the number n of double bonds (see Fig. 21):

$$\lambda_1 = K' \cdot \sqrt{n} + K''$$

The absorption spectra found for synthetic polyenes were of considerable importance for structural investigations on natural carotenoids.

Another wide field of work opened up in connection with water-soluble vitamins. It was fortunate that *Paul György* worked at that time at the Heidelberg

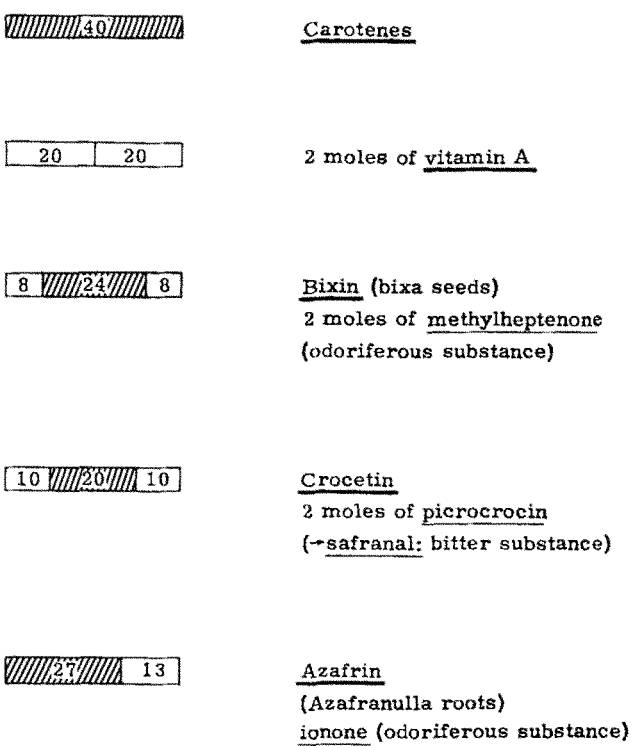


Fig. 20. Biochemical cleavage reactions of carotenes, after *R. Kuhn* [28].

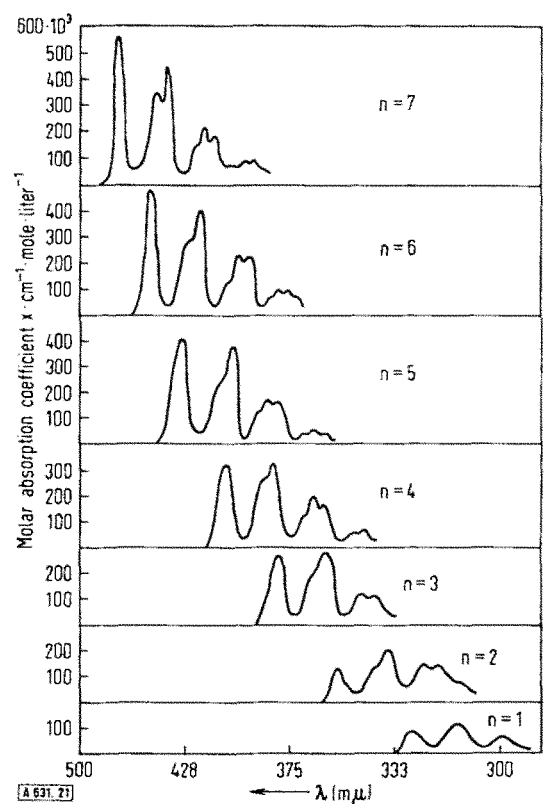


Fig. 21. Absorption spectra of diphenylpolyenes C_6H_5-$(CH{=}CH)_n$-C_6H_5 in ether-alcohol mixtures at −196 °C [29].

[28] *R. Kuhn*, J. Soc. chem. Ind., Chem. and Ind. *52*, 981 (1933).
[29] *K. W. Hausser, R. Kuhn, et al.*, Z. physik. Chemie (B) *29*, 363, 384, 391, 417 (1953); *H. A. Staab*: Einführung in die theoretische Organische Chemie. Verlag Chemie, Weinheim 1959, p. 343.

Children's Clinic. He was interested in problems of infant nutrition, and saw clearly that vitamins are of decisive importance for the growing child. How many and which vitamins important for life could be present in milk? Together with *György* and *E. Lederer*, *Kuhn* tried to isolate the antiseborrheic skin factor (vitamin H) described by *György*. It seemed worthwhile to work on this skin factor in order to distinguish it from vitamin B_2 which was considered in those days as a substance preventing pellagra. *Wagner-Jauregg*, who had just completed his habilitation thesis, volunteered to undertake this work. He soon observed that B_2 concentrates are always yellow and exhibit green fluorescence. Starting from very large quantities of whey and using many refining stages, he isolated a crystalline substance, lactoflavin, which was shown to be pure vitamin B_2 [30, 31]. This was the first step in the chemistry of flavins.

In connection with *Otto Warburg*'s work on oxidation enzymes, *Kuhn* and his co-workers showed that lactoflavin was a component of *Warburg*'s yellow ferment. Together with *Hermann Rudy*, *Friedrich Weygand*, and *Wagner-Jauregg*, *Kuhn* determined the structure and carried out a synthesis of lactoflavin [32] and then prepared lactoflavin phosphate [33]. Combining the protein carrier of the yellow enzyme from yeast with synthetic lactoflavin phosphate, *Kuhn* and *Rudy* [34] succeeded in synthesizing *Warburg*'s yellow oxidation enzyme (Fig. 22) in 1935/1936. This proved to be fully effective enzymatically, and was thus the first

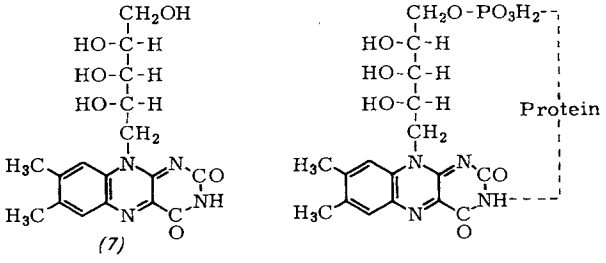


Fig. 22. Vitamin B_2 (lactoflavin) and its relationship to the yellow oxidation enzyme [34].

instance of partial synthesis of an enzyme. A photograph of *Richard Kuhn* taken in those days is shown in Fig. 23.

Those who had an opportunity at that time to hear *Richard Kuhn* lecturing on his work were held irresistibly by the magic of his personality. This was particularly so at the Heidelberg Chemical Society. He never tried to disguise his Viennese accent; his vocal powers ranged from a factual mezzo piano to

Fig. 23. *Richard Kuhn* in Heidelberg in 1935.

a mighty, almost theatrical, forte. He polished his lectures with great care, so that they became almost works of art. During the lectures his imagination was at full pitch – one could almost see the thoughts seething in his mind. The author also came under the influence of such lectures, which provided for many young scientists the frequently decisive contact with genius, and decided to strive for the privilege of working under *Richard Kuhn*.

In connection with the synthesis of lactoflavin and of many lactoflavin analogs, the need arose to study *N*-glycosides; this led to important work with *Weygand* and *L. Birkofer* on the Amadori rearrangement and its mechanism [35].

In 1937 *Richard Kuhn* and *Rudolf Ströbele* published a fundamental paper on the action of lactoflavin as an oxidation catalyst [36] entitled "On verdo-, chloro-, and rhodoflavins". On the basis of the red reduction stage of lactoflavin as described by *Kuhn* and *Wagner-Jauregg* [36], *Kuhn* and *Ströbele* succeeded in isolating intermediate stages of the oxidation-reduction system flavin $\rightleftarrows$ leukoflavin as crystals of brilliant deep colors and definite compositions. It was shown that these could be reconverted into lactoflavin by 0.25, 0.5, and 0.75 moles of O_2 respectively, and the intermediate oxidation stages were characterized as dimers with different paramagnetic properties (Fig. 24). The paramagnetism is due to the 1:1 ratio of monohydroflavin (semiquinone) and of the fully oxidized or fully reduced stage in molecular compounds of the type of quinhydrone. The biological significance of these two basic chemical principles – formation of quinhydrone-type complexes on the one hand and of radical ions on the other – ensuring stabilization of the intermediate stages was clearly recognized. The yellow enzyme can only be hydrogenated in four stages if two flavin molecules are associated in the enzyme complex. Only in this manner can the energy of the $^1/_4$-quinone and

[30] *P. György*, *Th. Wagner-Jauregg*, and *R. Kuhn*, Mitt. Kaiser-Wilhelm-Ges. *1933*, No. 1. p. 4; *R. Kuhn*, *P. György*, and *Th. Wagner-Jauregg*, Ber. dtsch. chem. Ges. *66*, 407, 1034, 1950 (1933).

[31] *P. György*, *R. Kuhn*, and *Th. Wagner-Jauregg*, Naturwissenschaften *21*, 560 (1933); Klin. Wschr. *12*, 1241 (1933); *P. György*, J. Nurit. *91*, Suppl. *1*, 5 (1967).

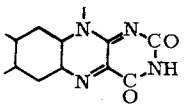
[32] *R. Kuhn* and *F. Weygand*, Ber. dtsch. chem. Ges. *67*, 2084 (1934); *68*, 1282 (1935).

[33] *R. Kuhn* and *H. Rudy*, Ber. dtsch. chem. Ges. *68*, 383 (1935); *R. Kuhn*, *H. Rudy*, and *F. Weygand*, *ibid. 69*, 1543 (1936).

[34] *R. Kuhn* and *H. Rudy*, Ber. dtsch. chem. Ges. *69*, 1974, 2557 (1936).

[35] *R. Kuhn* and *F. Weygand*, Ber. dtsch. chem. Ges. *70*, 769 (1937); *R. Kuhn* and *L. Birkhofer*, *ibid. 71*, 621 (1938).

[36] *R. Kuhn* and *R. Ströbele*, Ber. dtsch. chem. Ges. *70*, 753 (1937); see also *R. Kuhn* and *Th. Wagner-Jauregg*, *ibid. 67*, 361 (1934).



	Empirical formula	O_2-consumption on regeneration of 1 flavin
Flavin, yellow	$C_{17}H_{20}O_4N_4$	0.00
Verdo-flavin, bronze-green	$C_{17}H_{21}O_6N_4$ $C_{17}H_{19}O_6N_4Na$	0.25
Chloro-flavin, grass-green (mainly dimeric)	$C_{17}H_{21}O_6N_4$	0.50
Rhodo-flavin, crimson	$C_{17}H_{21}O_6N_4$ HCl $C_{17}H_{22}O_6N_4$ HCl	0.75
Leuko-flavin, white	$C_{17}H_{22}O_6N_4$	1.00

Fig. 24. Intermediate stages of the oxidation-reduction lactoflavin ⇌ leukoflavin [36].

of the $^3/_4$-quinone be distributed over the two halves of the molecular compound.

We are only now beginning to understand the mechanism of the cooperation of the protein-bound coenzyme molecules of different reduction stages, postulated by *Kuhn* in a stroke of genius as far back as 1937. One of the highlights of the 1967 International Biochemistry Congress in Tokyo was the demonstration by *Kunio Yagi*[37] of crystallized intermediate stages of the anaerobic reduction of D-amino acid oxidase. These are exactly the compounds discussed in the paper by *Kuhn* and *Ströbele*[36] published 30 years earlier. What *Kuhn* called "distribution of energy" is now called "complex formation by electron transfer between two molecules of flavin of different oxidation levels (charge transfer complexes according to *Mulliken*, 1950) and formation of semiquinone".

This example is one of many illustrating *Richard Kuhn*'s powers of conception and comprehensive foresight.

From here the path led to the vitamin B group. Vitamin B_6 (pyridoxin) – which *Kuhn* called "Adermin" because it cured a dermatitis in deficient rats – was concentrated from yeast and rice bran, and was obtained in the crystalline state by *G. Wendt*[38]. The structural formulation (Fig. 25) and the synthesis were achieved by *Wendt* jointly with *K. Westphal* and *O. Westphal*[39].

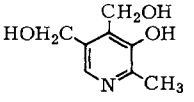


Fig. 25. Vitamin B_6.

Pantothenic acid was isolated, and was synthesized by *Theodor Wieland*[40]. The growth factor vitamin H' was identified as *p*-aminobenzoic acid[41]. Numerous analogs of all these vitamins or growth factors were synthesized, *e.g.* dichlorolactoflavin and flavins with other polyol residues such as ribital; derivatives were prepared of *p*-aminobenzoic acid, among them 4,4'-diaminobenzil (Fig. 26), and of salicil, *e.g.* dibromosalicil. Several of these substances exhibited growth-promoting vitamin effects, others were ineffective, but some analogs, tested in bacterial growth experiments, exhibited antagonistic effects with respect to the corresponding natural growth factors, *i.e.* acted as antivitamins[42,43].

A short time earlier, British workers had postulated antagonism between *p*-aminobenzoic acid and sulfanilic acid. *Kuhn* showed that sulfanilic acid and some of its derivatives do indeed strongly inhibit the growth-promoting action of *p*-aminobenzoic acid [42] (Fig.26)

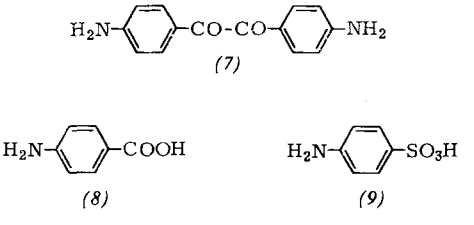


Fig. 26. On the vitamin/antivitamin antagonism. Antagonists of *p*-aminobenzoic acid [42]: *(7)*, 4,4'-diaminobenzil (→ salicil derivatives) (inhibitors); *(8)*, *p*-aminobenzoic acid (growth factor), *(9)*, sulfanilic acid (sulfonamides).

[37] *K. Yagi*, VII. int. Biochem. Congr., Tokyo, Aug. 1967, Abstr. I, p. 167.

[38] *R. Kuhn* and *G. Wendt*, Ber. dtsch. chem. Ges. *71*, 1118 (1938).

[39] *R. Kuhn, G. Wendt*, and *K. Westphal*, Ber. dtsch. chem. Ges. *72*, 310 (1939); *R. Kuhn, K. Westphal, G. Wendt*, and *O. Westphal*, Naturwissenschaften *27*, 469 (1939).

[40] *R. Kuhn* and *Th. Wieland*, Ber. dtsch. chem. Ges. *73*, 971, 1134 (1940).

[41] *R. Kuhn* and *K. Schwarz*, Ber. dtsch. chem. Ges. *74*, 1617 (1941).

[42] *R. Kuhn*, Die Chemie *55*, 1 (1942); see also *R. Kuhn, E. F. Möller, et al.*, Ber. dtsch. chem. Ges. *76*, 900 (1943).

[43] *R. Kuhn*, Chemie-Arb. Werk Labor *67*, 241 (1944).

and that this inhibition explains the bacteriostatic effectiveness of sulfonamides: the antivitamin displaces the vitamin from its natural acceptor (*e.g.* an enzyme protein) in a specific manner, thus inhibiting the metabolic process concerned, and this inhibition may often be reversibly counteracted by increased doses of the vitamin. *Kuhn* pioneered these concepts, and the principles which he formulated are valid for almost all the antibiotics discovered since then.

On November 9, 1939, the Nobel Committee in Stockholm decided to award *Richard Kuhn* the Nobel Prize in chemistry "for his work on carotenoids and vitamins".

When the award of this highest scientific distinction was announced, *Richard Kuhn*, similarly to *A. Butenandt* and *G. Domagk*, was forced by the German National-Socialist Government, under threat of sanctions, to decline the prize. The Swedish Academy later acknowledged that the refusal was made under duress, and accepted it as null and void.

In the field of carotenoids there is a chapter which later caused *Richard Kuhn* much pain. The biologist *Max Hartmann*, of Berlin-Dahlem, suggested studies on the copulation substances of the green alga *Chlamydomonas eugametos*. He strongly recommended to *Kuhn* his student, *Franz Moewus*, to carry out these studies. In their experiments, *Moewus* and his wife proclaimed the effectiveness of a series of carotenoids purportedly isolated from green algae. On this basis an extensive theory of the "relative sexuality" and the effectiveness of light was constructed for these unicellular organisms. However, detailed and careful checks carried out by several researchers after the war, some of them in *Moewus*' presence, invariably gave totally negative results. Several biologists held it against *Kuhn* that it was not until 1960 that he publicly dissociated himself from *Moewus*' assertions and results [44]. In this disclaimer it was stated that *Moewus*' claims to the effect that crocin, the dimethyl ester of crocetin, rutin, quercetin, isorhamnetin and peonin, which had been isolated in Heidelberg from other plant material, were also formed by *Chlamydomonas*, were unverified and in fact doubtful. The alleged biological effectiveness of picrocrocin and safranal, crocin, the dimethyl esters of *cis*- and *trans*-crocetin, a flavonol glycoside from crocus, isorhamnetin, boric acid, and other substances on *Chlamydomonas* cells was also declared as unverified. Nevertheless, *Kuhn* and *Löw* concluded the disclaimer with the sentence: "It should be noted that the purely chemical results of this work, relating to methods of isolation, crystallization, and structural formulation, are free of the reservations expressed above" [44].

As *Max Hartmann* and *Franz Moewus* are no longer alive, this chapter should be closed at this point, but only after stating that *Kuhn*'s trust in the two biologists had remained unshaken for a long time.

In nearly 30 years of belonging to *Kuhn*'s working circle, *Irmentraut Löw* distinguished herself by purifying and crystallizing numerous plant glycosides. She has contributed substantially to clarifying the structures of flavonol and alkaloid glycosides, as well as of oligosaccharides from *crocus*, *Solanum* species, *Forsythia*, and *lycopersicum*, and was also a chemical partner of *Hartmann* and *Moewus*' biological group. This part of the work yielded many interesting new natural products.

Work on carotenoids and polyenes led to the cumulenes, again as a result of a simple thought: synthesis of substances with the highest possible cumulation of double bonds. In this context, on the occasion of being awarded the 1942 Goethe Prize of the City of Frankfurt, the first time this prize was awarded to a natural scientist, *Kuhn* said [45]: "It is only gradually that a student of nature, and especially a chemist working on syntheses, comes to discover the natural laws and then, following his intuition, to go beyond that which he finds in nature. He thus becomes in a certain sense an artist developing freely within the limits drawn by nature". He was again referring to *van't Hoff*, who had postulated at the turn of the century that in the case of an isolated double bond one may expect *cis-trans* isomerism but that, with two cumulated double bonds, one should expect right-handed and left-handed isomers, *i.e.* d,l isomers (Fig. 27). In general,

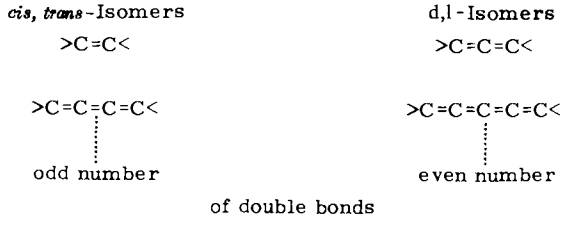


Fig. 27. d,l and *cis-trans* isomerism depending on the number of cumulated double bonds (after *J. H. van't Hoff* [46]).

one should expect *cis-trans* isomerism with an odd number of cumulated double bonds, and d,l isomerism with an even number, as implied by the tetrahedral form of carbon.

Syntheses of cumulenes were started in 1938. *Kurt Wallenfels* distinguished himself greatly by preparing such substances starting from diacetylene [47,48]; substances with cumulated double bonds were thus obtained, which were stabilized *e.g.* by phenyl residues at the ends.

It was shown, for example, that it is possible to obtain from diacetylenedimagnesium bromide and acetophenone a high yield of 1,1,6,6-tetraphenyl-2,4-hexadiine-1,6-diol [47], [Fig. 28, formula *(10)*], and from this, with HCl and $CrCl_2$ in ether [48], also a virtually quantitative yield of tetraphenylhexapentaene [48,49] [Fig. 28, formula *(11)*].

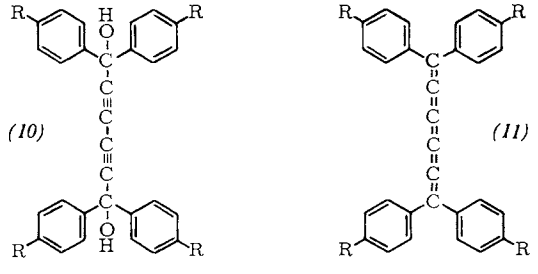


Fig. 28. Preparation of cumulenes.
(10) Tetraphenylhexadiinediol precursor: R = H, m.p. 141 °C; R = CH_3, m.p. 158 °C; R = Cl, m.p. 169 °C; R = OCH_3, m.p. 130 °C.
(11) Tetraphenylhexapentaene: R = H, decomp. at 302 °C; R = CH_3, decomp. at 326 °C; R = Cl, decomp. at 218 °C.

[44] *R. Kuhn* and *I. Löw*, Chem. Ber. *93*, 1009 (1960).

[45] *R. Kuhn* in: Goethe-Kalender *1942*, 21.

[46] *J. H. van't Hoff*: Lagerung der Atome im Raume. F. Vieweg, Braunschweig, 1st Edit. 1877; 2nd Edit. 1894.

[47] *R. Kuhn* and *K. Wallenfels*, Ber. dtsch. chem. Ges. *71*, 783 (1938).

[48] *R. Kuhn* and *K. Wallenfels*, Ber. dtsch. chem. Ges. *71*, 1510 (1938).

[49] *R. Kuhn* and *G. Platzer*, Ber. dtsch. chem. Ges. *73*, 1410 (1940).

The second world war caused an increasingly severe curtailment of scientific effort at almost all German Institutes. *Kuhn*'s creative work was also severely cut. He nevertheless fought behind the scenes in high places, as can be seen from numerous letters. He fought for the preservation of German chemical literature, especially for the authors of important books regardless of personalities, only according to quality. He was concerned with preserving what he called the "100000 man army" of chemists, so that after the war Germany could immediately begin reconstruction as in 1918.

Many letters preserved from the years 1936/1944 show that *Kuhn* was motivated by a great admiration and love for Germany. He now acted for the Germany of the open-minded spirit of research so rich in tradition, of the great chemical and technological achievements which he had praised in his inaugural lecture in Zurich in 1927[7]. He had welcomed Austria's unification with Germany from a deeply felt sense of togetherness of the two German-speaking nations with so much common history. But he was undemonstrative and disliked heroics. He was essentially an introvert and a sensitive man who revealed himself seldom and then only to a few friends. He could be described as a "master of silence". Subsequent accounts of his relations with the regime of those days, particularly in various English-speaking scientific circles, had frequently done him injustice.

The work on cumulenes was resumed after the war (1951). While the earlier investigations[47,48] were performed mostly from a preparative point of view, more stereochemical aspects now came to the fore with *H. Jahn*, *K. L. Scholler*, *D. Blum*, and especially *Herbert Fischer* and *B. Schultz*. *Cis-trans* isomerism was demonstrated, for example, for mixed phenylated and nitrophenylated butatrienes[49,50], using dipole measurement techniques. *Cis* (m.p. 142–143 °C) and *trans* (m.p. 127–128 °C) isomers of 1,4-diphenyl-1,4-di-*tert*-butylbutatriene, [Fig. 29, formula *(12)*] were separated by column chromatography[51]. In contrast, 1,6-diphenyl-1,6-di-*tert*-butylhexapentaene [Fig. 29, formula *(13)*][52], could not be separated by laboratory methods, but the nuclear resonance spectrum in [D_6]-dimethyl sulfoxide showed two sharp bands at 100 MHz, corresponding to the two *tert*-butyl groups of the *cis* and the *trans* forms. From the coalescence point (coalescence temperature 100 °C) of the two bands, the free activation enthalpy of the *cis-trans* transformation in dimethyl sulfoxide was assessed at $\Delta G^{\ddagger} = 20$ kcal/mole[52], the $\Delta G^{\ddagger}$ of the butatriene *(12)* at about 30 kcal/mole. It follows, as theoretically predicted, that the stability of the steric arrangement decreases with increasing number of cumulated double bonds. *R. Kuhn* and *H. Zahn*[53] also obtained tetraphenylated octaheptaenes

$$Ar_2C{=}C{=}C{=}C{=}C{=}C{=}C{=}CAr_2$$

by transforming triacetylene with benzophenone, or with fluorenone, into octatriinediols and reducing these with P_2I_4.

In the series of compounds with an even number of cumulated double bonds, *Kuhn et al.*[54]

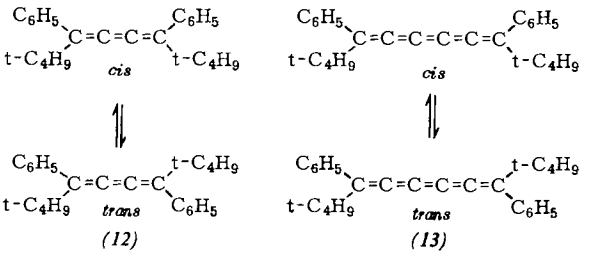


Fig. 29. Diphenyl-di-*tert*-butylbutatriene *(12)* and diphenyl-di-*tert*-butylhexapentaene *(13)*.

could only reach tetraphenylated pentatetraenes. A number of sketches were found among *Kuhn*'s papers, including one for a lecture on problems of cumulenes (Fig. 30).

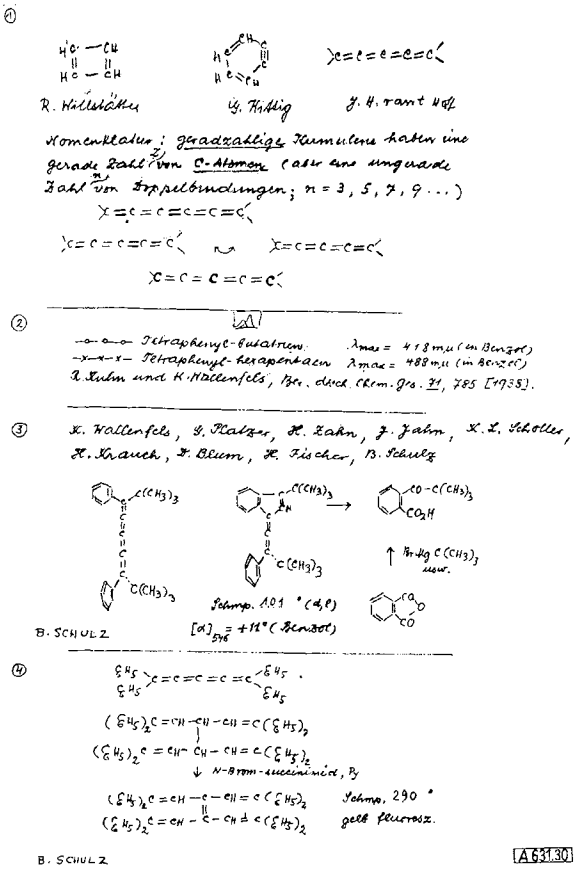


Fig. 30. Sketches by *R. Kuhn* (1963) regarding problems of cumulenes; cf. [55].

Closely related to the work on cumulenes were the investigations on highly acidic hydrocarbons which started in 1961[56] and which were conducted mainly in collaboration with *Herbert Fischer* and *Franz Neugebauer*. The colorless 1,5-bis-(2,2′-biphenylylene)-1,4-pentadiene [Fig. 31, formula *(14)*], which forms a deep blue salt in aqueous NaOH[57], may be cited as a

[50] *R. Kuhn* and *D. Blum*, Chem. Ber. *92*, 1483 (1959).

[51] *R. Kuhn* and *B. Schulz*, Chem. Ber. *98*, 2611 (1965).

[52] *R. Kuhn*, *B. Schulz*, and *J. C. Jochims*, Angew. Chem. *78*, 449 (1966); Angew. Chem. internat. Edit. *5*, 420 (1966).

[53] *R. Kuhn* and *H. Zahn*, Chem. Ber. *84*, 566 (1951).

[54] *R. Kuhn*, *Herb. Fischer*, and *H. Fischer*, Chem. Ber. *97*, 1760 (1964).

[55] *R. Kuhn* and *B. Schulz*, Angew. Chem. *74*, 292 (1962); Angew. Chem. internat. Edit. *1*, 211 (1962); Angew. Chem. *75*, 452 (1963); Angew. Chem. internat. Edit. *2*, 395 (1963).

[56] *R. Kuhn* and *Herb. Fischer*, Angew. Chem. *73*, 435 (1961).

[57] *R. Kuhn*, *Herb. Fischer*, *F. A. Neugebauer*, and *H. Fischer*, Liebigs Ann. Chem. *654*, 64 (1962); see also *R. Kuhn*, *Herb. Fischer*, *D. Rewicki*, and *H. Fischer*, *ibid. 689*, 1 (1965); *R. Kuhn* and *D. Rewicki*, *ibid. 690*, 50 (1965).

typical example[57]. *Kuhn* could not deny himself the pleasure of demonstrating this colorful experiment during his *van't Hoff* lecture[58].

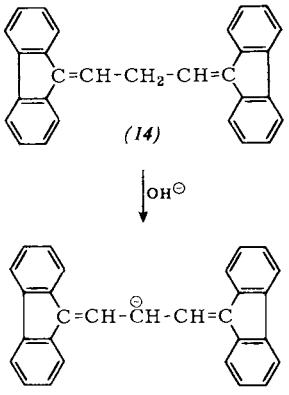


Fig. 31. 1,5-Bis-(2,2'-biphenylylene)-1,4-pentadiene [bis-(9-fluorenylidene)propane] *(14)*.

The anions of highly acidic hydrocarbons can be discharged into free paramagnetic radicals by oxidizing agents. For example, the colorless hydrocarbon *(15)* (Fig. 32) changes in aqueous NaOH into the red anion *(16)*, which is discharged by potassium hexacyanoferrate(III) to give the dimeric hydrocarbon *(17)* obtainable as colorless crystals. In solution, however, this dimer dissociates into yellow free radicals *(18)*[57,58], which are very stable, for example, to oxygen, due to delocalization of the radical electron, as has also been demonstrated by ESR. This delocalization is related to mesomeric stabilization, corresponding to stabilization of the anions of the corresponding highly acidic hydrocarbons.

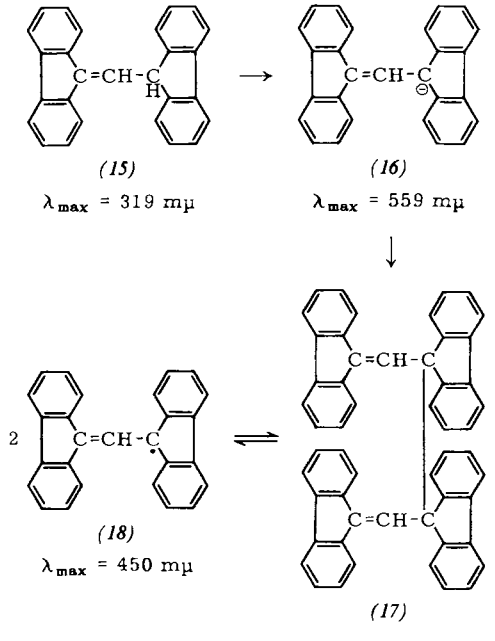


Fig. 32. Example of formation of radicals from highly acidic hydrocarbons [58]. *(15)* colorless; *(16)* red; *(17)* colorless; *(18)* yellow.

[58] *R. Kuhn*, Naturwiss. Rdsch. *15*, 1 (1962).

[59] *R. Kuhn* and *F. A. Neugebauer*, Mh. Chem. *94*, 1 (1963).

Nitrogen-containing radicals[59] such as the tetraazapentenyl radical[60]

$$Ar_2N-N=CH-\dot{N}-NAr_2$$

were prepared from aza-isologs of highly acidic hydrocarbons. The green "verdazyls"[61] discovered jointly with *H. Trischmann* are similar N-radicals. The stability of such verdazyls was demonstrated, more or less as a game, by preparing the deep green triradical 1,3,5-tris(1,5-diphenylverdazyl-3-yl)benzene[62] containing ten conjugated six-membered rings.

Verdazyls are derived from triphenylformazan (Fig. 33), which was used by *Kuhn* and *D. Jerchel*[63] as early as 1941 as an intermediate product in the synthesis of triphenyltetrazolium chloride. Within the framework of joint investigations with *H. J. Bielig*, *D. Jerchel*, and *O. Westphal* on the so-called invert soaps and their biological properties[64], several surface-active ammonium salts were synthesized, including some with N-containing heterocycles, such as triazolium[65] and tetrazolium[63] salts. Of these, triphenyltetrazolium chloride (TTC) proved to be particularly interesting because it can be used as a biological reduction indicator[66]. For example, if TTC is introduced into the nutrient solution of germinating plants, the cotyledons appear deep red owing to the presence of formazan formed by reduction. As *Kuhn* and *Trischmann*[61] found in 1964, triphenylformazan is easily transformed by dimethyl sulfate, methyl iodide, or formaldehyde into the green radical called verdazyl (Fig. 33).

Kuhn's colleagues report an episode from the difficult days after the end of the war, at a time when there was an acute danger of the Institute being closed by US forces and when an

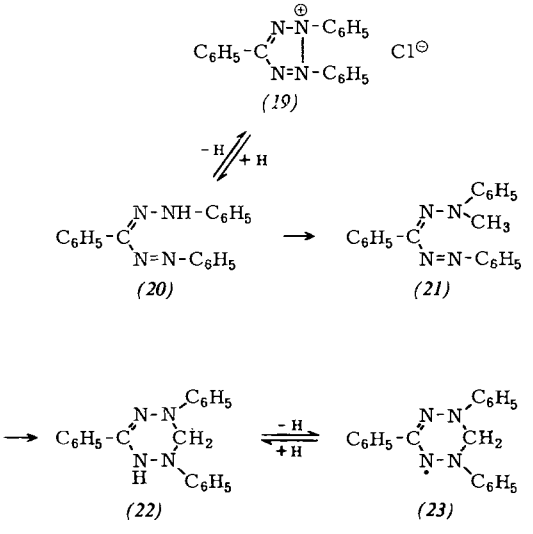


Fig. 33. The relationship of triphenylformazan *(20)*, deep red, to triphenyltetrazolium chloride (TTC) *(19)*, colorless, and to triphenylverdazyl *(23)*, green. *(21)* is orange.

[60] *R. Kuhn*, *F. A. Neugebauer*, and *H. Trischmann*, Angew. Chem. *76*, 230 (1964); Angew. Chem. internat. Edit. *3*, 232 (1964).

[61] *R. Kuhn* and *H. Trischmann*, Angew. Chem. *75*, 294 (1963); Angew. Chem. internat. Edit. *2*, 155 (1963); Mh. Chem. *95*, 457 (1964); *R. Kuhn*, Angew. Chem. *76*, 691 (1964); Angew. Chem. internat. Edit. *3*, 762 (1964).

[62] *R. Kuhn*, *F. A. Neugebauer*, and *H. Trischmann*, Angew. Chem. *77*, 43 (1965); Angew. Chem. internat. Edit. *4*, 72 (1965).

[63] *R. Kuhn* and *D. Jerchel*, Ber. dtsch. chem. Ges. *74*, 941 (1941).

[64] *O. Westphal* and *D. Jerchel*, Kolloid-Z. *101*, 213 (1942).

[65] *R. Kuhn* and *O. Westphal*, Ber. dtsch. chem. Ges. *73*, 1109 (1940).

[66] See *e.g. R. Kuhn*, *G. Pfleiderer*, and *W. Schulz*, Liebigs Ann. Chem. *578*, 159 (1952).

ordinance was in force that "by order of the Headquarters of the Military Government, all Austrian citizens must be repatriated forcibly to Austria with 50 kg of luggage each". One day, an American colonel appeared in this connection and was engaged in conversation by *Kuhn*. It transpired that the colonel's wife, back in the States, was an enthusiastic amateur gardener. *Kuhn* told the colonel that he could, in a simple way, turn green plants a gorgeous red. The colonel was sceptical, but decided to send his wife a sample of TTC... with resounding success. By return of mail came the news that the lady's friends invited to witness the experiment were highly delighted, and that more of the wonder drug should be sent. *Kuhn*'s imminent repatriation was postponed.

The 1950's saw the second period of great creative activity in the life of *Richard Kuhn* (Fig. 15) connected with investigations on resistance factors[67] and with the related work on oligosaccharides of human milk and gangliosides of the brain. Among the first investigations after the end of the war was *Kuhn*'s work on the resistance of certain *solanum* species to attack by the Colorado beetle. In 1947, *Kuhn* together with *I. Löw* isolated demissin, an alkaloid glycoside from *solanum demissum*[68]. In collaboration with *A. Gauhe*[69] he demonstrated the importance of this substance for resistance against the Colorado beetle larva. During the following ten years, *Kuhn*, together with *I. Löw* and *H. Trischmann* carried out extensive studies[70] on the structure of demissin and other closely related alkaloid glycosides.

Work on resistance factors led again to processing of the contents of milk. *Paul György*, in Philadelphia since 1936, resumed contact with *Kuhn*, and thus the two working groups found themselves, some 30 years after the first joint work on lactoflavin, working together again on the old question of the importance of mother's milk (compared to cow's milk) with regard to the resistance of the infant to infections. On the basis of investigations on *bifidus* factors and on the virus-inhibiting properties of mother's milk[71], *Kuhn* concentrated his interest (together with *H. H. Baer* and *Adeline Gauhe*, and later also with *R. Brossmer*) on the oligosaccharides. From 1954 onwards, numerous lacto-oligosaccharides were prepared in pure form and defined structurally with masterly skill. A key substance proved to be lacto-*N*-tetraose (Fig. 34) which was isolated in 1954[72] and whose structure was established in 1956[73]. The isomeric lacto-*N*-neotetraose (Fig. 34) was defined in 1962[74]. Both tetrasaccharides consist of glucose, galactose, and *N*-acetylglucosamine in the ratio of 1:2:1, the galactose at the non-reducing end being bound β-1,3 in lacto-*N*-tetraose and β-1,4 in lacto-*N*-neotetraose.

[67] *R. Kuhn*, Naturwissenschaften *46*, 43 (1959).

[68] *R. Kuhn* and *I. Löw*, Chem. Ber. *80*, 406 (1947); see also *81*, 552 (1948).

[69] *R. Kuhn* and *A. Gauhe*, Z. Naturforsch. *2b*, 407 (1947).

[70] *R. Kuhn, I. Löw*, and *A. Gauhe*, Chem. Ber. *83*, 448 (1950); *R. Kuhn, I. Löw*, and *H. Trischmann, ibid. 85*, 416 (1952); *86*, 372, 1027 (1953); Angew. Chem. *68*, 212 (1956).

[71] *K. Hummeler, P. György, J. R. E. Hoover*, and *R. Kuhn*, Science (Washington) *118*, 781 (1953); *P. György, R. Kuhn, et al.*, Arch. Biochem. Biophysics *48*, 202, 210, 214 (1954).

[72] *R. Kuhn, A. Gauhe*, and *H. H. Baer*, Chem. Ber. *87*, 289 (1954).

[73] *R. Kuhn* and *H. H. Baer*, Chem. Ber. *89*, 504 (1956).

[74] *R. Kuhn* and *A. Gauhe*, Chem. Ber. *95*, 518 (1962).

In the course of investigations on gangliosides undertaken in 1960, the key substance ganglio-*N*-tetraose[75] was isolated from these glycolipids, which proved to be structurally very similar to the two tetraoses from human milk (Fig. 34) inasmuch as the only difference is that galactosamine, instead of glucosamine, is the amine found in ganglio-*N*-tetraose (bound β-1,4 to the median galactose). All three tetrasaccharides are derivatives of galactosido-β-1,4-glucose (Fig. 34). It remained *Kuhn*'s unfulfilled wish to study the genetic background of these relationships.

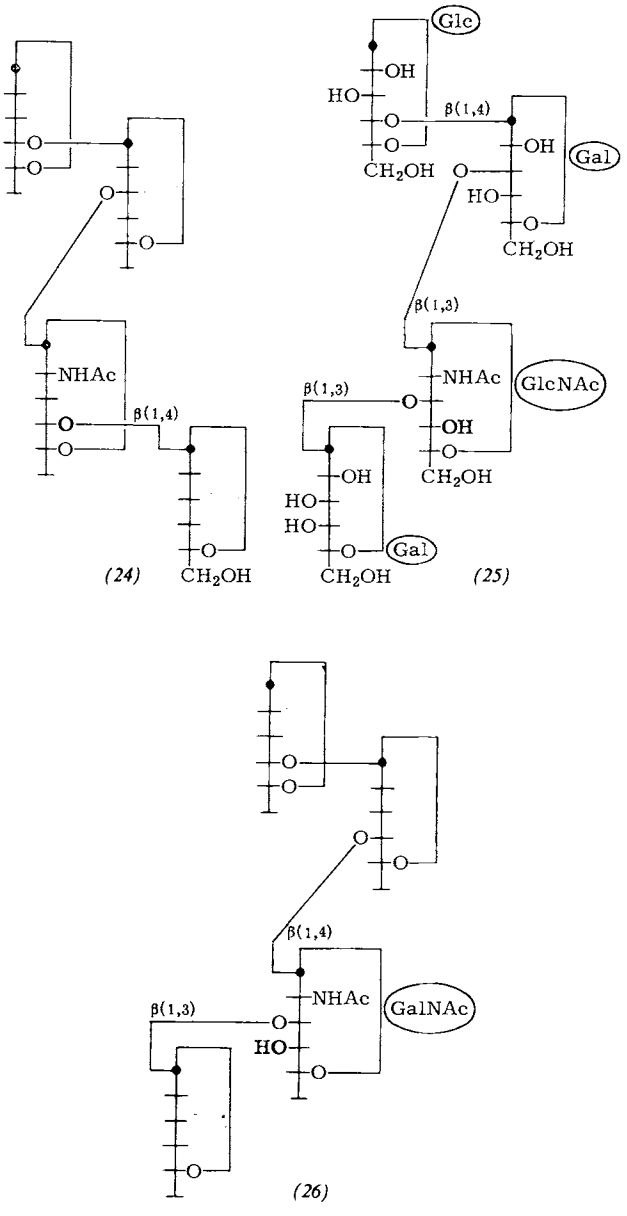


Fig. 34. *(24)*: Lacto-*N*-neotetraose; *(25)*: lacto-*N*-tetraose; *(26)*: ganglio-*N*-tetraose.

Almost all the oligosaccharides found in human milk[76] are either cleavage products such as the lacto-*N*-trioses I and II[77], or substitution products

[75] *R. Kuhn* and *H. Wiegandt*, Chem. Ber. *96*, 866 (1963).

[76] For a summary, see *R. Kuhn*, Angew. Chem. *67*, 184 (1955); Bull. Soc. Chim. biol. *40*, 297 (1958); *R. Kuhn et al.*, Angew. Chem. *69*, 23 (1957).

[77] *R. Kuhn, A. Gauhe*, and *H. H. Baer*, Chem. Ber. *89*, 1027 (1956).

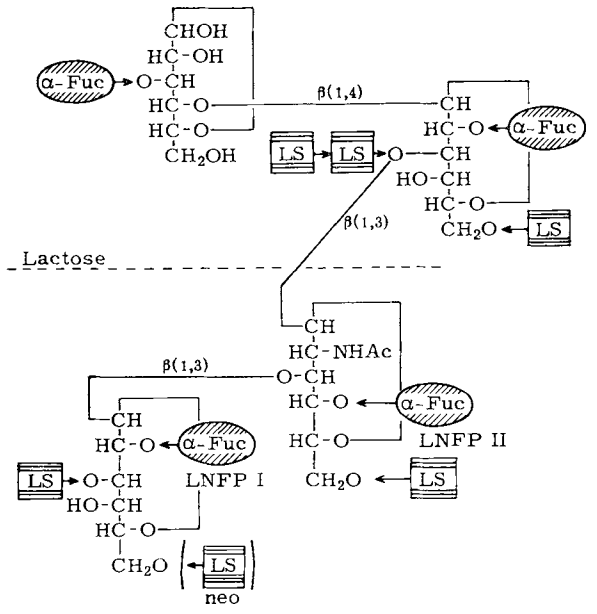


Fig. 35. Oligosaccharides from human milk derived from lacto-*N*-tetraose (or -neotetraose) by substitution of fucosyl or lactaminyl residues. LNFP I and II = lacto-*N*-fucopentaose I and II.
(*R. Kuhn, H. H. Baer, R. Brossmer, A. Gauhe, et al.*).

Table 1. Fucosido- and lactaminyl-oligosaccharides isolated from human milk.

Lactose	Gal-β(1,4)→Glc<
Lacto-*N*-tetraose	Gal-β(1,3)→GlcNac-β(1,3)→Gal-( )→Glc<
Lacto-*N*-neotetraose	Gal-β(1,4)→GlcNac-β(1,3)→Gal-( )→Glc<
Fucosido-lactose	Gal-( )→Glc< α(1,2) Fuc
Lacto-difuco-tetraose	Gal-( )→Glc< ( ) α(1,3) Fuc Fuc
Lacto-*N*-fuco-pentaose I	Gal-β(1,3)→GlcNac-β(1,3)→Gal-( )→Glc< α(1,2) Fuc
Lacto-*N*-fuco-pentaose II	Gal-( )→GlcNac-( )→Gal-( )→Glc< α(1,4) Fuc
Lacto-*N*-difuco-hexaose	Gal-( )→GlcNac-( )→Gal-( )→Glc< ( ) ( ) Fuc Fuc
Le^a-active hexa-saccharide	Gal-( )→GlcNac-( )→Gal-( )→Glc< ( ) α(1,3) Fuc Fuc
3'-Lactaminyl-lactose	Gal-( )→Glc< (2,3) LAA
6'-Lactaminyl-lactose	Gal-( )→Glc< (2,6) LAA
Dilactaminyl-lactose	Gal-( )→Glc< (2,3) LAA-(2,8)-LAA
Pentasaccharide a	Gal-β(1,3)→GlcNac-β(1,3)→Gal-( )→Glc< (2,3) LAA
Pentasaccharide b	Gal-( )→GlcNac-( )→Gal-( )→Glc< (2,6) LAA
Pentasaccharide c	Gal-β(1,4)→GlcNac-( )→Gal-( )→Glc< (2,6) LAA

of correspondingly low oligosaccharides, *e.g.* lactose, or can be obtained from the tetraoses shown in Fig. 34 by substitution with fucosyl or lactaminyl residues (Fig. 35 and Table 1).

Among the substances which were isolated and identified were fucosidolactose [78], lactodifucotetraose [79], lacto-*N*-fucopentaose I (LNFP I) and II (LNFP II) [80], lacto-*N*-difucohexaose, and a (crystallized) hexasaccharide with two fucosyl residues [81] which showed strong Le^a blood group activity. A list of all the oligosaccharides which were isolated or prepared for comparison up to 1957 is given in the synopsis on amino sugars [76]. The finding that lactaminic acid-containing oligosaccharides are cleaved by influenza virus [82,83] was of great interest. The simplest cleavable oligosaccharides were found to be the 3'- and 6'-lactaminyl-lactoses [84,85]. It was shown that influenza virus, as well as the so-called receptor-destroying enzyme (RDE) of cholera vibrios split the glycosidic bond of lactaminic acid derivatives, *i.e.* possess α-ketosidase activity. Lactaminyl oligosaccharides were identified

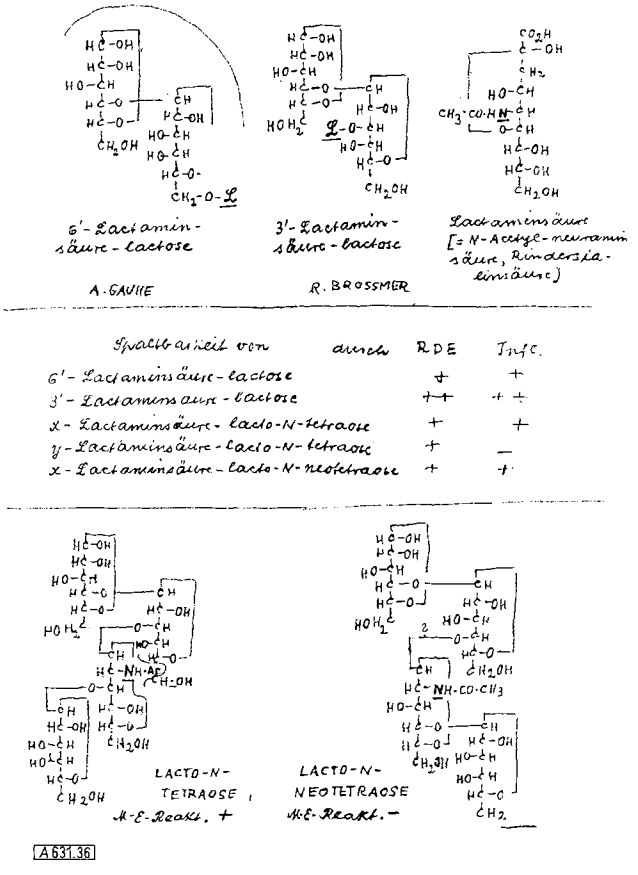


Fig. 36. *Kuhn*'s note on oligosaccharides from human milk and on cleavage experiments with influenza virus and with receptor-destroying enzyme (RDE); see also [94].

[78] *R. Kuhn, A. Gauhe*, and *H. H. Baer*, Chem. Ber. *89*, 2513 (1956).

[79] *R. Kuhn* and *A. Gauhe*, Liebigs Ann. Chem. *611*, 249 (1958).

[80] *R. Kuhn, H. H. Baer*, and *A. Gauhe*, Chem. Ber. *89*, 2514 (1956); *91*, 364 (1958).

[81] *R. Kuhn* and *A. Gauhe*, Chem. Ber. *93*, 647 (1960).

[82] *R. Kuhn* and *R. Brossmer*, Angew. Chem. *68*, 211 (1956).

[83] *R. Kuhn* and *R. Brossmer*, Chem. Ber. *89*, 2013 (1956).

[84] *R. Kuhn* and *R. Brossmer*, Angew. Chem. *70*, 25 (1958).

[85] *R. Kuhn* and *R. Brossmer*, Chem. Ber. *92*, 1667 (1959).

as receptors for influenza virus, thus explaining[86,87] the virus-inhibiting effectiveness of human milk. In his lecture on resistance problems[67], given at the 100th Meeting of the Gesellschaft Deutscher Naturforscher und Ärzte in 1958 in Wiesbaden, *Kuhn* suggested that cells that do not form such lactaminyl-oligosaccharide structures on their surfaces must be resistant to influenza virus. A note from that time found in *Kuhn*'s papers (Fig. 36) shows the structure of the oligosaccharides obtained and their substrate effectiveness toward influenza virus and RDE.

Lactaminic acid was found to be identical with *N*-acetylneuraminic acid (sialic acid)[88]; it may therefore be considered as a condensation product of *N*-acetyl-D-mannosamine with pyruvic acid (Fig. 36). Lactaminic acid was synthesized in 1962 by *Kuhn* and *G. Baschang*[89].

Gangliosides are oligosaccharide derivatives of sphingosin with a long-chain fatty acid (Fig. 37). The gangliosides I, II, III, and IV isolated from brain by *Kuhn*, mainly in collaboration with *H. Wiegandt*, are derivatives of ganglio-*N*-tetraose (Fig. 34) with one, two, or three lactaminyl residues, as shown in Fig. 38; the higher substituted gangliosides IV, III, and II are transformed by influenza virus into ganglioside I, as shown by the arrows[91].

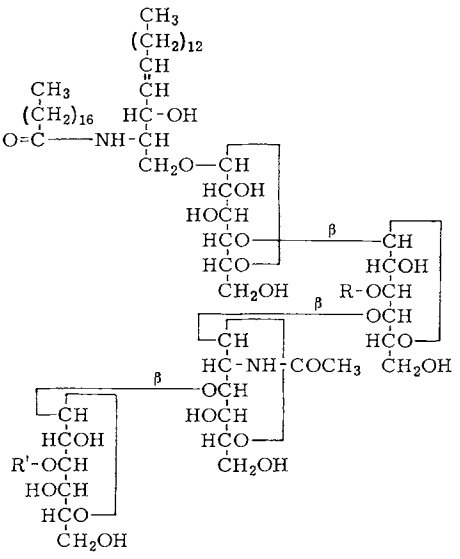


Fig. 37. Structural principle of gangliosides [90]. Ganglioside G_I: R = lactaminic acid, R' = H; Ganglioside G_{II}: R = R' = lactaminic acid.

These results were obtained at the beginning of a large program of detailed research on gangliosides, and are of a provisional nature[92,93]. *Kuhn* did not live to see

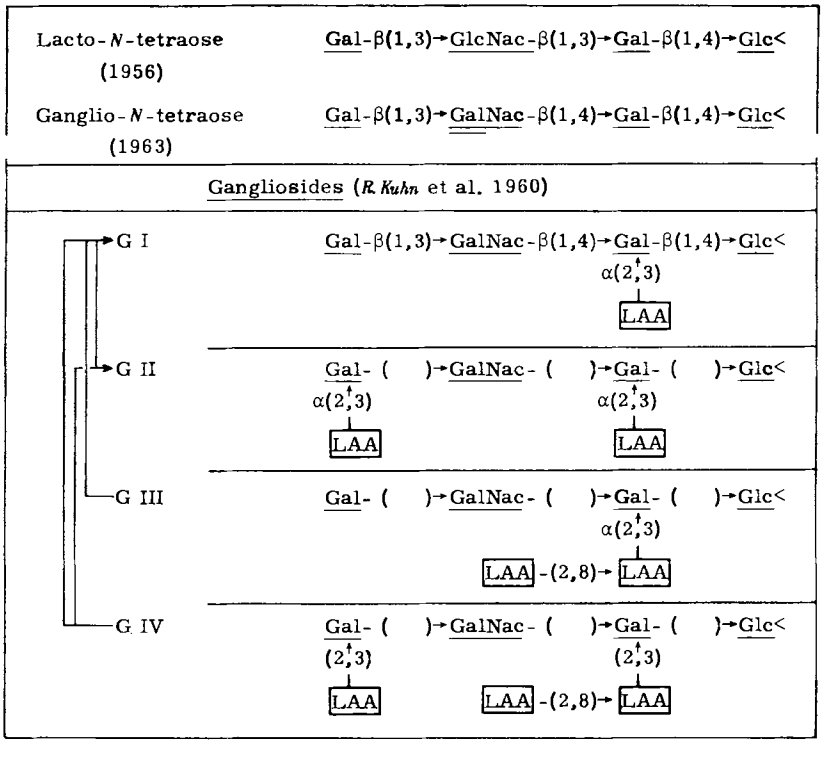


Fig. 38. The acidic oligosaccharides of gangliosides I, II, III, and IV (see [91]).

the fulfilment of the great expectations he had of further ganglioside and brain research[93a].

"We live in an age of electronics. Electronic computers, or electronic brains as they are also called, can perform with

[86] *R. Kuhn* and *A. Gauhe*, Chem. Ber. *95*, 513 (1962).

[87] *R. Kuhn* and *A. Gauhe*, Chem. Ber. *98*, 395 (1965).

[88] *R. Kuhn* and *R. Brossmer*, Angew. Chem. *69*, 534 (1957); *74*, 252 (1962); Angew. Chem. internat. Edit. *1*, 218 (1962); Liebigs Ann. Chem. *616*, 221 (1958); *R. Kuhn* and *G. Baschang*, Chem. Ber. *95*, 2384 (1962).

[89] *R. Kuhn* and *G. Baschang*, Liebigs Ann. Chem. *659*, 156 (1962).

[90] *R. Kuhn*, *H. Wiegandt*, and *H. Egge*, Angew. Chem. *73*, 580 (1961).

[91] *R. Kuhn*, *H. Wiegandt*, and *H. Egge*, Chem. Ber. *96*, 866 (1963); *R. Kuhn* and *H. Wiegandt*, Z. Naturforsch. *18b*, 541 (1963); see also *R. Kuhn* and *H. Egge*, Chem. Ber. *96*, 3338 (1963).

[92] See also *R. Kuhn* and *H. Wiegandt*, Z. Naturforsch. *19b*, 80, 256 (1964).

[93] *R. Kuhn* and *H. Müldner*, Naturwissenschaften *51*, 635 (1964); Angew. Chem. *77*, 176 (1965); Angew. Chem. internat. Edit. *4*, 160 (1965).

[93a] See *H. Wiegandt*, Angew. Chem. *80*, 89 (1968); Angew. Chem. internat. Edit. *7*, 87 (1968).

lightning speed computations that would require scarcely imaginable times with a pencil and log tables. Research on the human brain has not kept pace with the rapid development of electronics" [94].

A method frequently used for the detection and quantitative determination of *N*-acetylamino sugars is the Morgan-Elson reaction [95]. After treatment with dilute caustic soda, *p*-dimethylaminobenzaldehyde (Ehrlich's aldehyde) is added to the acidified solution, resulting in a purple coloration. *Kuhn* and *G. Krüger* [96] elucidated the mechnism of this important color reaction and defined the structural conditions required for the formation of the chromogen (splitting off of two molecules of H_2O from the acetylaminohexose and closure of the furan ring); they also determined the structure of "chromogen III", which was identified as D-5-dihydroxyethyl-3-acetaminofuran (Fig. 39). They showed that, in the formation of the chromogen, the *N*-acetylhexosamine reacts in its furanose form and that consequently the hydroxyl groups on carbons 1 and 4 must be free. The above assumptions make it possible to apply this color reaction to structural studies of hexosamine derivatives.

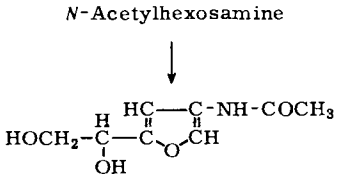


Fig. 39. The "chromogen III" of the Morgan-Elson reaction [96,97].

In connection with research on lacto- and ganglio-*N*-oligosaccharides and on their amino sugar-containing cleavage products, it became necessary to improve the methods available for the synthesis of amino sugars and derived disaccharides, *etc.* Together with *W. Kirschenlohr*, *W. Bister*, *G. Baschang*, and others, *Kuhn* did a considerable amount of work on syntheses of amino sugars [97].

The well known synthesis, due to *E. Fischer* and *H. Leuchs* [98], in which a 2-amino sugar is built up from a sugar containing one less carbon atom by conversion with ammonia and HCN into the corresponding aminonitrile, then transformation of the aminonitrile into the acid and its lactone, and reduction of the lactone to the amino sugar with Na amalgam (which gives only a 1 to 2% overall yield) was decisively improved [97] by introduction of semihydrogenation of aminonitriles [99] as well as of arylamino- and benzylaminonitriles [100]. In less than ten years, 25 papers were published on syntheses of amino sugars. Among the substances synthesized were the eight possible 2-amino-2-deoxyhexoses (hexosamines) of the D-series [101], the four 2-amino-2-deoxypentoses [102], and the two 2-aminotetroses (D-threosamine and D-erythrosamine) [103]. L-Fucosamine [104] and other amino sugars of the deoxy series also became easily accessible. A very elegant synthesis based on the same principle was that of the disaccharide *N*-acetyllactosamine from lactose (galactosyl-β-1,4-glucose) [105]. Lactose is first degraded to galactosyl-β-1,3-arabinose, which is then transformed into lactosamine *via* the aminonitrile.

The cyanohydrin reaction was also developed for a substantially improved synthesis of L-glucose and L-mannose starting from L-arabinose [106].

Kuhn's amino sugar syntheses have enriched considerably the preparative chemistry of carbohydrates.

In the last years of his life and in keeping with his position as President of the Gesellschaft Deutscher Chemiker *Richard Kuhn* did considerable biographical work, in which he occupied himself with the great men of chemistry, especially with those whose thoughts and theories had permanently influenced progress in chemistry. He was interested in their letters and had an extraordinary memory for everything he could find out about them. Thus arose some delightful documents, such as the commentary [107] to the reprint of *J. H. van't Hoff*'s inaugural lecture on "Imagination in Science", delivered on the occasion when *van't Hoff*, like *Kuhn*, became a Professor at the age of 26 (1878 in Amsterdam). *Kuhn* was always working on this theme, which fascinated him because he too had a great gift of imagination [*]. Imagination is of immense importance in scientific work, and it is the teacher's duty to stimulate it in his students.

The papers left by *Kuhn* include innumerable sketches, beautifully written formulas – virtually works of art – reflecting his thoughts.

Kuhn has exerted great attraction on many people and was often in touch with important men. He enjoyed the meetings of Nobel Prize winners at Lindau. We find

Fig. 40. *Richard Kuhn* and the former President of the Federal Republic *Theodor Heuss* in Göttingen at the 80th birthday of *Otto Hahn* (March 8, 1959).

[94] *R. Kuhn et al.*, Angew. Chem. *72*, 805 (1960).

[95] *W. T. J. Morgan* and *L. A. Elson*, Biochem. J. *28*, 988 (1934).

[96] *R. Kuhn* and *G. Krüger*, Chem. Ber. *89*, 1473 (1956).

[97] *R. Kuhn et al.*, Angew. Chem. *69*, 23 (1957).

[98] *E. Fischer* and *H. Leuchs*, Ber. dtsch. chem. Ges. *36*, 24 (1903).

[99] *R. Kuhn* and *W. Kirschenlohr*, Angew. Chem. *67*, 786 (1955).

[100] *R. Kuhn* and *W. Kirschenlohr*, Liebigs Ann. Chem. *600*, 115 (1956); see also *R. Kuhn* and *H. J. Haas*, *ibid. 611*, 57 (1958).

[101] *R. Kuhn*, *W. Bister*, and *H. Fischer*, Liebigs Ann. Chem. *617*, 109 (1958).

[102] *R. Kuhn* and *C. Baschang*, Liebigs Ann. Chem. *628*, 193 (1959).

[103] *R. Kuhn* and *H. Fischer*, Liebigs Ann. Chem. *641*, 152 (1961).

[104] *R. Kuhn*, *W. Bister*, and *W. Dafeldecker*, Liebigs Ann. Chem. *628*, 186 (1959).

[105] *R. Kuhn* and *W. Kirschenlohr*, Liebigs Ann. Chem. *600*, 135 (1956).

[106] *R. Kuhn* and *P. Klesse*, Chem. Ber. *91*, 1989 (1958).

[107] *R. Kuhn*: Die Phantasie in der Wissenschaft. "Ruperta Carola", Mitt. d. Vereinigg. Freunde d. Stud. Univ. Heidelberg, XIII, Vol. 30, p. 3 (Dec. 1961).

[*] "Die Phantasie in der Wissenschaft", read by *R. Kuhn*, is available on record No. 13/1 of the series Stimme der Wissenschaft, issued by the Akademische Verlagsgesellschaft, Frankfurt a. M.

again and again the expression of his interest in thinking and creative people.

The years 1944/1945, when *Theodor Heuss* left the increasingly unsafe Berlin after the July 1944 plot and came to quieter Heidelberg, saw the development of a warm friendship; *Heuss* and *Kuhn* sought and found mutual contact (Fig. 40). On the occasion of BASF president *Carl Wurster*'s 60th birthday, on December 2, 1960, in Ludwigshafen, *Heuss* learned that *Kuhn*'s 60th birthday was on the following day. On his return to Stuttgart, *Heuss* sent *Kuhn* a handwritten letter which he posted in the small hours "as an experiment on whether they manage it in time". A few lines may be quoted ... "You, my dear Herr *Kuhn*, have a refreshingly meager talent for getting excited. My greatest pleasure in your company is the relaxed serenity of your observant eyes. May this searching look serve you for many years to discover that which is hidden and to enjoy your discoveries. With best wishes, *Theodor Heuss*".

In September 1965, at the Kekulé festival in Bonn, *Kuhn* was told by doctors that he was incurably ill. Those who had the privelege of being near him during the last period of his life know with what inner and outer discipline, spiritually unbroken to the last, he put his affairs in order, and with what passionate dedication he made arrangements for the future of his Institute and of his colleagues. We remember him as he appears in a photograph in 1965 (Fig. 41) gazing at distant horizons, in the background his devoted wife who stood by his side in both good and bad times, and especially in the last two years of his life. All his students and friends know how much she did for him in her quiet way.

Richard Kuhn died on July 31, 1967, in Heidelberg. It will take time to appreciate fittingly the life's work of this great chemist. In numerous discussions with former students, *Friedrich Ebel*, *Heinz Staab*, *Theodor Wagner-Jauregg* and *Kurt Wallenfels* (to whom, as well as to *A. Lüttringhaus*, the author is indebted for

Fig. 41. *Richard Kuhn* and his wife at the 75th Anniversary of the Deutsche Pharmazeutische Gesellschaft, Berlin, in October 1965. (Copyright by Raillon & Baldenins, Berlin).

advice and discussion), who assisted in assembling the biographical data and particulars of *Kuhn*'s work, it became very obvious that the task of appraising the work of *Richard Kuhn* is beyond the capacity of any one individual, at least at the present time. This is a task for future research. We, however, will always retain the indelible impression of *Kuhn*'s unique personality. We, his students, often used to say of him: You can only love him, or else you do not understand him. Let us take earnestly his precept that our most precious possession is man's creative force directed to beauty and progress. "The greatest happiness is to observe the birth of new ideas, and to foster and stimulate them, because they shape the future" [7]. The memory of *Richard Kuhn* binds us all to this precept. His achievements are part of the history of natural science.

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Free Radical Studies at Low Temperatures

BY B. MILE[*]

Free radicals can be produced in the gas phase and then condensed together with the molecules of an inert gas; they can also be generated and trapped in isolated sites in rigid solids. IR and ESR spectra of trapped radicals provide information concerning their structure and chemical properties. The techniques employed for producing and studying radicals are reviewed and a number of recent IR and ESR investigations of trapped radicals are discussed. The last part of the article deals exclusively with the applications of the rotating cryostat to the study of the ESR spectra and reactions of trapped radicals at low temperatures.

1. Introduction

Free radicals (molecular fragments containing an unpaired electron) are active participants in a wide variety of systems undergoing chemical change [1]. For example, the pyrolysis and combustion of organic materials involve highly reactive free radicals and the extensive conversions that occur are due to the high efficiency of the reactions between radicals and molecules. The high reactivity of free radicals can also result in extreme complexity since the conversion of reactants to products occurs through a maze of numerous, very fast radical-molecule reactions taking place in sequence and in parallel. The very efficient reaction between two radicals to form molecular products also causes the concentration of radicals in most systems to be so low that, not only have the concentrations not been measured, but even the presence of radicals in the system has usually been inferred from the nature of the products and has not been directly demonstrated.

The fact that the radical concentrations have not been measured inevitably means that there are more reaction steps than there are products and that, consequently, there is uncertainty both in the reaction scheme adopted and in the rate constants assigned to the assumed reaction steps. The consistency of the data for the same radical reaction studied in entirely different systems does, in most cases, lend support to the reaction steps proposed and to the existence of the radicals postulated; but, clearly, these proposed reaction mechanisms would be put on a firmer basis if the radicals postulated could be shown to exist and if the reactions could be observed directly and in isolation. Of equal, if not greater, importance is the fact that the physical and thermodynamic properties of radicals (*i.e.*, the orbital of the unpaired electron, the vibration frequencies, *etc.*) must be known before any reliable theory of radical-molecule reaction rates can be formulated. Thus, there are strong arguments for attempting to obtain sufficient concentrations of free radicals in a high state of purity so that their physics and chemistry can be studied more directly.

There are two ways of producing radicals in sufficient concentrations to be detected by physical techniques such as ESR spectroscopy: (a) the rate of radical generation can be increased; this is done in flash photolysis [2], pulse radiolysis [3], and recently in the radiolysis of liquid hydrocarbons [4]; (b) the rates of radical-radical termination reactions can be reduced; this is the approach adopted in the study of trapped radicals at low temperatures, and it is with this method that this review is concerned. The collision between radicals, which is the prerequisite of reaction, is reduced to a very small value by forming and trapping the radicals in isolated sites in rigid solids at low temperatures. The rates of diffusion of the radicals through the solid matrix can be made so low that the radicals can be preserved for years without any significant decrease in their concentration.

Work on trapped free radicals was begun by *G. N. Lewis* and his students [5] in the early 1940's. They showed that photolysis of frozen solutions of aromatic hydrazines with ultraviolet light resulted in the formation of free radicals which could be kept for long periods of time. In 1951, *Rice* and *Freamo* [6] demonstrated another way of generating trapped radicals when they decomposed hydrazoic acid by passing it through a heated tube at low pressures, and trapped out reactive intermediates from the gas phase onto a surface cooled with liquid nitrogen. (For reviews and details of work carried out on this topic up to 1960 see [7].)

The article will be divided into four sections dealing with: (1) experimental methods, (2) the infrared

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[1] *E. W. R. Steacie*: Atomic and Free Radical Reactions. Reinhold, New York 1954, 2nd Edition, Vol. I, p. 14.

[2] *G. Porter*: Technique of Organic Chemistry. Interscience Publ., New York 1963. 2nd Edition, Vol. III/2, p. 1055.

[3] *L. M. Dorfman* and *M. S. Matheson* in *G. Porter*: Progress in Reaction Kinetics. Pergamon Press, Oxford 1965, Vol. 3, p. 237.

[4] *R. W. Fessenden* and *R. H. Schuler*, J. chem. Physics *39*, 2147 (1963).

[5] *G. N. Lewis* and *D. Lipkin*, J. Amer. chem. Soc. *64*, 2801 (1942).

[6] *F. O. Rice* and *M. Freamo*, J. Amer. chem. Soc. *73*, 5329 (1951).

[7] *A. M. Bass* and *H. P. Broida*: Formation and Trapping of Free Radicals. Academic Press, New York 1960.

spectra of free radicals, (3) recent ESR studies, and (4) the use of the rotating cryostat in trapped radical studies.

2. Experimental Methods of Preparing and Trapping Radicals

2.1. Matrices: The Matrix Isolation Technique[8]

It is impossible to prevent collisions between radicals in the liquid and gas phases (except in the extremely dilute regions of a molecular beam) and it is only in inert solids that radicals can be kept apart. The solid matrix used for holding the radicals in dispersed sites several molecules apart should satisfy the following requirements.

Rigidity – Clearly the matrix must be sufficiently rigid to prevent radicals diffusing and this is usually ensured by working at low temperatures. However, some work has been done with ionic solids containing trapped radicals as, for instance, in studies of γ-irradiated single crystals of carboxylic acids and their salts[9]. It is worthwhile noting that radical diffusion occurs at a temperature well below the melting point of the matrix; usually the radicals begin to disappear when the temperature rises to between one-tenth and one-third of the melting point (°K).

Inertness – The matrix must not react with the free radicals being studied. Otherwise, not only will radicals from the matrix be generated rather than the radicals of interest, but there is also the possibility of "chemical" diffusion whereby the free valences migrate through the matrix by a series of atom-transfer reactions between adjacent molecules. Additionally, the matrix must not be decomposed by the light which is used to photodissociate the guest reagent molecules into radicals.

Transparency – For visible, ultraviolet, and infrared spectroscopic studies, ideally the matrix should not absorb radiation in the same wavelength regions as the radicals do. The rare gases are obviously the most suitable matrices from this viewpoint. In the case of electron spin resonance spectroscopy, the spectra are often considerably better resolved if the radicals are trapped in sites in which they can undergo extensive "tumbling" motion. This helps to average out the effects on the spectrum of the orientation of the free radical in the magnetic field. (In most trapped radical studies, amorphous solids are used so that if the free radicals are in a fixed orientation, there is an overall random distribution of all possible orientations with a consequent broadening of the lines.) Thus, the best matrix would be one having large cavities in which the radicals can be trapped and still rotate in three dimensions, as well as having sufficient rigidity to prevent translational motion of the radicals.

Volatility – Apart from those cases where solutions are frozen and then irradiated, most of the techniques require that the matrix be deposited from the vapor phase onto a cooled surface. The matrix must therefore have sufficient volatility ($\approx$1 torr) at temperatures below those at which the matrix molecules decompose. The rare gases are the most commonly used matrices but hydrocarbons, fluorocarbons, and even water have also proved useful.

2.2. Formation of Radicals Prior to Trapping

There are two distinct ways of preparing the radicals that are to be trapped: (a) the radicals can be formed in the gas phase and subsequently trapped in the solid phase by co-condensing the radicals with molecules of inert gas; (b) the radicals can be both formed and trapped in the solid phase.

2.2.1. Formation of Radicals in the Gas Phase

Electric discharges are most frequently used for dissociating gaseous molecules (especially for making simple radicals, like H, NH, *etc.*). The gas mixture, consisting mainly of a rare gas with a small amount of the compound to be dissociated, is passed through either an electrodeless discharge or a discharge employing electrodes (Woods tube) and the resulting dissociated mixture is then quickly condensed onto a cold surface located close to the end of the discharge. This technique is simple and straight-forward to use, but it suffers from the disadvantage that the processes occurring in the discharge are complex and the identity and degree of purity of the radicals produced are sometimes uncertain.

Gaseous molecules can also be dissociated by pyrolysis[6]. *Klein* and *Scheer*[10] have studied the reactions of dissociated hydrogen atoms by heating a tungsten filament to a high temperature (2000 °K) in a stream of hydrogen and then bombarding frozen solid olefins with the partially dissociated gas. Atoms and small molecules of carbon can also be generated by thermal methods[11]. These methods are more useful for producing atoms by the dissociation of diatomic molecules than for producing polyatomic free radicals.

Only atoms and simple radicals such as OH, CH, C_2, NH_2, and PH_2, have been trapped from the gas phase and there is a simple reason for this. The combination of atoms and simple radicals can only occur in the presence of a third molecule which can remove some of the energy released on combination. (If this energy is not removed the nascent molecule will dissociate at the end of the first vibration.) Because of this third-body requirement, the rate of combination of atoms in the gas phase can be reduced considerably by reducing the pressure and thus sufficient concentrations of atoms can be built up to ensure the trapping of ap-

[8] *E. D. Becker* and *G. C. Pimentel*, J. Chem. Physics *25*, 224 (1956).

[9] *A. Horsfield, J. R. Morton*, and *D. H. Whiffen*, Molecular Physics *4*, 327 (1961).

[10] *R. Klein* and *M. D. Scheer*, J. physic. Chem. *62*, 1011 (1958).

[11] *R. L. Barger* and *H. P. Broida*, J. chem. Physics *43*, 2364, 2371 (1965).

preciable numbers when the gas is condensed. More complex radicals with a larger number of bonds to absorb the energy released on combination do not require a third body for combination so that it is very difficult to achieve sufficiently large concentrations of these radicals in the gas phase. The condensation process itself probably results in extensive combination since the gaseous molecules and radicals are brought much closer together as they form the solid phase. Nevertheless, it would be of considerable interest to be able to trap and identify radicals from complex gaseous systems where, for example, pyrolysis or oxidation occurs. Possibly the use of techniques similar to those used for the mass spectrometric [12] examination of free radicals might be helpful in this connection.

2.2.2. Formation of Radicals in the Solid Phase

The molecules to be dissociated are dispersed widely in the inert matrix by condensing the reagent and the inert matrix on a cold surface from the gas phase. The frozen solid is then irradiated with visible or ultraviolet or far-ultraviolet light, which causes photodissociation of the reagent molecules into free radicals. Radiolysis can also be used but the reagent itself must then serve as the matrix since the absorption of ionizing irradiation is non-selective. Photolysis of well-chosen molecules can be clean and can result in the formation of one or only a small number of radicals.

The major problem with this method is the possible occurrence of the "cage" effect which can reduce the quantum yield of radical formation to very low values. Photolytic dissociation of a molecule always results in the formation of two radicals (of opposite spin) and not one, and these radicals must separate from each other if they are not to recombine to form the parent molecule. This separation can be difficult in the solid phase where the two radicals are "caged" together and prevented by surrounding molecules from diffusing apart. Although the cage effect can be an important factor, it can be overcome by a suitable choice of conditions [13, 14]. For instance, if a molecule dissociates to give one small fragment that can move readily through the matrix, then the other larger fragment will be trapped. A simple reorientation of the radicals can also result in stabilization [15].

A hybrid of the two methods of gas and solid phase formation of radicals has also been employed. In this method the sample is photolyzed while it is being condensed and in some cases there is a considerable enhancement in yield over the simple photolysis of the condensed solid solution [16]. This may be due both to a reduction in the cage effect and to the fact that every region of the deposit has been irradiated and not merely the surface layers. (Absorption of a large amount of light in the first few layers of a solid can lead to the generation of a large number of radicals in close proximity with resultant loss of the radicals by combination.

Once the radicals have been formed and trapped, a variety of techniques can be used for their identification and characterization. Emission and absorption spectrometry, X-ray diffraction, calorimetry, infrared spectrometry, and electron spin resonance spectrometry have all been used for this purpose. Only the latter two techniques will be discussed in this article.

3. Infrared Spectra of Trapped Radicals

The characteristics of the ultraviolet and visible absorption spectra of trapped small radicals are well known, but it is only recently that it has been possible to obtain the infrared spectra of radicals [17]. The problem has been one of obtaining sufficiently high concentrations of radicals so that infrared absorption by the radicals is detected above the background absorption by the matrix.

The infrared spectrum of a radical can yield information about the frequencies of the various vibrations in the radical and also about the structure and thermodynamic properties of the radical. For instance, it is often possible to decide whether a radical is planar or non-planar, or whether two atoms of the same element are equivalent or non-equivalent. Thermodynamic functions such as the entropy and heat capacity can be calculated by statistical mechanics if the vibration frequencies and the bond lengths and angles of the radicals are known. The frequencies can be obtained from the infrared spectra but in most cases the bond lengths and angles have to be guessed – this is a serious gap in our knowledge and can only be removed by observation of rotational fine structure in the infrared spectra or by the observation of the microwave spectra of radicals.

3.1. Infrared Cells Used for Trapped Radical Studies

Most of the infrared work has been carried out in a cell similar to that first described by *Becker* and *Pimentel* [8] and shown schematically in Figure 1. A Dewar vessel containing the refrigerant, liquid hydrogen, helium, or nitrogen, is sur-

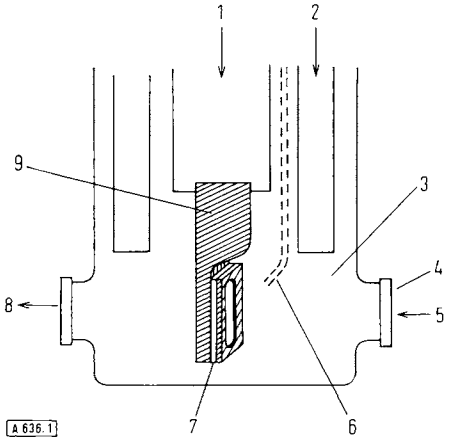

Figure 1. Schematic diagram of a low temperature cell used for infrared examination of deposits.
1 — Liquid helium. 2 — Liquid nitrogen. 3 — Evacuated space. 4 — CsBr window. 5 — IR and UV radiation. 6 — Inlet tube for matrix and reactants. 7 — AgI window. 8 — To IR spectrometer. 9 — Copper block and rod.

[12] *F. P. Lossing* and *A. W. Tichner*, J. chem. Physics *20*, 907 (1952).

[13] *G. C. Pimentel* in *A. M. Bass* and *H. P. Broida*: Formation and Trapping of Free Radicals. Academic Press, New York 1960, p. 95.

[14] *I. Norman* and *G. Porter*, Proc. Roy. Soc. (London), Ser. A *230*, 399 (1955).

[15] *H. Linschitz* in: Informal Discussion on Free Radical Stabilization. Faraday Society, Sheffield 1958, p. 37.

[16] *E. L. Cochran*, *F. J. Adrian*, and *V. A. Bowers*, J. chem. Physics *40*, 213 (1964).

rounded by another Dewar vessel containing liquid nitrogen, this outer Dewar serving as a radiation shield. A copper rod protrudes from below into the refrigerant in the inner Dewar and to the lower end of this rod is attached a copper block holding a silver iodide window (or other window transparent to infrared radiation). The silver iodide window is thus cooled *via* the copper block and rod. The matrix and substance under examination are co-condensed on the window, photolyzed with ultraviolet radiation, and investigated infrared spectroscopically.

3.2. Infrared Spectra

3.2.1. The Formyl Radical, HCO

The formyl radical (see also Section 4.2.1) was the first radical whose infrared spectrum was recorded. *Ewing*, *Thompson*, and *Pimentel*[17] ingeniously avoided the cage effect by using a reactive matrix. HI or DI molecules were dispersed in solid carbon monoxide and the hydrogen or deuterium atoms produced by photodissociation reacted with the carbon monoxide to form formyl radicals, HCO or DCO. The radicals were detected by their absorption bands in the visible spectral region.

Subsequently, *Milligan* and *Jacox*[18] were able to produce much larger concentrations of HCO or DCO by the simultaneous condensation and photolysis of mixtures of H_2S or D_2S and CO. These workers assigned the following frequencies: C=O stretching frequency of 1861 cm^{-1} in HCO and 1800 cm^{-1} in DCO; C–H and C–D stretching frequencies of 2488 and 1937 cm^{-1}, respectively; and C–H and C–D bending frequencies of 1090 and 852 cm^{-1}, respectively. Perhaps the most interesting feature of the spectra is the very low value of the C–H stretching mode at 2488 cm^{-1} (C–H stretching frequencies in normal molecules occur at *ca.* 3000 cm^{-1}). This indicates strongly that the C–H bond in HCO is considerably weaker than that in H_2CO and this is entirely in accord with kinetic evidence which indicates that $D_{(CO-H)}$ is 18 kcal per mole compared with a value of 88 kcal per mole for $D_{(HCO-H)}$[19]. The electron spin resonance spectrum of HCO also provides evidence of a very weak C–H bond (see Section 4.2.1).

The thermodynamic functions of the formyl radical can now be calculated fairly accurately since the bond angles and bond lengths of this radical are known from the absorption spectrum of the radical in the gas phase[20,21].

3.2.2. The Hydroperoxyl Radical, HO_2

The HO_2 radical, believed to be one of the most important intermediates in oxidation systems, has proved to be one of the most elusive radicals to trap and identify. *Milligan* and *Jacox*[22] finally succeeded in obtaining its infrared spectrum in argon at 4 °K by employing a technique similar to that used for the study of the formyl radical. Argon, hydrogen iodide, and oxygen were deposited onto a cooled cesium bromide window with simultaneous photolysis of the cold film. Argon was used as a diluent to prevent possible reaction between HO_2 and the iodine atom also produced by photodissociation of the HI. Three absorption bands were obtained for $H^{16}O_2$ and these were assigned to the H–O_2 stretching mode (3414 cm^{-1}), the O–O stretching mode (1101 cm^{-1}), and the H–O_2 bending mode (1389 cm^{-1}). The values of the OH stretching and bending mode frequencies are near to those for these modes in H_2O_2 indicating a tightly bound hydrogen atom in the HO_2 radical. This is in accord with the recent estimation of $D_{(H-O_2)}$ = 47.1 ± 2 kcal/mole compared to $D_{(HO_2-H)}$ = 89.6 ± 2 kcal/mole[23]. The O–O stretching frequency is intermediate between that in H_2O_2 (880 cm^{-1}) and that in O_2 (1580 cm^{-1}). The spectra of $H^{16}O^{18}O/H^{18}O^{16}O$ mixtures are interesting in that they show that the two oxygen atoms are not equivalent. This contradicts theoretical calculations which indicate that HO_2 has the configuration of an isosceles triangle[24].

3.2.3. The Methyl Radical, CH_3

Although much effort has been expended in the search for the infrared spectrum of the simplest alkyl radical, the methyl radical, it is only very recently that an absorption due to the out-of-plane bending mode has been observed by *Andrews* and *Pimentel*[25]. The methyl radicals were generated by condensing methyl iodide in argon simultaneously with a beam of lithium atoms. Although bands attributable to lithium iodide and methyllithium were detected, an additional absorption at 730 cm^{-1}, which decayed on warming, was also observed. From a comparison of the corresponding band obtained when deuterated methyl iodide was used, the authors assigned the observed frequency to an out-of-plane bending mode and calculated a force constant of 0.2527 mdyn/Å. This is close to force constants for the same mode in BBr_3 (0.29) and BI_3 (0.24) and thus provides some support for the planar structure of the methyl radical. No infrared spectra of any other alkyl radicals have yet been reported (see also Section 4.3.1.).

3.2.4. The Trifluoromethyl Radical, CF_3

Milligan, *Jacox*, and *Comeford*[26] have succeeded in recording the spectrum of CF_3 in a variety of matrices. The radical was prepared by a number of different

[17] *G. E. Ewing*, *W. E. Thompson*, and *G. C. Pimentel*, J. chem. Physics *32*, 927 (1960).

[18] *D. E. Milligan* and *M. E. Jacox*, J. chem. Physics *41*, 3032 (1964).

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[20] *G. Herzberg* and *D. A. Ramsay*, Proc. Roy. Soc. (London), Ser. A, *233*, 34 (1955).

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[22] *D. E. Milligan* and *M. E. Jacox*, J. chem. Physics *38*, 2627 (1963).

[23] *S. N. Foner* and *R. L. Hudson*, J. chem. Physics *36*, 2681 (1962).

[24] *M. E. Boyd*, J. chem. Physics *37*, 1317 (1962).

[25] *W. L. Andrews* and *G. C. Pimentel*, J. chem. Physics *44*, 2527 (1966).

[26] *D. E. Milligan*, *M. E. Jacox*, and *J. J. Comeford*, J. chem. Physics *44*, 4058 (1966).

methods but the infrared spectra from the deposits had three features in common and all these features decayed on warming. The three bands occur at 703 cm^{-1}, 1084 cm^{-1}, and 1250 cm^{-1} and have been assigned to an umbrella mode, to a symmetric, and to an asymmetric stretching mode respectively. The finding of two absorptions (1084 cm^{-1} and 1250 cm^{-1}) in the region of the C–F stretching fundamentals is very important since it shows that the CF_3 radical is non-planar. (In a planar molecule only the asymmetric stretching mode would be seen since the symmetric mode would involve no change in dipole moment.) In the case of CF_3 a direct comparison is possible between results in the gas phase and those in the solid phase since *Carlson* and *Pimentel* [27] have also succeeded in obtaining the infrared spectrum of the CF_3 radical in the gas phase by using rapid-scan infrared techniques in conjunction with flash photolysis. Transient absorption bands were observed whose positions were nearly identical with those observed for the trapped CF_3 radicals. Recent examination of the electron spin resonance spectrum of CF_3 has also shown that the radical is non-planar (*vide infra*).

3.2.5. Other Radicals

The foregoing should suffice to illustrate the application of infrared spectroscopy to trapped radicals. The spectra of the following radicals have also been observed and interpreted but will not be described in detail here: NH_2 [28,29]; NH [29,30]; NF_2 [31]; NF, NCl and NBr [32]; NCN [33]; CCO [34]; FCO [35]; ClCO [36]; CF_2 [37]; and the radical anion CO_2^- [38].

4. The Electron Spin Resonance Spectra of Trapped Radicals

Electron spin resonance spectroscopy has several advantages for the study of radicals: it only "sees" species containing free electrons so that matrix transparency is not a problem; it "sees" the very part that causes the high reactivity of the free radical; and it is extremely sensitive and can detect free radical concentrations as low as 10^{-8} molar (cf. [39,40]).

The technique depends on the fact that the electron has a magnetic moment (associated with its spin) which can lie either parallel or antiparallel to a magnetic field in which the electron is placed. In a sample containing many free electrons those with magnetic moments lying parallel to the field have a slightly lower energy than those lying anti-parallel to it, the relative numbers in each state (N_p and N_{ap} respectively) being given by the Botzmann equation:

$$N_{ap}/N_p = \exp(-\Delta E/kT)$$

where ΔE is the energy of separation which is equal to $g\beta H$, g is a dimensionless number (g-factor) having the value of 2.0023 for a free electron, β is the Bohr magneton, and H is the field strength in gauss (G). When electromagnetic radiation of the correct frequency falls on the sample ($h\nu = g\beta H$) it is absorbed and some of the electrons in the low energy state are raised to the high energy state. (ν is in the microwave region, 9000 MHz, when fields of 3000 G are used.) Of great interest to the chemist is the fact that nuclei close to the electron can cause hyperfine structure in the absorption if these nuclei themselves possess a magnetic moment. For example, in a hydrogen atom (nuclear spin quantum number, $I = 1/2$) the magnetic moment of the nucleus, like that of an electron, can lie parallel or anti-parallel to the field and these different orientations will result in the magnetic field experienced by the electron being either greater or less than the externally applied field. Two absorption lines are thus observed

$$h\nu_1 = g\beta\,(H + H_p) \text{ and } h\nu_2 = g\beta\,(H - H_p).$$

For hydrogen atoms, H_p, the effective field due to the proton at the electron, has a value of about 250 G. The presence of more than one proton in the vicinity of the electron, as in alkyl radicals, causes further splitting of these lines and clearly this hyperfine structure gives direct information about the environment of the unpaired electron and hence about the orbital which it occupies.

The interaction of the free electron with neighboring nuclei is of two types, isotropic and anisotropic. The latter is simply the dipole-dipole interaction between the magnetic moments of the electron and that of the nucleus, and its magnitude is inversely proportional to the cube of their separation and also dependent on the relative orientation of the two spins and hence on the orientation of the radical in the magnetic field. If the radicals are rigidly held and their orientations are random, this interaction can lead to considerable broadening of the hyperfine lines with consequent loss in resolution. A "tumbling" motion of the radicals in their sites results in the anisotropic interaction being averaged out to zero. The isotropic interaction, or the Fermi contact interaction [41], only occurs when there is a finite unpaired electron density at the neighboring nucleus. This isotropic interaction is not averaged out to zero by molecular motion and it is this interaction which is usually measured in the spectra of randomly orientated trapped radicals.

ESR experiments can be carried out in a similar way to infrared experiments. The copper rod and windows (Figure 1) are replaced by a non-conducting sapphire rod (electric insulator) and this rod is located in a microwave cavity between the pole

[27] *G. A. Carlson* and *G. C. Pimentel*, J. chem. Physics *44*, 4053 (1966).

[28] *D. E. Milligan* and *M. E. Jacox*, J. chem. Physics *43*, 4487 (1965).

[29] *D. E. Milligan* and *M. E. Jacox*, J. chem. Physics *41*, 1199 (1964).

[30] *K. Rosengren* and *G. C. Pimentel*, J. chem. Physics *43*, 507 (1965).

[31] *M. D. Harmony* and *R. J. Myers*, J. chem. Physics *35*, 1129 (1961).

[32] *D. E. Milligan* and *M. E. Jacox*, J. chem. Physics *40*, 2461 (1964).

[33] *D. E. Milligan*, *M. E. Jacox*, and *A. M. Bass*, J. chem. Physics *43*, 3149 (1965).

[34] *M. E. Jacox* and *D. E. Milligan*, J. chem. Physics *43*, 3734 (1965).

[35] *D. E. Milligan*, *M. E. Jacox*, *A. M. Bass*, *J. J. Comeford*, and *D. E. Mann*, J. chem. Physics *42*, 3187 (1965).

[36] *M. E. Jacox* and *D. E. Milligan*, J. chem. Physics *43*, 866 (1965).

[37] *D. E. Milligan*, *D. E. Mann*, and *M. E. Jacox*, J. chem. Physics *41*, 1199 (1964).

[38] *K. O. Hartmann* and *J. C. Hisatsume*, J. chem. Physics *44*, 1913 (1966).

[39] *D. J. E. Ingram*: Free Radicals as Studied by Electron Spin Resonance. Butterworths, London 1958.

[40] *J. E. Wertz*, Chem. Reviews *55*, 829 (1955); *A. Carrington*, Quart. Rev. (Chem. Soc., London) *17*, 67 (1963); *C. Jen*, in [3], Chapter 3; *M. C. R. Symons*, Advances physic. org. Chem. *1*, 283 (1963).

[41] *E. Fermi*, Z. Physik *30*, 320 (1930).

pieces of a powerful magnet. Alternatively, the free radicals can be formed and trapped in samples outside the spectrometer and then subsequently placed in the cavity. The samples must, of course, be prepared, transferred, and measured at low temperatures and silica glass Dewars are used for these purposes.

4.1. σ and π-Radicals

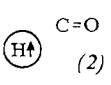
The classification into σ and π-radicals is dependent on the structure and symmetry of the orbital of the free electron; it also has important chemical implications. In σ-radicals the free electron is in an sp-hybridized orbital with contributions from both the s and p orbitals of the atom at which the free valence formally occurs; this usually results in the free electron orbital being non-perpendicular to the bonds attached to the free valence atom. In π-radicals the free electron orbital has a contribution from only the p orbital of the free valence atom and is perpendicular to the bonds to this atom; these bonds may themselves be sp-hybrid bonds and may be either co-linear or co-planar.

4.2. σ-Radicals

4.2.1. The Formyl Radical, HCO

The formyl radical could be either linear, $H-\overset{|}{C}=O$ (π-radical), or bent, $\overset{H}{\diagdown}C=O$ (σ-radical). *Adrian*, *Cochran*, and *Bowers*[42] produced the radical by reaction of hydrogen with solid carbon monoxide and also by photolysis of solid formaldehyde and methyl alcohol. The most striking feature of this work is the large proton hyperfine interaction of 137 G observed. (Since the resonance frequency ν and the magnetic field H are related by $h\nu = g\beta H$, the hyperfine interaction or splitting constant can be expressed in gauss or in megahertz.) This large interaction together with the pronounced anisotropy of the g-factor show that the formyl radical is a σ-type radical with the bent structure, *(1)*.

(1)



(2)

The other canonical form, *(2)*, with a loose interaction between a free hydrogen atom and a carbon monoxide molecule, also makes an important contribution. This is in complete accord with the information obtained from the infrared and kinetic studies (see Section 3.2.1).

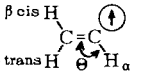
Brivati, *Keen*, and *Symons*[43] have also observed the ESR spectrum of the formyl radical and come to similar conclusions.

Recently *Cochran*, *Adrian*, and *Bowers*[44] have observed the ^{13}C hyperfine splittings in the HCO radical, and have determined the HCO angle as 125 °, thus confirming the bent structure.

4.2.2. The Ethynyl and Vinyl Radicals, $HC\equiv C\bullet$ and $H_2C=\dot{C}H$[16]

Photolysis of acetylene while being co-deposited with argon results in the formation of the ethynyl radical, $HC\equiv C$. The ESR spectrum shows a hyperfine interaction of 16.1 G with the proton. Unfortunately, the interpretation of this interaction in terms of the structure of the radical is complex but it does seem likely that the radical is of σ- and not π-type. Observation of the ^{13}C interactions (^{13}C has a magnetic moment, ^{12}C does not) would provide more information about the structure of the radical.

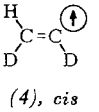
Vinyl radicals, $CH_2=\dot{C}H$, were formed by addition of hydrogen atoms to acetylene diluted with argon (analogous to the system used to generate HCO). The ESR spectrum showed that the unpaired electron interacted with three non-equivalent protons and from the effect of deuteration and from theoretical considerations it



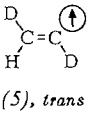
(3)

was shown that the hyperfine splitting constants could be assigned as follows: $a_{H\alpha} = 16.0$ G; $a_{Hcis} = 34$ G; $a_{Htrans} = 68$ G. *Cochran*, *Adrian*, and *Bowers*[16] calculate the Θ angle to be between 140 ° and 150 °.

In the formyl radical the α proton interaction is considerably greater (137 G). This is explained in part by the larger resonance of the carbon monoxide molecule and in part by the fact that the interaction is greater the less the angle Θ (in $\hat{HCO}$, Θ = 125 °). An interesting finding in this work is the fact that only the *trans* isomer is found when hydrogen atoms are added to dideuterioacetylene.



(4), cis



(5), trans

This is likely to be due to the zero point vibrational energies of the two isomers being sufficiently different so that only the more stable isomer is present in detectable concentrations at temperatures below 32 °K.

The ESR spectrum of the vinyl radical has also been observed recently in liquid ethylene by *Fessenden* and *Schuler*[4] and the only significant difference between the [solid] liquid and solid phases is that in liquid ethylene the α proton is inverting from one side of the molecule to the other at such a rate that the interactions with the β protons are averaged.

[42] *F. J. Adrian*, *E. L. Cochran*, and *V. A. Bowers*, J. chem. Physics *36*, 1661 (1962).

[43] *J. A. Brivati*, *N. Keen*, and *M. C. R. Symons*, J. chem. Soc. (London) *1962*, 237.

[44] *E. L. Cochran*, *F. J. Adrian*, and *V. A. Bowers*, J. chem. Physics *44*, 4626 (1966).

Fessenden [45] has recently observed the $\alpha^{13}C$ splitting in the vinyl radical (107.57 G) and from this has calculated Θ to be 151 ° which is in the range suggested by *Cochran, Adrian,* and *Bowers.* (The magnitude of the hyperfine splitting constant of the $\alpha^{13}C$ is dependdent on the amount of s character in the hybridize orbital and this in turn will also determine the bond angle.) All the features of the ESR spectrum of the vinyl radical, especially the $\alpha^{13}C$ interaction, show conclusively that it is a σ-type radical.

4.2.3. Trifluoromethyl, CF_3, and Other Fluorinated Methyl Radicals

Fessenden and *Schuler* [46] have observed the spectra of the interesting fluorinated methyl radical trapped in inert gas matrices, and also of CF_3 in liquid C_2F_6 (see also Section 3.2.4). In solid krypton and xenon the concentrations of radicals were sufficient for the ^{13}C splitting to be detected. From the value of the ^{13}C interaction, these authors have calculated that the free electron orbital has 21 % carbon 2s character and that the radical is non-planar (there is an angle of 17.8 ° between the C–F bonds and the plane normal to the threefold symmetry axis). In CHF_2 the orbital has 10 % C 2s character and the angle is 12.7 °; the CH_2F radical is nearly planar. There is thus a slow change from a planar radical to a pyramidal radical as the hydrogen atoms of the methyl group are replaced by fluorine atoms (see Section 4.3.1). The CF_3 and CF_2H radical ara again σ-type radicals.

4.2.4. The Cyclopropyl Radical

The ESR spectrum of the cyclopropyl radical in the liquid phase has been seen only by *Fessenden* and *Schuler* [4] and although it was not possible to observe any ^{13}C interaction, it is clear from the value of the α hydrogen splitting that the three bonds to the free valence carbon atom do not lie in a plane and that the radical is of the σ-type.

4.3. π-Radicals

4.3.1. The Methyl Radical

The ESR spectrum of methyl radicals has been observed in the solid phase [47] and in the liquid phase [4].

The hyperfine interaction with the protons is 23 G and with ^{13}C is 38.5 G, indicating that the radical is nearly planar, in agreement with the conclusion based on the absorption spectrum of the radical in the gas phase [48]. The methyl radical is thus a π-type radical with the free electron located in a carbon 2p orbital, the hydrogen atoms being bound to the carbon through sp^2-hybrid orbitals. An interesting result that follows from the different values of the ^{13}C interaction in CH_3, CD_3, CD_2H, and CDH_2 has been determined by *Fessenden* [45]. These values show that there is incomplete orbital following in these species (*i.e.*, the bonding electrons lag behind the nuclei as the nuclear skeleton undergoes bending vibrations). This is thought to be due to a decrease in electron repulsions caused by the occurrence of "bent" bonds [49].

4.3.2. Other π-Radicals

Most of the alkyl radicals appear to be of this type and these are discussed in Section 6.1.1. The benzyl radical [50], $C_6H_5\dot{C}H_2$, also belongs to this type and in this case the planar configuration about the $-CH_2$ group is favored by the occurrence of overlap of the p orbital on this carbon atom with the π-orbitals of the benzene ring.

4.4. Oxygen-containing Radicals

4.4.1. Alkoxy Radicals

Unfortunately, there is a conspicuous lack of information on the ESR spectra of alkoxy radicals. The samples from the γ-irradiation of frozen ethanol [51] and ultraviolet photolysis of H_2O_2/ethanol mixtures [52], followed by annealing of the samples at 100 °K, give rise to a slightly asymmetric single-line ESR spectrum which has been assigned to ethyl and methyl alkoxy radicals. No structural information is obtainable from these spectra and the assignments cannot be regarded as certain. The electron may not have an appreciable interaction with protons in the alkyl group but much more work is needed before any conclusions can be drawn with confidence.

5. The Rotating Cryostat

5.1. Principle of the Technique

The rotating cryostat is really a means of mixing two solids together intimately at the molecular level and in a controlled fashion so that single-step chemical reactions can occur and the primary products can be preserved for further study of their chemical and phys-

[45] *R. W. Fessenden,* Meeting of Amer. chem. Soc. Division of Physical Chemistry, Michigan August 1966, p. I 1.

[46] *R. W. Fessenden* and *R. H. Schuler,* J. chem. Physics *43,* 2704 (1965).

[47] *W. Gordy* and *C. G. McCormick,* J. Amer. chem. Soc. *78,* 3243 (1956); *C. K. Jen, S. N. Foner, E. L. Cochran,* and *V. A. Bowers,* Physic Reviews *112,* 1169 (1958); *B. Smaller* and *M. Matheson,* J. chem. Physics *28,* 1169 (1958); *T. Cole, H. O. Pritchard, N. B. Davidson,* and *H. M. McConnell,* Molecular Physics *1,* 406 (1958).

[48] *G. Herzberg,* Proc. Roy. Soc. (London) Ser. A, *262,* 291 (1961).

[49] *D. M. Schrader* and *M. Karplus,* J. chem. Physics *40,* 1593 (1964).

[50] *A. Carrington* and *I. C. Smith,* Molecular Physics *9* (2), 137 (1965).

[51] *C. Chacaty* and *E. Mayer,* Nature *200,* 59 (1963); J. chem. Physics *61,* 1115 (1964).

[52] *B. N. Shelimov, N. V. Fok,* and *V. V. Voevodskii,* Kinetika i Kataliz *5,* 1008 (1964).

ical properties. For example, the reaction between a halohydrocarbon and alkali atoms,

$$RX + Na^{\bullet} \rightarrow R^{\bullet} + NaX,$$

has been used to generate hydrocarbon radicals.

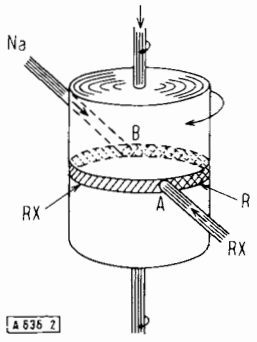


Fig. 2. Principle of the rotating cryostat.

The principle of the method is illustrated in Figure 2. Alternate layers of the two reactants are deposited from the gas phase onto the outer surface of a stainless steel drum which contains liquid nitrogen and is rotated rapidly (*ca.* 2400 r.p.m.) in a high vacuum ($<10^{-5}$ torr). The gaseous reactants are directed onto the drum from jets located close to the surface and on opposite sides of the drum so that each is deposited on a freshly formed surface of the other. The flow rates are adjusted so that about nine monolayers of halohydrocarbon are deposited per revolution but only about 1/25 of a monolayer of sodium. This "sprinkling" of the surface with sodium atoms ensures that very few alight adjacent to each other so that the radicals are formed in isolated sites. These radicals, immobilized on the surface, are then covered and trapped by the next layer of halohydrocarbon, and a small number of the surface molecules of this next layer are then converted into radicals by bombardement with further sodium atoms. This whole process is repeated many times until a solid deposit about 1 cm wide and about 1 mm thick is formed which is an interleaving spiral of a very dilute, free-radical layer and a much more dense halohydrocarbon layer. At the end of the experiment this deposit which contains about 10^{18-19} radicals per gram is transferred from the drum, still at 77 °K and under high vacuum, into a glass tube suitable for electron spin resonance measurements.

The technique can be slightly modified so that radicals can be prepared and trapped in materials other than the parent halohydrocarbon. This is achieved simply by deposition of the matrix as a third layer which forms the bulk of the deposit, the flux of halohydrocarbon being reduced to a value similar to that of sodium. In this case three jets are used instead of two. A similar modification allows the reactions of radicals with molecules to be studied. Before the radicals are covered up they are bombarded with a stream of the reactant molecules from the third jet. For example, the radicals can be bombarded with oxygen molecules, when the reaction

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}$$

takes place and the product radicals, RO_2, together with any unchanged R, are covered by the next matrix layer and trapped. If the ESR spectra of the reactant and product radicals differ sufficiently, the extent of the conversion can be calculated directly from the composite spectrum. Clearly, other reactions and other methods of generating radicals can be used in conjunction with the technique.

The rotating cryostat has a number of advantages over the simpler co-deposition methods where the vapors of different compounds are condensed on a stationary cold surface. The motion of the cold surface in the rotating cryostat allows the two processes of condensation and chemical reaction to be separated from each other and therefore allows more control of the system. It is also possible to study further reactions of the radicals initially formed, and this again can be done in a controlled way.

5.2. Experimental Equipment

A vertical section through the apparatus is shown in Figure 3. The drum itself is constructed from stainless steel and the parts are argon-arc-welded or vacuum-brazed together.

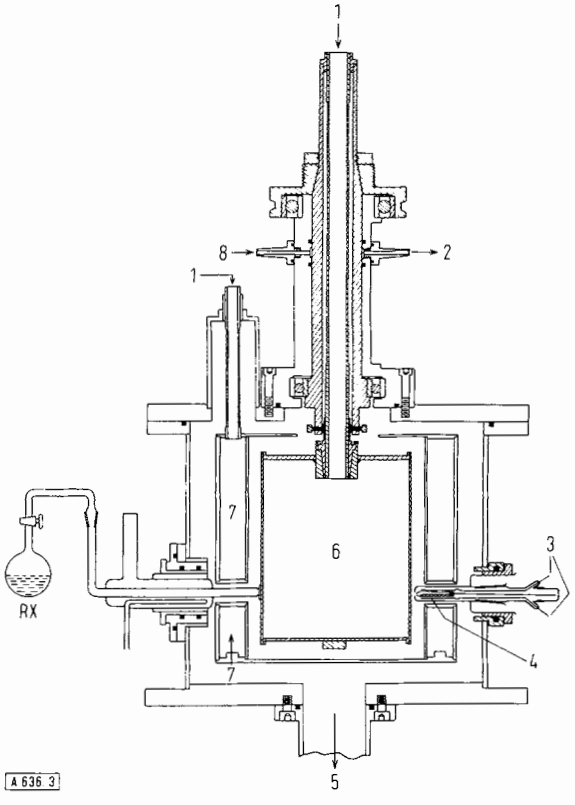


Fig. 3. General arrangement of cryostat (all hatched parts rotate; others are stationary), about 1/6 natural size.
1 — Filling tube for liquid nitrogen. 2 — Outlet for coolant. 3 — Terminals for heater windings. 4 — Sodium wire. 5 — To vacuum pumps. 6 — Spinning drum containing liquid nitrogen. 7 — Liquid nitrogen. 8 — Inlet for coolant.

The assembly is rotated by a belt-driven pulley attached to the outer tube, and it is the outer tube which carries the rotating seal. The "heart" of the apparatus is the seal around the outer shaft, which must allow the drum to be rotated at high speeds but must also seal the shaft so that pressures of less than 10^{-5} torr can be maintained in the main vessel (a high speed pump and wide-bore tubes are also used to help to maintain these low pressures). Two rubber O-rings, manufactured for rotating seals, are housed in two grooves with a 1 cm separation between them. The lower O-ring is the vacu-

um seal, while the upper one is a retaining ring which allows silicone oil to be pumped around the rotating shaft between the two O-rings. This flow of oil serves both to lubricate the seals and also to carry away the frictional heat which is generated by rotation of the shaft. (For further details see[53,54].)

6. Applications of the Rotating Cryostat

The results obtained can be divided into two categories: those that give information about the structure of the radicals and those that give direct information about the chemical reactions of radicals.

6.1. ESR Spectra and Structure of Radicals

6.1.1. Alkyl Radikals

Several radical species may be formed in the initial stages of photolysis or radiolysis and these primary radicals can either react with matrix molecules to form new radicals (the photon energy in excess of that required for bond breaking can be used for these reactions) or themselves be photolyzed into new species. With the rotating cryostat technique, the radicals are formed by the reaction

$$RX + Na\cdot \rightarrow R^{\bullet} + NaX$$

so that the position of the free valence in the radical is determined by the position of the halogen atom in the parent halohydrocarbon molecule. The ESR spectra of the deposits can therefore be assigned to definite radical species with considerable confidence.

A large number of alkyl radicals of each radical type have been prepared in a variety of matrices and the ESR spectra in each case can be interpreted in terms of the radical expected from the sodium-halohydrocarbon reaction. Some typical ESR spectra are shown in Figure 4. The results[54,55] are in general agreement with those of *Ayscough* and *Thomson*[56] who avoided some of the difficulties accompanying radiolysis by preparing the radicals by γ-irradiation of the parent halohydrocarbon. One difference is the finding of a readily interpretable spectrum for the isopropyl iodide-sodium system with the rotating cryostat, whereas a very complex spectrum was observed by *Ayscough* and *Thomson* after the radiolysis of isopropyl iodide.

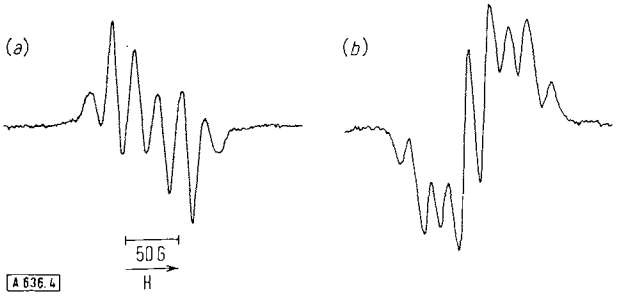


Fig. 4. The first derivative ESR spectra of: (a) *n*-heptyl radical $CH_3-(CH_2)_5-\dot{C}H_2$; (b) 4-heptyl radical $CH_3-(CH_2)_2-\dot{C}H-(CH_2)_2-CH_3$.

The spectra of the alkyl radicals can be interpreted on the following basis:

1) in all the alkyl radicals only the α and β protons (*i.e.* those attached to the free valence carbon atom and the adjacent carbon atoms) show any resolvable interaction with the unpaired electron (interaction with γ protons from 0.4 to 1.1 G can be observed in the liquid phase where the lines are narrower[4]);

2) the α protons, all three protons of a βCH_3 group and one of the protons of a βCH_2R group have similar hyperfine splitting constants of about 22 to 25 G;

3) the other proton in a βCH_2 group and the one proton in a βCH group have a hyperfine splitting constant of about 42 to 45 G.

These features can be explained by assuming that the α carbon atom adopts an sp^2 hybridization with a coplanar arrangement of the bonds around it and with the unpaired electron occupying a p-orbital whose axis is perpendicular to this plane. In order to explain the inequality of the two βCH_2R protons, it must be assumed that the hyperfine interaction depends on the orientation of the βCH bond with respect to the axis of the p-orbital. *Horsfield*, *Morton*, and *Whiffen*[9] have shown that this is so in free radicals formed by γ-irradiation of carboxylic acids and have also shown that the angular dependence of the interaction is given by

$$H_\beta = B_0 + B_1 \cos^2\Theta$$

where H_β is the β proton splitting, B_0 and B_1 are constants, and Θ is the angle between the βC–H bond and the p-orbital axis projected onto a plane perpendicular to the C–C bond. From the values of the hyperfine interaction the angles for the two β protons in alkyl radicals were calculated to be 12° (44 G interaction) and 48° (22 G interaction). The fact that the two β C–H bonds are non-equivalent shows that there is a barrier to rotation about the C–C bond. This does not necessarily mean that the molecule is fixed rigidly in any configuration but indicates that the lifetime in any of the four possible orientations which have these angles must be greater than 10^{-7} sec (the reciprocal of the hyperfine splitting).

From the chemical viewpoint the interaction with the α and β protons must mean that the α and β C–H bonds in the radical are weaker than in the corresponding alkane. In simple valence bond theory, this can be described in terms of contributions from canonical structures such as $H\cdot CH_2{=}CH_2$. For an isolated hydrogen atom the hyperfine interaction has a value of about 500 G so that a 22 G interaction can be interpreted on this basis to mean that the hydrogen is about 4% (22/500) dissociated in the radical. It is known from kinetic data that the C–H bond strengths in alkyl radicals are lower than those in the corresponding alkane (for example: $D_{(C_2H_5-H)} = 98.0$ kcal per mole while $D_{(\dot{C}H_2CH_2-H)} = 39$ kcal per mole)[19]

The results from these solid phase studies are in good accord with those obtained by *Fessenden* and *Schuler*[4] for alkyl

[53] *A. Thomas*, Trans. Faraday Soc. *57*, 1979 (1961).

[54] *J. E. Bennett* and *A. Thomas*, Proc. Roy. Soc. (London) Ser. A, *280*, 123 (1964).

[55] *J. E. Bennett*, *B. Mile*, and *A. Thomas*, unpublished.

[56] *P. B. Ayscough* and *C. Thomson*, Trans. Faraday Soc. *58*, 1471 (1962).

radicals in the liquid phase. Any differences between corresponding spectra are due to effects of temperature and phase on the rates of intramolecular internal reorientation of the radicals.

6.1.2. Substituted Allyl Radicals[57]

Because the free allyl radicals can be formed with the free valence at a specific site, the rotating cryostat allows an interesting direct demonstration of the phenomenon of resonance in organic molecules. In two separate experiments sodium atoms were caused to react with 3-chloro-1-butene *(6)* and with 1-chloro-2-butene *(7)*. In the absence of resonance, radicals *(8)* and *(9)* should have quite different ESR spectra.

$$\underset{(6)}{CH_2{=}CH{-}CHCl{-}CH_3} + Na\cdot \rightarrow \underset{(8)}{CH_2{=}CH{-}\dot{C}H{-}CH_3} + NaCl$$

$$\underset{(7)}{ClCH_2{-}CH{=}CH{-}CH_3} + Na\cdot \rightarrow \underset{(9)}{\cdot CH_2{-}CH{=}CH{-}CH_3} + NaCl$$

In fact, the radicals from both chloro compounds gave identical spectra consisting, at 77 °K, of seven lines with an equal separation of 15 G. This shows that the unpaired electron is interacting equally with six equivalent protons and is entirely in accord with the generally held view that structures *(8)* and *(9)* are canonical forms of the same radical species. The one proton that does not show any interaction at 77 °K is that on C-2.

6.1.3. The Phenyl Radical[58]

The phenyl radical is considered to be one of the most reactive hydrocarbon radicals[59,60]. This radical can be prepared in a rotating cryostat from phenyl iodide and can be trapped when matrices of water, benzene, deuteriobenzene, and perfluorocyclohexane are used; however, when matrices such as camphane, hexamethylethane, and cyclohexane are used the radical abstracts a hydrogen atom from a matrix molecule to form a matrix radical. The ESR spectrum indicates that the unpaired electron interacts with the two *ortho* protons (18.1 G) and to a lesser extent with the two *meta* protons (6.4 G) but not with the *para* proton. This shows that the unpaired electron remains in an sp^2 orbital on the carbon atom at which bond scission has occurred and the radical is thus of the σ-type. The projection of the sp^2 orbital outwards from the aromatic ring helps to explain the very high reactivity of the phenyl radical since appreciable bonding interactions can occur with adjacent molecules at distances where the repulsive interactions are still low. The extreme reactivity of the phenyl radical is shown by the fact that radicals such as methyl do not attack matrices such as cyclohexane while the phenyl radical does so with great ease.

6.1.4. The $CO_2^{\ominus}$ and $CS_2^{\ominus}$ Radical Anions[61,62]

Deposition of sodium or potassium onto solid carbon dioxide or solid carbon disulfide at 77 °K resulted in the formation of ion pairs, $Na^{\oplus}CO_2^{\ominus}$, *etc.* There was a small hyperfine coupling to the alkali metal nucleus which showed that the unpaired electron was not completely transferred to the carbon dioxide or carbon disulfide molecule. Similar ion pairs can be formed by γ-irradiation of alkali formate crystals[63,64] and the differences between the hyperfine splitting constants of the alkali metal atoms in the two cases (one a molecular solid, the other an ionic solid) demonstrates the marked effect the environment can have on the unpaired electron distribution between the members of an ion pair.

6.1.5. Aliphatic Ketyl Radical Anions[65]

The ketyl radical anions *(10)* of acetone, biacetyl, cyclopentanone, and cyclohexanone were prepared by reaction of sodium (or potassium) atoms with the solid ketones at 77 °K,

$$\underset{\underset{O}{\|}}{R{-}C{-}R} + Na^{\cdot} \rightarrow \underset{\underset{O^{\ominus}}{|}}{R{-}\dot{C}{-}R} + Na^{\oplus}$$

(10)

No differences in spectra were detectable when potassium was used instead of sodium, showing that the electron had been transferred completely to the ketone molecule. From the values of the proton hyperfine splitting constants, the unpaired spin density at the carbonyl carbon was calculated to be only 70% of that in the corresponding alkyl radical in which hydrogen replaces the $O^{\ominus}$ group. This reduction is due to the occurrence of an appreciable spin density at the carbonyl oxygen atom, *i.e.*, structures such as *(11)*

$$R{-}\overset{\ominus}{\underset{\underset{O\cdot}{|}}{C}}{-}R \quad (11)$$

are important.

6.1.6. Trapped Electrons

Radiation chemistry has recently undergone a major development since it has been shown that the primary reducing species produced by the passage of ionizing

[57] *J. E. Bennett, B. Mile,* and *A. Thomas,* unpublished.

[58] *J. E. Bennett, B. Mile,* and *A. Thomas,* Chem. Commun. *1965,* 265; Proc. Roy. Soc. (London) Ser. A, *293,* 246 (1966).

[59] *F. J. Duncan* and *A. F. Trotman Dickenson,* J. chem. Soc. (London) *1962,* 4672.

[60] *W. Fielding* and *H. O. Pritchard,* J. physic. Chemistry *66,* 821 (1962).

[61] *J. E. Bennett, B. Mile,* and *A. Thomas,* Trans. Faraday Soc. *61,* 2357 (1965).

[62] *J. E. Bennett, B. Mile,* and *A. Thomas,* Trans. Faraday Soc. *63,* 262 (1967).

[63] *D. W. Ovenall* and *D. H. Whiffen,* Molecular Physics *4,* 135 (1961).

[64] *P. W. Atkins, N. Keen,* and *M. C. R. Symons,* J. chem. Soc. (London) *1962,* 2873.

[65] *J. E. Bennett, B. Mile,* and *A. Thomas,* J. chem. Soc. (London) *A, 1968,* 298.

radiation through polar media such as water are solvated electrons and not hydrogen atoms[66] as was formerly supposed. A solvated electron is not associated with one molecule but is stabilized by interaction with an assembly of solvent molecules. ESR spectra of solvated electrons can be observed in liquid ammonia[66a], in frozen alkaline water, and in alcohols[67,68]. However, their spectrum is obscured by the spectra of other paramagnetic species such as $O^{\ominus}$, OH, and α-hydroxyalkyl radicals.

The rotating cryostat has been used to prepare trapped electrons as the sole paramagnetic species by the reaction of alkali metal atoms with ice and solid alcohols at 77 °K[69]. All the deposits were intensely colored and at 77 °K their ESR spectra consisted of a single narrow line. At 170 °K the spectrum Fig. 5 of trapped electrons in water became better resolved to reveal the presence of seven equally spaced lines (5.6 G apart) indicating an equal interaction with six protons of neighboring water molecules. The most likely arrangement of the water molecules around the electron is one with an octahedral disposition of the protons.

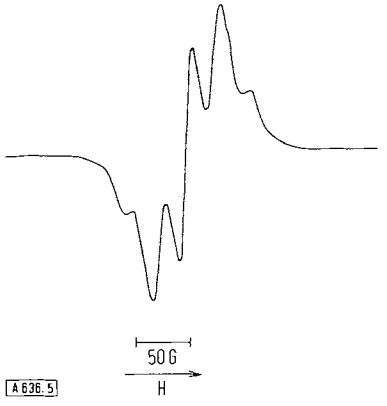


Fig. 5. The first derivative ESR spectrum of trapped electrons in ice at 170 °K.

When the samples containing trapped electrons in alcohols were either warmed slightly or exposed to visible light, the color of the samples faded and the spectrum changed to that of the corresponding α-hydroxyalkyl radical, R^1R^2COH[70]. The rate of this conversion could be measured from the change in the ESR spectrum with time, and it appeared that the rate-controlling step was a reorientation of the molecules around the electron trap into a configuration in which reaction could occur.

It is interesting that solvated electrons are not formed with hydrogen sulfide. Instead, simple negative ions $H_2S^{\ominus}$ are formed in which the electron is attached to one hydrogen sulfide molecule[71]. This marked difference between water and hydrogen sulfide is understandable because (1) the molecules in H_2S are not highly associated and have a lower dipole moment than molecules of water or alcohol and are thus less likely to form suitable electron traps; (2) the sulfur atoms has low-lying 3d orbitals which can accommodate the extra electron, whereas the oxygen does not.

6.2. Reaction Studies with the Rotating Cryostat

In these experiments the conditions under which reaction can occur are somewhat unusual in that a radical and a reactant molecule are "caged" or locked together in adjacent sites in the solid phase at 77 °K. The reactants are continually "colliding" with each other as they undergo lattice vibrations and librations of varying energy and amplitude. During the time of twenty minutes between the formation of the "caged" radical-molecule pair in the deposit and the recording of the ESR spectrum, reaction can occur when the energy in the caged region exceeds a critical activation energy with the reactants correctly orientated for reaction. If it is assumed that the energy flows in and out of the cage region with a frequency similar to that of lattice vibrations ($\nu = 10^{12}$ sec^{-1}) and that the pseudo-unimolecular reaction rate is given by $\nu P \exp(-E_A/RT)$, it can be readily shown that virtually complete reaction of all radical-molecule pairs occurs in the time available if $E_A < 5$ kcal per mole ($T = 77$ °K) and the steric factor $P = 10^{-1}$ to 10^{-4} sec^{-1}. Reactions with activation energies in excess of 5 kcal per mole cannot be conveniently studied because of the long times which would be involved.

6.2.1. Addition of Radicals to Oxygen

The reaction

$$R\bullet + O_2 + M \rightarrow RO_2\bullet + M \quad [72]$$

and the subsequent reactions of the peroxyl radicals, RO_2, are amongst the most important steps in any hydrocarbon oxidation at moderate temperatures (< 500 °C). The reaction has been investigated for a large number of radicals of widely different types (*e.g.*, alkyl, benzyl, and CF_3 radicals) by bombarding the radicals with molecular oxygen.

Since the ESR spectra of the radicals R• are usually very different from those of the corresponding peroxyl radicals, it is a relatively simple matter to estimate the extent of conversion of R• into RO_2 from a composite spectrum. The changes that occur in the case of the *tert*-butyl radical are shown in Figure 6. It is worth emphasizing that this is a direct observation on frozen radicals and does not involve the analysis of products

[66] See, for instance, the papers in Rad. Res. Suppl. *4* (1964).

[66a] *C. A. Hutchinson* and *R. C. Pastor*, J. chem. Physics *21*, 1959 (1953).

[67] *D. Schulte-Frohlinde* and *K. Eiben*, Z. Naturforsch. *17*, 445 (1962).

[68] *M. J. Blandamer, L. Sheilds*, and *M. C. R. Symons*, Nature *199*, 902 (1963).

[69] *J. E. Bennett, B. Mile*, and *A. Thomas*, Nature *201*, 919 (1964).

[70] *J. E. Bennett, B. Mile*, and *A. Thomas*, J. chem. Soc. (London) *A*, *1967*, 1394, 1399.

[71] *J. E. Bennett, B. Mile*, and *A. Thomas*, Chem. Commun. *1966*, 182.

[72] *J. E. Bennett, B. Mile*, and *A. Thomas*, Eleventh International Symposium on Combustion. The Combustion Institute, Pittsburgh 1967, p. 853.

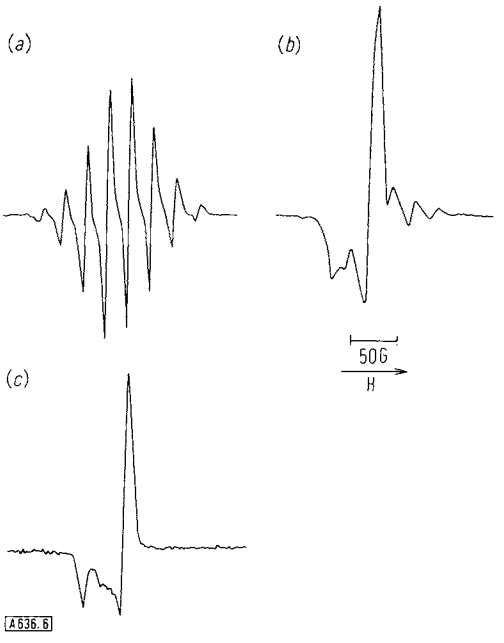


Fig. 6. Reaction between *tert*-butyl radical and oxygen at 77 °K. First derivative ESR spectra of (a) *tert*-butyl; (b) *tert*-butyl after bombardment with less than the stoichiometric quantity of oxygen; and (c) *tert*-butyl after bombardment with an excess of oxygen.

of further reaction. In all cases, even at 77 °K, complete conversion to the peroxyl radical occurred when sufficient oxygen was used, indicating a reaction of high efficiency and low activation energy. This extends to other radicals the previous conclusion about the high efficiency of this reaction made by *Dingledy* and *Calvert*, and *Hoare* and *Walsh* who studied the reactions of methyl and ethyl radicals with oxygen in the gas phase [73, 74].

The ESR spectra of the different peroxyl radicals are striking in that they are almost identical, being independent of the nature of the group R, and showing no hyperfine interaction with the protons in this group. This indicates that the free electron occupies an orbital that is confined almost entirely to the O–O region of the radical and is unaffected by the substituent group. Since the reactivity of radicals in terms of activation energy is determined principally by the orbital of the free electron it follows that all peroxyl radicals will have similar activation energies in bond-forming reactions.

6.2.2. The Addition of Radicals to Olefins

Early studies with the rotating cryostat showed [75] that not all radicals react with a particular olefin. For example, phenyl radicals react with ethylene at 77 °K, whereas *tert*-butyl and trichloromethyl radicals do not. Alkyl radicals do not react with tetradeuteroethylene at 77 °K [76]. The model used in the earlier work must be modified since it assumed that reaction occurred either on direct first collision between the radical and the alighting molecule or very soon afterwards. Subsequent work has shown that reaction can occur at any time from the collision of the molecule with the surface to the recording of the ESR spectrum of the deposit [77]. The uncertainty in time and in the value of ν (the lattice vibration frequency) means that only upper limit estimates of E_A and P can be made. It is therefore more profitable to study the site of radical addition in asymmetric olefins, than to attempt such estimates.

Phenyl radical addition to 1-hexene [76] leads to the formation of a radical the ESR spectrum of which shows that addition occurs exclusively at the terminal CH_2 group. This is a direct observation and no inferences have to be made to arrive at this conclusion. In the case of phenyl radical addition to $CH_2{=}CD_2$ [76] a secondary deuterium isotope effect could be studied since the phenyl radicals could add to the deuterium end of the olefin to give the radical $C_6H_5{-}CD_2{-}CH_2\bullet$ or to the hydrogen end to give $C_6H_5{-}CH_2CD_2\bullet$. The ESR spectra of these two radicals were different and the relative amounts of each radical could be evaluated from the composite spectrum. In this way it was found that $C_6H_5{-}CD_2{-}CH_2\bullet / C_6H_5{-}CH_2{-}CD_2\bullet = 4$ showing that the phenyl radical had a marked preference to add at the deuterium end of the olefin. This indicates that the sum of the carbon-hydrogen/deuterium vibration frequencies in the activated complex is greater than that in the ground state. This arises because, during the reaction, a soft out-of-plane bending C–H vibration in the olefinic trigonal carbon is converted into a harder bending vibration in the tetrahedral product radical.

$$C_6H_5^{\bullet} + CH_2{=}CH_2 \rightarrow C_6H_5{-}CH_2{-}\dot{C}H_2$$

trigonal tetrahedral

From the observed inverse isotope ratio of 4 and a simplified form of *Bigeleisen*'s equation [77, 78] the difference between the sum of the frequencies in the activated complex and in the ground state was calculated to be 570 cm^{-1}. The total change in the sum of frequencies for complete conversion of phenyl to phenylethyl was estimated to be 900 cm^{-1}, and a value of 570 cm^{-1} for the activated complex is a clear proof that the complex is product-like and that a strong bond exists between the phenyl radical and the olefin in the activated complex.

The advantages of the rotating cryostat for this type of study are clearly shown here; the low temperature accentuates small differences in reactivity (for instance, an isotope effect of 1.4 is predicted for this reaction at 25 °C) and the direct determination of the site of radical addition by ESR avoids difficulties that might arise because of isotope effects that can occur in product analysis.

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[75] *J. E. Bennett* and *A. Thomas*, Lecture at the Sixth International Symposium on Free Radicals, Cambridge 1963, Paper N.

[76] *J. E. Bennett, B. Mile*, and *A. Thomas*, unpublished.

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[78] *A. Streitweiser jr., R. H. Jagow*, and *S. Suzuki*, J. Amer. chem. Soc. *80*, 2326 (1958).

6.2.3. Abstraction Reactions

$R\cdot + R_1H \rightarrow RH + R_1\cdot$

The activation energies for hydrogen abstraction by most radicals are too high for detectable reaction to occur at 77 °K. Phenyl, cyclopropyl, vinyl, and CF_3 radicals are the exceptions and these attack other molecules with great ease even at 77 °K [58, 76]. This clearly demonstrates their higher reactivity and it is of some interest to note that all these radicals are of the σ-type, in which the free electron is in a localized orbital projecting away from the rest of the molecule.

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Modification of the Orientation of Substitution Reactions on Thiophene and Furan Derivatives

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Under normal conditions, thiophene and furan derivatives are substituted in the α position, and no convenient alternative methods for the preparation of β-substitution products have been available until now. The present article describes a method that permits the synthesis of many β-substituted thiophenes and furans. In this method, the carbonyl group in α-aldehydes or ketones of the thiophene and furan series is blocked by complex formation with an excess of aluminum chloride, so that electrophilic substitution takes place in position 4. In another useful method, the carbonyl group is blocked by acetalization. The acetals can be metalated in the ring by organolithium compounds.

1. Introduction

Though the term "aromaticity" [**] was first introduced more than a century ago, there is still no satisfactory definition or experimental test that could be applied to establish whether or not a system is aromatic. Our present ideas on aromatic systems are dominated by generalizations that follow from *Hückel*'s application of the MO theory to aromatic molecules and from the further development of this author's views. Despite the simplifications and approximations involved, the resulting physical picture enables us to explain some of the properties of such systems more or less precisely, and to predict the existence of new, similar compounds. However, questions concerning the properties of individual types of aromatic compounds were largely ignored for a long time.

Peculiarities in the behavior even of compounds that are formally very similar have in the meantime attracted considerable attention, from both the theoretical and the practical points of view. A comparison of the thiophenes with the furans shows that many properties are changed when a sulfur atom is replaced by an oxygen. Greater differences are observed on comparison of these and other heteroaromatic compounds with benzene derivatives. These differences are particularly obvious in substitution reactions; the unsubstituted heteroaromatic compounds can very often be regarded purely formally as monofunctional compounds.

One peculiarity of thiophene and furan is the strict orientation of electrophilic and protophilic substitutions, in which the substituent always becomes attached to the α position of the ring [***]. In the few cases in which β-substitution products were found, these were probably formed by isomerization of the α-substituted compound formed initially [4, 5]. Thus β-substituted products can generally be obtained only indirectly.

How can the orienting effect of the hetero atom be overcome in thiophene and furan chemistry? A solution to this problem would be valuable, since *e.g.* many natural products are β-substituted furans and thiophenes. The β-substitution products may also include physiologically active compounds.

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[**] The term "aromatic" is also used for heteroaromatic systems in this paper.

[***] The deuterium exchange kinetics show that the α position of thiophene reacts three orders of magnitude faster than the β position in electrophilic substitutions [1, 2] and six orders of magnitude faster in protophilic substitutions [2]. The α position in furan reacts three orders of magnitude faster than the β position in protophilic substitutions [3].

[1] *K. Halvarson* and *L. Melander*, Ark. Kemi *8*, 29 (1955).

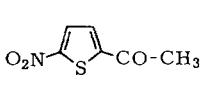
[2] *A. I. Šatenštein, A. G. Kamrad, I. O. Šapiro, Ju. I. Ranneva*, and *E. N. Zvjaginceva*, Doklady Akad. Nauk SSSR *168*, 364 (1966).

[3] *A. I. Šatenštein, A. G. Kamrad, I. O. Šapiro, Ju. I. Ranneva*, and *S. A. Giller*, Chim. geterocikličeskich Soedinenij 1966, 643.

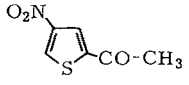
[4] *H. Wynberg* and *U. E. Wiersum*, J. org. Chemistry *30*, 1058 (1965).

[5] *N. I. Šuikin, B. L. Lebedev, V. G. Nikolskij, O. A. Korytina, A. V. Kessenich*, and *E. P. Prokofev*, Izvest. Akad. Nauk SSSR, Ser. chim. *1967*, 1618.

Significant work on the synthesis of 2- and 3-substituted thiophenes and their biological action in comparison with one another and with benzene derivatives has been carried out by *Campaigne et al.* [6]. Having examined the literature data (cf. *e.g.* [7]), we can agree with *Campaigne*'s opinion that the biological activity of 3-substituted thiophene cannot be estimated from the activity of the corresponding 2-substituted thiophene or of a benzene analog. Thus the β-substituted isomer should not be forgotten in the testing of thiophene analogs of biologically active benzene derivatives. There is a very high probability that this isomer is more active than the α-isomer. We know of only one case in which the antibiotic activity present in the α isomer (5-nitro-2-acetylthiophene) *(1)* does not occur in the β isomer *(2)* [8].



(1)



(2)

There is considerably less literature on the comparison of the physiological activities of α- and β-substituted furans, since β-substituted furans are much more difficult to obtain. However, many of the β derivatives again exhibit greater biological activity than the α isomer (analgesics [9], antihistaminics [10], antiseptics [11, 12]).

Four methods are available for the synthesis of β-substituted thiophenes:

1. Ring closure of bifunctional aliphatic compounds.

2. Side-chain bromination of 3-methylthiophene with *N*-bromosuccinimide.

3. Introduction of functional groups into a 2,5-disubstituted thiophene, followed by removal of the original substituents (generally halogen).

4. Reactions of 3-bromothiophene.

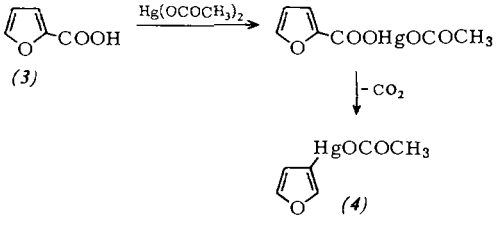
Though method 1 has been used for the synthesis of several interesting compounds, it is not very promising, since the bifunctional aliphatic compounds required as starting material are generally difficult to obtain. Moreover, thiophene derivatives can be synthesized from thiophene itself and its lower homologs, which are formed on thermal decomposition of natural raw materials or can be obtained from aliphatic hydrocarbons and sulfur or simple sulfur compounds. Quite apart from that, the tendency in thiophene chemistry is more toward the opposite course, *i.e.* the preparation of aliphatic compounds from thiophenes.

Method 2, which was proposed by *Campaigne* [13], is more feasible; however, it is fairly laborious and yields 2-bromo-3-methylthiophene as a by-product, although it has given satisfactory yields of 3-substituted thiophenes in some cases [14].

2,5-Dichloro-3-chloromethylthiophene [15], alkyl 2,5-dichloro-3-thienyl ketones [16, 17], and 2,5-dichloro-3-thiophenecarboxylic acid [18] have so far been obtained by method 3. It is very difficult in this case to eliminate the halogen atoms without alteration of the functional group introduced.

In our view the most suitable method for the preparation of 3-substituted thiophenes is that based on the use of 3-bromothiophene (method 4). The latter compound is generally obtained from 2,3,5-tribromothiophene by elimination of two bromine atoms. The simplest method of dehalogenation is that described by *Gronowitz* [19], in which zinc dust and acetic acid are used. This author also showed that the bromine in 3-bromothiophene can be almost quantitatively replaced by lithium under the action of *n*-butyllithium at −70 °C [20]. It would be difficult to overestimate the possibilities offered by 3-thienyllithium.

The range of reactions available for the synthesis of β-substituted furans is even smaller than that given for β-substituted thiophenes. We know of only two cases in which substituents were introduced directly into the β-position of a furan ring having at least one free α position. One was the reaction of mercury acetate with 2-furancarboxylic acid *(3)* to form a β-mercurated compound *(4)* [21], while the other was the formation of 4-isopropylfurfural from furfural [22] by alkylation with 2-chloropropane.



(3) *(4)*

In the first case the reaction proceeds *via* a mixed mercury salt of acetic acid and 2-furancarboxylic acid. Isomerization of 2-isopropylfurfural into the 3-isomer cannot be ruled out in the second case (cf. [5]).

In view of these difficulties, 3-monosubstituted and 2,3- and 2,4-disubstituted furans are usually obtained by cyclization of aliphatic compounds or by removal

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[8] *M. Bellenghi, G. Carrara, F. Fava, E. Ginoulhiac, C. Martinuzzi, A. Vecchi*, and *G. Weitnauer*, Gazz. chim. ital. *82*, 773 (1952); *48*, Chem. Abstr. 2029 (1954).

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[12] *C. N. Anderson*, US-Pat. 2022997; (Dec. 3, 1935) Lever Bros. Co.; Chem. Abstr. *30*, 820 (1936).

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[18] *J. A. Blanchette* and *E. V. Brown*, J. Amer. chem. Soc. *73*, 2779 (1951).

[19] *S. Gronowitz*, Acta chem. scand. *13*, 1045 (1959).

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[21] *H. Gilman* and *G. F. Wright*, J. Amer. chem. Soc. *55*, 3302 (1933).

[22] *H. Gilman, N. O. Calloway*, and *R. R. Burtner*, J. Amer. chem. Soc. *57*, 906 (1935).

of substituents from 2,3,5-trisubstituted furans. All these reactions proceed less readily than in the thiophene series, and the desired products are formed in lower yields.

2. Modification of the Orientation by Complex Formation

2.1. Problem

None of the preparative methods permits the direct introduction of substituents into the β-position of thiophenes or furans containing at least one free α position. We attempted to develop a direct method of β substitution suitable for at least some types of compounds of these series. As our first model we chose derivatives having a carbonyl group in one α position in the ring.

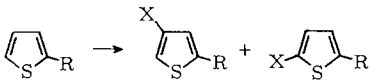
The directing influences of the ring hetero atom and of the electron-attracting substituent in position 2 of thiophene are superimposed in such a complex manner that the direction of electrophilic substitution cannot be predicted accurately for such compounds (for review see [23]).

However, it was observed some time ago [24] that the *ortho*, *meta*, and *para* positions of benzene approximately correspond to the 3, 4, and 5 positions in a 2-substituted thiophene. MO calculations [25] and dipole moment measurements [26] confirm that, to a satisfactory approximation, these positions can in fact be compared. On applying the Hammett equation to heterocycles, *Imoto et al.* [27,28] found that the constants ρ for reactions of thiophene and benzene derivatives do not differ greatly if σ_{para} is used for 2,5-disubstituted thiophenes and σ_{meta} for 2,4-disubstituted thiophenes.

Owing to the competition of the 4-directing effect of the substituent and the α-directing effect of the hetero atom, electrophilic substitutions on furan and thiophene derivatives having class II substituents in the α position practically always lead to mixtures of the 4- and 5-substitution products. The proportion of the 4 isomer formed increases with the strength of the −M effect of the substituent in position 2 [23].

Intensification of the electron-attracting properties of the substituent, *e.g.* by protonation of the carbonyl group in a strongly acidic medium, increases the percentage of the 4 isomer. Thus the 4 isomer predominates on nitration of 2-thiophenecarbaldehyde with nitric acid/sulfuric acid, whereas bromination of the aldehyde in chloroform leads almost exclusively to 5-bromo-2-thiophenecarbaldehyde [29]. Literature data relevant to this problem are listed in Table 1.

Table 1. Directing effects of class II substituents in position 2 of the thiophene ring.



(5) *(6)*

R	Reaction	Amount of *(5)* (%)	Amount of *(6)* (%)	Ref.
NO_2	Nitration	80–85	15–20	[10, 11]
CHO	Nitration	75	25 [a]	[32]
$COCH_3$	Nitration	52	48	[32, 38]
CN	Nitration	43	[57 [b]	[32]
COOH	Nitration	31	69	[32, 40]
$CH(OCOCH_3)_2$	Nitration	14	86	[32]
SO_3H	Nitration	little	much	[30]
SO_2Cl	Nitration	much	little	[31]
NO_2	Sulfonation	little	much	[30]
SO_3H	Sulfonation	little	much	[30]
SO_2Cl	Chlorination	much	little	[30]
SO_2Cl	Sulfochlorination	much	little	[30]
CHO	Bromination	3	97	[41,42] [c] [43] [c]
$COCH_3$	Isopropylation	99	1	[44]
$COCH_3$	Acetylation	—	≈ 100[d]	[45]
$COCH_3$	Chloromethylation	—	≈ 100[d]	[46]

[a] For further data on the nitration of 2-thiophenecarbaldehyde, see [33–37].

[b] For further data on the nitration of 2-thiophenecarbonitrile, see [39].

[c] These articles report: 5 isomer — very large proportion, 4 isomer — very little.

[d] Product yield about 6%.

In the furans, the directing influence of the hetero atom adequately explains the results in almost every case. Exceptions to these rules are (i) the formation of β-furylmercury acetate *(4)* by the action of mercury acetate on 2-furancarboxylic acid *(3)* [21], (ii) the β-alkylation of furfural with 2-chloropropane [22] (see

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[26] *R. Keswani* and *H. Freiser*, J. Amer. chem. Soc. *71*, 1789 (1949).

[27] *Y. Otsumi* and *E. Imoto*, J. chem. Soc. Japan, pure Chem. Sect. (Nippon Kagaku Zasshi) *80*, 1297 (1959); Chem. Abstr. *55*, 6476g (1961).

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[43] *N. P. Buu-Hoi* and *D. Lavit*, J. chem. Soc. (London) *1958*, 1721.

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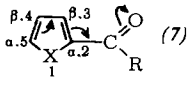
[45] *H. D. Harthough* and *A. I. Kosak*, J. Amer. chem. Soc. *69*, 3093 (1947).

[46] *R. Lukeš*, *M. Janda*, and *K. Kefurt*, Collect. czechoslov. chem. Commun. *25*, 1058 (1960).

Section 1), and (iii) the reaction of methyl furoate with caproic anhydride in the presence of tin tetrachloride, which yields a mixture of the 4- and 5-caproylated products [47].

Thus to introduce an electrophilic substituent into the β position of thiophene or furan, it is necessary to reduce the mobility of the α hydrogen atom in the ring without appreciably altering the mobility of the β hydrogens. Moreover, any side chains present must not be attacked. To achieve this purpose, it seemed reasonable to make use of the conjugation resulting from the presence of an electronegative group such as the carbonyl group in the molecule [see *(7)*].

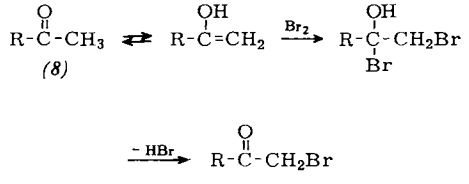


(7)

The carbonyl compound can react with an excess of a Lewis acid (particularly aluminum chloride) to form a complex in which the substituent is more strongly electron-attracting than in the free aldehyde or ketone; this increases the probability of formation of the 4-substituted, but not of the 5-substituted product. On the other hand, the complex formation hinders or prevents substitution in the side chain. Finally, the well-known catalytic effect of Lewis acids on electrophilic substitutions is particularly important for the less active β position.

It was shown as early as 1926 [48] that *m*-xylene, which gives no diketone under the usual conditions for the Friedel-Crafts reaction, reacts in the presence of 3 moles of aluminum chloride and without a solvent to give the diketone in a satisfactory yield. *Campbell* and *Spaeth* [49] obtained *m*-isopropylacetophenone by reaction of acetophenone with 2-chloropropane in a 4.5-fold molar excess without a solvent or in a 2-fold molar excess with a solvent. Practically pure 4-isopropyl-2-acetylthiophene has been prepared in a similar manner by alkylation of 2-acetylthiophene with 2-chloropropane and an excess of aluminum chloride [44].

Pearson et al. [50, 51] investigated the effect of the quantity of aluminum chloride on the direction of halogenation. It is well known that alkyl aryl ketones are normally halogenated in the side chain, α to the carbonyl group. The first step is the enolization of the ketone *(8)* [52].



In the halogenation of acetophenone and its homologs in the presence of 2–3 moles of aluminum chloride and without a solvent, *Pearson et al.* found that the halogen was introduced, not into the side chain, but into the ring position *meta* to the carbonyl group.

The main action of the aluminum chloride is probably the blockage of the carbonyl group by complex formation. The methyl group of the ketone is then no longer attacked, since enolization is practically or completely prevented in the complex. One mole of aluminum chloride is thus used for complex formation, and the remainder acts as a catalyst by participation in the formation of the attacking agent.

$$X_2 + AlCl_3 \rightleftarrows X^{\oplus} + AlCl_3X^{\ominus}$$

This assumption is confirmed by the fact that the rate of the reaction decreases when the quantity of catalyst added is reduced from 2.5–3 mole to 1.2 mole. However, the aluminum chloride also acts as a medium having a high dielectric constant, and so promotes dissociation [*].

This effect ("swamping catalyst effect") also enabled the authors to obtain satisfactory yields in the halogenation of several aromatic aldehydes and ketones [51] and several derivatives of aromatic acids [53], aniline [54], pyridine, picoline [55], isoquinoline, and quinoline [56].

2.2. Bromination of Aldehydes and Ketones of the Thiophene and Furan Series in the Presence of an Excess of Aluminum Chloride

We decided to prepare the complex of 2-acetylthiophene with aluminum chloride first, and to examine it by UV and IR spectroscopy [57], since complex formation with the hetero atom, which is possible in principle though not very probable in our case, could not be ruled out. The 600 Å increase in the wavelength of the UV absorption maximum in relation to the spectrum of the free ketone and the 70 cm^{-1} decrease in the characteristic carbonyl frequency in the IR spectrum confirm that complex formation takes place at the carbonyl group, as previously reported in the literature [58–61]. The complex is dissociated in very dilute solutions in chloroform.

[47] *G. Robinson*, J. org. Chemistry *31*, 4252 (1966).

[48] *O. Wulf*, DRP 515540 (1926); Chem. Abstr. *25*, 2439 (1931).

[49] *B. N. Campbell* and *E. S. Spaeth*, J. Amer. chem. Soc. *81*, 5939 (1959).

[50] *D. E. Pearson* and *H. W. Pope*, J. org. Chemistry *21*, 381 (1956).

[51] *D. E. Pearson, H. W. Pope, W. W. Hargrowe*, and *W. E. Stamper*, J. org. Chemistry *23*, 1412 (1958).

[52] *A. Lapworth*, J. chem. Soc. (London) *85*, 30 (1904).

[*] As has been shown in our laboratory, operation in the absence of solvents is not essential to successful halogenation (see Section 2.3).

[53] *D. E. Pearson, W. E. Stamper*, and *B. R. Suthers*, J. org. Chemistry *28*, 3147 (1963).

[54] *B. R. Suthers, P. H. Piggins*, and *D. E. Pearson*, J. org. Chemistry *27*, 447 (1962).

[55] *D. E. Pearson, W. W. Hargrowe, K. T. Judith*, and *B. R. Suthers*, J. org. Chemistry *26*, 789 (1961).

[56] *M. Gordon* and *D. E. Pearson*, J. org. Chemistry *29*, 329 (1964).

[57] *Ju. B. Volkenštein, B. V. Lopatin*, and *V. A. Petuchov*, Izvest. Akad. Nauk SSSR, Otdel. chim. Nauk *1962*, 917.

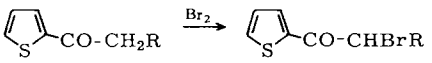
[58] *N. N. Lebedev*, Ž. obšč. Chim. *21*, 1788 (1951).

[59] *B. Susz* and *J. Cooke*, Helv. chim. Acta *37*, 1273 (1954).

[60] *B. Susz*, C.R. hebd. Séances Acad. Sci. *248*, 2569 (1959).

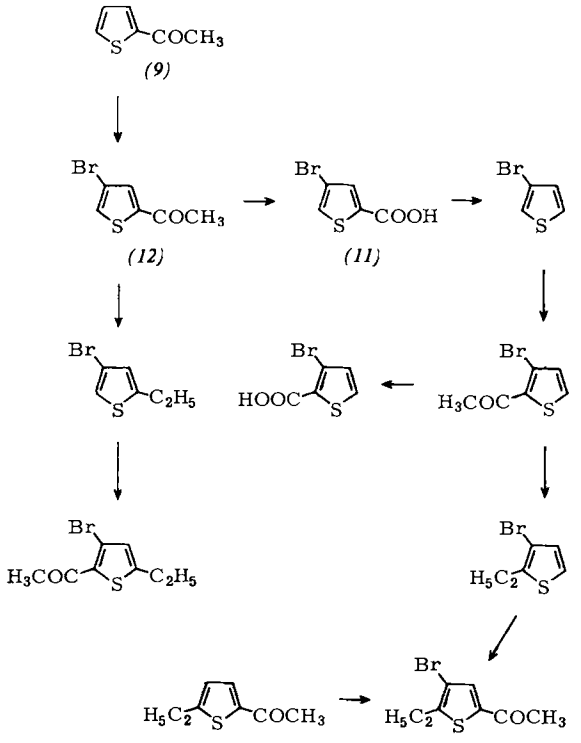
[61] *A. N. Terenin, V. N. Filimonov, D. S. Bystrov*, Izvest. Akad. Nauk SSSR, Ser. fiz. *22*, 1100 (1958).

2-Acetylthiophene *(9)* [62] and other alkyl 2-thienyl ketones *(10)* [63] are brominated in the side chain in the presence of catalytic quantities of aluminum chloride in solution.



(9), R = H
(10), R = Alkyl

Bromination without a solvent and in an excess of aluminum chloride [2.5 moles per mole of *(9)* or *(10)*] yields 4-bromo-2-thienyl ketones [63,64]. Some of the reactions of 4-bromo-2-acetylthiophene *(12)* are shown in Scheme 1.



Scheme 1

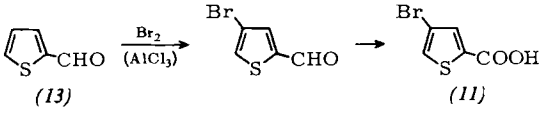
The structure of *(12)* is confirmed by chemical reactions, particularly by oxidation to the known acid *(11)*, as well as by its UV and IR spectra [65]. Polarographic measurements [66] indicate that the distilled 4-bromo-2-acetylthiophene *(12)* contains at most 0.5% of 5-bromo-2-acetylthiophene.

The only impurity isolated from *(12)* was 4,5-dibromo-2-acetylthiophene. The yield of 4-bromo-2-acetylthiophene was about 70%, that of its homologs (in the reactions of higher alkyl 2-thienyl ketones) 43–62%, and that of 4,5-dibromo-2-acetylthiophene 12%.

In view of the high reactivity of the α-methylene hydrogen in ketones, it could be assumed that the first step in the bromination is the formation of the 2-(α-bromoacyl)thiophene, independent of the reaction conditions. In the presence of more than the molar quantity of aluminum chloride, this product could isomerize to give the ring-brominated product. However, our experiments with 2-(α-bromopropionyl)thiophene and with 2-(α-bromobutyryl)thiophene in the presence of an excess of aluminum chloride and in the absence of solvent showed that a rearrangement of this type does not take place. It was also found that 5-bromo-2-acetylthiophene could be recovered unchanged after having been heated for several hours with an excess of aluminum chloride while hydrogen bromide gas was passed through the mixture.

The experiments thus show that bromine, presumably as Br^+, attacks alkyl thienyl ketones directly on C-4 of the ring.

We have also used this method for the bromination of 2-thiophenecarbaldehyde *(13)*, which is brominated almost exclusively in position 5 under normal conditions [42,43]. The bromination of the complexed aldehyde [41] leads to 4-bromo-2-thiophenecarbaldehyde (yield about 90%), the structure of which was proved by oxidation to the carboxylic acid *(11)* and by its spectra.



If the quantity of bromine is increased to 2.5–3 moles per mole of carbonyl compound, the bromination of 2-thiophenecarbaldehyde and of the alkyl 2-thienyl ketones with an excess of aluminum chloride and in the absence of solvent can be made to give very high yields of the 4,5-dibromo derivatives of the carbonyl compounds.

It was of interest to study the reaction of 2-acetylfuran *(14)* with bromine in the presence of an excess of aluminum chloride. According to *E. V. Brown*, *(14)* is brominated in the side chain when little or no catalyst is present [67]. It is also known [68–71] that in the halogenation of furan derivatives having electronegative substituents in position 2, the α-directing effect of the ring oxygen (which evidently influences the substitution direction more strongly than the sulfur in thiophene) predominates. Nevertheless, under the conditions used by *Pearson* the question of orientation in the bromination of 2-acetylfuran was difficult to decide.

We found that the action of one mole of bromine on 2-acetylfuran *(14)* at room temperature in the presence of three moles of aluminum chloride and without a solvent results in attack on the furan ring. However, this reaction, unlike that of 2-acetylthiophene, cannot be stopped at the stage of the monobromo derivative [72]. A little 2-acetyl-5-bromofuran can be isolated

[62] *F. Kipnis, H. Soloway*, and *J. Ornfelt*, J. Amer. chem. Soc. *71*, 10 (1949).

[63] *Ju. B. Volkenštein* and *Ja. L. Goldfarb*, Doklady Akad. Nauk SSSR *138*, 115 (1961).

[64] *Ja. L. Goldfarb* and *Ju. B. Volkentšein*, Doklady Akad. Nauk SSSR *128*, 536 (1959).

[65] *Ju. B. Volkenštein, B. V. Lopatin*, and *V. A. Petuchov*, Izvest. Akad. Nauk SSSR, Otdel. chim. Nauk *1961*, 1880.

[66] *S. G. Mairanovskij, N. V. Baraškova*, and *Ju. B. Volkenštein*, Izvest. Akad. Nauk SSSR, Ser. chim. *1965*, 1539.

[67] *E. V. Brown*, Iowa State Coll. J. Sci. *11*, 221 (1936–37).

[68] *Z. N. Nazarova*, Ž. obšč. Chim. *24*, 575 (1954).

[69] *H. Gilman* and *G. F. Wright*, J. Amer. chem. Soc. *52*, 1170 (1930).

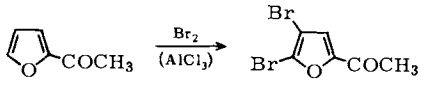
[70] *A. F. Shepard, N. R. Winslow*, and *J. R. Johnson*, J. Amer. chem. Soc. *52*, 2083 (1930).

[71] *H. B. Hill* and *C. R. Sanger*, Liebigs Ann. Chem. *232*, 67 (1886).

[72] *Ja. L. Goldfarb* and *L. D. Tarasova*, Izvest. Akad. Nauk SSSR, Otdel. chim. Nauk *1960*, 1304.

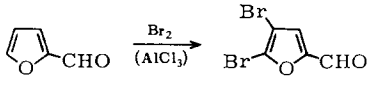
only at low temperatures and with short reaction times, together with 2-acetyl-4,5-dibromofuran *(15)*, which is the principal product at room temperature.

The yield of 2-acetyl-4,5-dibromofuran *(15)* rises from 34 to 62% when the molar ratio of bromine to 2-acetylfuran is increased to 2:1. The structure of *(15)* is proved by oxidation to the known 4,5-dibromo-2-furancarboxylic acid, which is also obtained directly by bromination of 2-furancarboxylic acid [71].



(14) *(15)*

It was later found that furfural [41, 73] behaves in the same way as 2-acetylfuran on bromination in the presence of an excess of aluminum chloride, *i.e.* two atoms of bromine enter the nucleus at the same time, and 4,5-dibromofurfural *(16)* is formed as the sole product (identification by oxidation to the carboxylic acid).



(16)

The bromination of furfural itself [68] and of its diacetate [69] in the absence of catalyst leads exclusively to 5-bromofurfural.

2.3. Influence of the Solvent

According to *Pearson et al.*, the bromination of an alkyl aryl ketone such as acetophenone, or of an aromatic aldehyde, without a solvent and with 2.5–3 moles of aluminum chloride per mole of aldehyde or ketone exhibits the "swamping catalyst effect". *Pearson* claims that three conditions are essential to ring halogenation [51]:

1. The carbonyl compound must be present as the aluminum chloride complex until the bromine is added.
2. Solvents must not be used.
3. The complex must be liquid, so that the mass can be stirred during the addition of the bromine.

Critical investigation of these conditions [74] has shown that the absence of solvents is not necessary, and sometimes actually hinders the isolation of the product from the reaction mixture and leads to low yields. It can be concluded from the proposed course of the reaction (see Section 2.1) that an excess of aluminum chloride and a practically homogeneous medium are essential to the success of the bromination. Any solvent that is inert under the conditions of the reaction may be used if it dissolves the complex of the aluminum chloride and the carbonyl compound without noticeable dissociation, and does not prevent the activation of the halogen by formation of a stable complex with the excess of aluminum chloride. The quantity of solvent that may be used is naturally limited, since the complex may dissociate if the solution is too dilute.

Even a small excess of aluminum chloride should direct the reaction in the desired direction; however, the optimum quantity that ensures an adequate reaction rate must be determined experimentally.

These conclusions have been fully confirmed by experiment. In the bromination of acetophenone in chloroform, we obtained the same results as under the conditions described by *Pearson*, and it was unnecessary to use 2.5 moles of aluminum chloride per mole of carbonyl compound. The same reaction direction and yield were obtained with only 1.5 mole of aluminum chloride per mole of ketone. A further decrease in the quantity of aluminum chloride leads to a decrease in the rate of the reaction, but the bromination, as before, still takes place on C-4 (see Table 2).

Table 2. Bromination of acetophenone in chloroform with various quantities of aluminum chloride [a].

$AlCl_3$:acetophenone (mole)	Acetophenone recovered (%)	Yield of *m*-bromoacetophenone (%)
2.5:1	4.2	57.0
1.5:1	11.6	60.0
1.3:1	24.0	45.0
1.1:1	69.0	29.5
1.0:1	68.0	— [b]

[a] In all the experiments the aluminum chloride was added to a solution of 0.1 mole of acetophenone in 50 ml of chloroform, and 0.1 mole of bromine was then added. The mixture was heated for 2 hours, allowed to stand for 18 hours at 20 °C, and then worked up in the usual way. The product was finally distilled off.

[b] In addition to the recovered acetophenone (68%), a high-boiling fraction (24% of the weight of acetophenone used) was obtained. Apart from acetophenone, this fraction contained traces of *m*-bromoacetophenone and phenacyl bromide (detected by gas chromatography).

The yield of *m*-bromoacetophenone increases to 80–85% when the bromination of acetophenone is carried out in dichloroethane. Methylene chloride, carbon tetrachloride, and carbon disulfide may also be used as solvents. On the other hand, bromination does not proceed in nitrobenzene; this is due to the low activity of the catalyst (the excess of aluminum chloride forms a complex with nitrobenzene). Saturated hydrocarbons are unsuitable, since the complex of acetophenone with aluminum chloride is completely insoluble in these solvents.

As expected, the bromination of 2-acetylthiophene, of 2-thiophenecarbaldehyde, and of furfural in solvents led to the same results as those obtained earlier under *Pearson*'s conditions. Both the products obtained by *Pearson*'s method and those obtained under our conditions contained 0.5–1.5% of the initial carbonyl compound, which was difficult to eliminate, and in the case of the ketone 0.5–1% of ω-bromo ketone.

The formation of the ω-bromo ketone in the presence of an excess of aluminum chloride can be attributed to the low equilibrium concentration of free ketone. An increase in the quantity of solvent used naturally favors the dissociation of the complex, and so leads to an increase in the quantity of ω-bromo ketone formed. Thus with 300 ml of chloroform instead of 50 ml per 0.1 mole of acetophenone (see Table 2), the bromination product consists almost entirely of phenacyl bromide.

Thus the solvent does not cause any essential change in the character of the reaction, and no specific "swamping catalyst effect" exists. In our opinion the only advantage of the large excess of aluminum chloride is that it lowers the melting point of the reaction mass. On the other hand, the use of a solvent permits an appreciable reduction of the quantity of aluminum chloride used, and also simplifies the isolation of the product; it is well known that when no solvent is used, the reaction mixture frequently solidifies toward the end of the reaction.

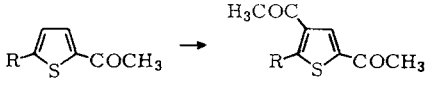
2.4. Acylation of Thienyl Ketones

On the assumption that bromination is not the only electrophilic substitution in the thiophene series to which the blockage of the carbonyl group by an excess of aluminum chloride could be applied, *Goldfarb* and *Litvinov* studied the acylation of some thienyl ke-

[73] *Ja. L. Goldfarb* and *L. D. Tarasova*, Izvest. Akad. Nauk SSSR, Ser. chim. *1965*, 1079.

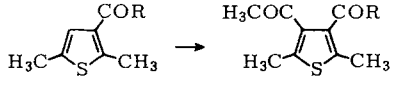
[74] *L. I. Belenkij, G. P. Gromova*, and *Ja. L. Goldfarb*, Izvest. Akad. Nauk SSSR, Ser. chim. *1967*, 1627.

tones [75]. It is known that the action of acetic anhydride on 2-acetylthiophene in the presence of zinc chloride leads to 2,5-diacetylthiophene [45], but only in 6% yield. It was hoped that 2,4-diacetylthiophene, possibly contaminated with the 2,5-isomer, might be obtained by the action of acetyl chloride in the presence of an excess of aluminum chloride and without a solvent, *i.e.* under *Wulf*'s conditions for the diacetylation of *m*-xylene [48]. However, the expected reaction did not take place, and the 2-acetylthiophene was recovered unchanged [75]. The introduction of the second acetyl group into position 4 proceeds only when the α position is occupied by an alkyl group, as in 5-methyl- *(17)* and 5-ethyl-2-acetylthiophene *(18)*.



(17), R = CH_3
(18), R = C_2H_5

It should be noted that 2,5-dimethyl-3-acetylthiophene *(19)* and *tert*-butyl 2,5-dimethyl-3-thienyl ketone *(20)* are acetylated in yields of up to 87% [75] with an excess of $AlCl_3$ and in absence of solvents, though in these cases, in contrast to the 5-alkyl-2-acetylthiophene, the orientation toward position 4 is absent.



(19), R = CH_3
(20), R = $(CH_3)_3C$

There are two possible reasons for this. The first is the high activity of the β position in 2,5-dialkylated thiophenes; the activity of this position in 2,5-dimethylthiophene is approximately the same as that of the α position in unsubstituted thiophene [76]. The second possible reason is that the carbonyl group in the β position is not coplanar with the thiophene ring [77] so that the withdrawal of electrons from position 4 by the −M effect is hindered.

2.5. Chloromethylation of Aldehydes and Ketones of the Thiophene and Benzene Series

It seemed interesting to examine the question of whether an excess of aluminum chloride can also be used for the chloromethylation of the ring in acetophenone, 2-acetylthiophene, and 2-thiophenecarbaldehyde. Little is known about the chloromethylation of aldehydes and ketones. In 1936, the chloromethylation products of pinacolone and of diethyl and dipropyl ketones [78] were obtained in 30–35% yield; acetone was later chloromethylated and the chloromethylation products of acetaldehyde and of methyl ethyl ketone were isolated in lower yields [79].

The unsubstituted aliphatic-aromatic and aromatic aldehydes and ketones (acetophenone [80–82], benzophenone [82], anthraquinone [83]) cannot be chloromethylated. However, two methyl groups in the ring of an aliphatic-aromatic ketone permit the introduction of the chloromethyl group into the ring [82]. Chloromethylation is even easier in ketones containing alkoxyl or hydroxyl groups. 4-Alkoxyacetophenones [84], 2-hydroxyacetophenone [85], and 2-hydroxypropiophenone [86] react in high yields. The chloromethylation of salicylaldehyde, of *o*-homosalicylaldehyde [87], and of anisaldehyde [88] has also been reported. Thus the reaction is facilitated by the presence of a hydroxyl or methoxyl group. Acetophenone, propiophenone, 4-methylacetophenone, and 3,4-dimethylacetophenone have been chloromethylated in the side chain in the presence of boron trifluoride-ether [89,90].

Even less work has been done on the chloromethylation of ketones of the five-membered heterocycles. It is interesting to note that in all the known cases prior to our work, the substituent entered the ring in position 5 (2-acetyl-5-chloromethylfuran [91], 2-acetyl-5-chloromethylselenophene [92], and 2-acetyl-5-chloromethylthiophene [46]). The yield in the case of 2-acetylthiophene was 5.7% based on the ketone introduced or 37% based on the ketone that reacted. According to the work of *Lukeš et al.* [46], *Hartough*'s report [93] that 2-acetylthiophene is chloromethylated in the side chain by formaldehyde and hydrochloric acid must be regarded as unsupported. We were unable to reproduce the work of *Janda* and *Dvořak* [94,95] on the orienta-

[75] *Ja. L. Goldfarb* and *V. P. Litvinov*, Ž. obšč. Chim. *30*, 2719 (1960).

[76] *Ja. L. Goldfarb*, *V. P. Litvinov*, and *V. I. Švedov*, Ž. obšč. Chim. *30*, 534 (1960).

[77] *V. P. Litvinov* and *V. A. Morozov*, Izvest. Akad. Nauk SSSR, Otdel. chim. Nauk *1961*, 166.

[78] *J. Colonge*, Bull. Soc. chim. France *3* (5), 2116 (1936).

[79] *O. C. Dermer* and *J. Newcombe*, J. Amer. chem. Soc. *74*, 3417 (1952).

[80] *G. Vavon*, *J. Bolle*, and *J. Calin*, Bull. Soc. chim. France *6* (5), 1023 (1939).

[81] *L. Schmid*, *W. Swoboda*, and *M. Wichtl*, Mh. Chem. *83*, 185 (1952).

[82] *R. C. Fuson* and *C. H. McKeever*, J. Amer. chem. Soc. *62*, 784 (1940).

[83] *H. Stephen*, *W. Short*, and *G. Gladding*, J. chem. Soc. (London) *117*, 510 (1920).

[84] *E. Profft* and *R. Drux*, J. prakt. Chem. *4*, 236 (1957).

[85] *R. Trave*, Gazz. chim. ital. *80*, 502 (1950).

[86] *P. DaRe* and *L. Verlicchi*, Ann. Chimica *46*, 910 (1956).

[87] *R. Stoermer* and *K. Behn*, Ber. dtsch. chem. Ges. *34*, 2455 (1901).

[88] *R. Quebt* and *J. Allard*, C.R. hebd. Séances Acad. Sci. *205*, 238 (1937).

[89] *M. N. Tiličenko* and *V. A. Popova*, Ž. obšč. Chim. *23*, 118 (1953).

[90] *V. A. Čaikovskaja*, Izvest. vyssich učebnych Zavedenij (Ivanovo), Chimija i chim. Technol. *2*, 895 (1959).

[91] *A. L. Mndžojan*, *V. G. Afrikjan*, and *M. G. Grigorjan*, Doklady Akad. Nauk Arm. SSR *17*, 97 (1953).

[92] *Ju. K. Jurev*, *N. K. Sadovaja*, and *E. N. Ljubimova*, Ž. obšč. Chim. *30*, 2732 (1960).

[93] *H. D. Hartough*: Thiophene and its Derivatives. Interscience Publishers, New York 1952, p. 189, 335.

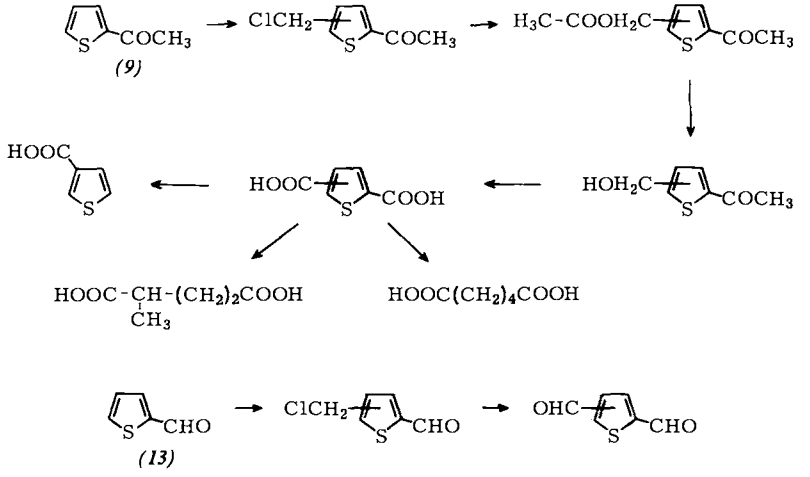
[94] *M. Janda* and *F. Dvořak*, Collect. czechoslov. chem. Commun. *27*, 327 (1962).

[95] *M. Janda* and *F. Dvořak*, ČSSR-Pat. 105005 (1962).

tion of the chloromethylation in 2-propionylthiophene [96].

The chloromethylation of acetophenone with chloromethyl methyl ether in the presence of 2.5 moles of aluminum chloride and without a solvent [97] led to *m*-chloromethylacetophenone (39% yield based on the acetophenone introduced, and 54% based on the acetophenone that had reacted), a compound that had not previously been described in the literature. The structure of the product was proved by oxidation to isophthalic acid, which was identified in the form of its dimethyl ester.

The chloromethylations of 2-acetylthiophene [97] and of 2-thiophenecarbaldehyde with an excess of aluminum chloride are not so simple. The product in both cases was a mixture of the 4- and 5-chloromethylation products, in which the 4 isomer predominated.



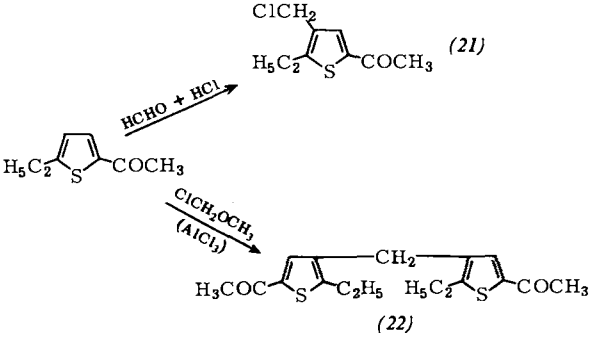
The reasons for the difference in orientation in the chloromethylation and in the bromination are not yet clear. There is still also some uncertainty concerning the action of the chloromethyl ether in normal chloromethylations; this evidently explains the contradictions in the literature [98,99,83].

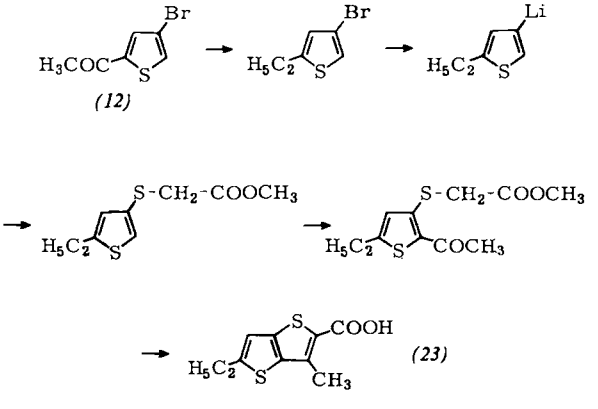
In the chloromethylation of aromatic compounds in the presence of aluminum chloride, diarylmethane derivatives are often formed as by-products. We found that acetophenone and 2-acetylthiophene are partly converted into derivatives of diphenyl- and dithienylmethane on chloromethylation [97].

It is interesting in this connection to note that 5-ethyl-2-acetylthiophene, which gives 5-ethyl-4-chloromethyl-2-acetylthiophene *(21)* in 47 or 76% yield when formaldehyde or paraformaldehyde, respectively, is used under normal conditions, is converted exclusively into bis(2-ethyl-5-acetyl-3-thienyl)methane *(22)* (yield 77%) by the action of chloromethyl methyl ether and an excess of aluminum chloride [100].

2.6. Some Reactions of the Synthesized Products

The blockage of a carbonyl group in derivatives of thiophene and furan permits the easy introduction of a functional group into position 4 of the ring. 4-Bromo-2-acetylthiophene, 4-bromo-2-thiophenecarbaldehyde, and 2-acetyl-4-bromofuran (which is obtained from 2-acetyl-4,5-dibromofuran by elimination of the bromine from the α position [101]) are readily obtainable starting materials for a number of syntheses. In particular, the reduction of the carbonyl group in these compounds, followed by replacement of the bromine in position 4 by lithium, offers a convenient method for the preparation of 5-ethyl- and 5-methyl-3-thiophenecarbaldehyde [102,41], 5-methyl-3-thiophene-





[96] *B. P. Fabričnyj, Ju. B. Volkenštein, V. I. Rogovik, I. B. Karmanova,* and *Ja. L. Goldfarb,* Chim. geterocikličeskich Soedinenij *1965,* 504.

[97] *Ja. L. Goldfarb* and *Ju. B. Volkenštein,* Ž. obšč. Chim. *31,* 616 (1961).

[98] *G. Ogata* and *M. Okano,* J. Amer. chem. Soc. *78,* 5423 (1956).

[99] *I. N. Nazarov* and *A. V. Semenovskij,* Izvest. Akad. Nauk SSSR, Otdel. chim. Nauk *1957,* 972.

[100] *Ja. L. Goldfarb* and *Ju. B. Volkenštein,* Izvest. Akad. Nauk SSSR, Otdel. chim. Nauk *1963,* 738.

[101] *Ja. L. Goldfarb* and *L. D. Tarasova,* Doklady Akad. Nauk SSSR *163,* 1393 (1965).

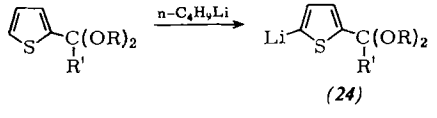
[102] *Ja. L. Goldfarb, M. L. Kirmalova,* and *M. A. Kalik,* Izvest. Akad. Nauk SSSR, Otdel. chim. Nauk *1962,* 701.

carboxylic acid [41], a series of new furan derivatives with a functional group in the β position, *etc.* 5-Ethyl-3-methylthieno[3,2-*b*]thiophene-2-carboxylic acid *(23)* has been prepared from 4-bromo-2-acetylthiophene [103].

3. Metalation of Acetals of the Thiophene and Furan Series; Syntheses on this Basis

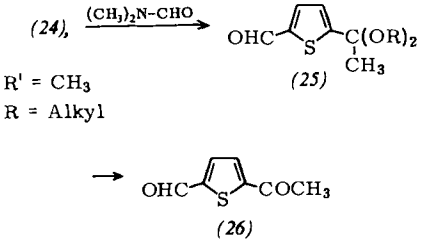
New synthetic paths are opened up by a reversible reaction in which a carbonyl derivative of thiophene or furan is converted in the usual manner into the acetal, which is then treated with an organolithium compound.

In contrast to the reaction of organomagnesium compounds with acetals [104, 105], the acetal group remains unchanged and lithium is introduced into position 5 of the ring. The resulting lithium-substituted acetal *(24)*, which need not be isolated, can be converted into a bifunctional compound [*e.g. (25)*]; the acetal group can, if necessary, be readily changed into an aldehyde or keto group, depending on the starting compound. The special feature of this method is that it permits the preparation of bifunctional thiophene derivatives having similar or different substituents, the synthesis of which is always very difficult, if not practically impossible, by other routes.

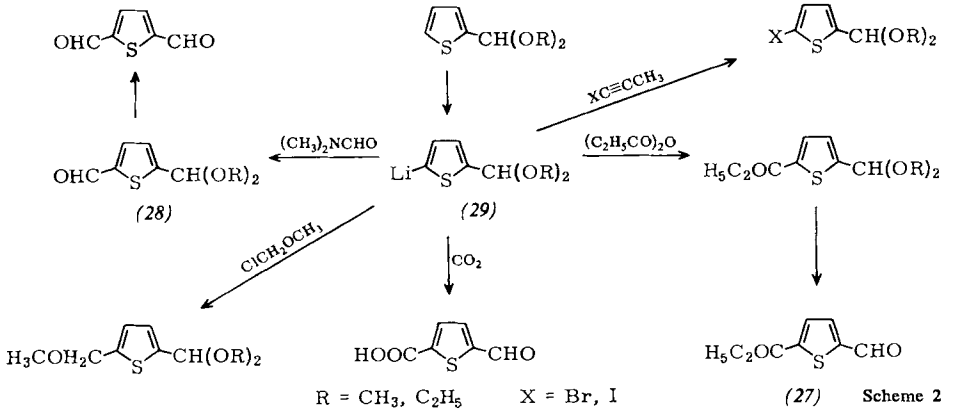


3.1. Syntheses of 2,5-Disubstitution Products

Ring metalation of compounds of the thiophene series containing a carbonyl group protected by acetalization, and subsequent replacement of the lithium with a second carbonyl group by the action of dimethylformamide, was first achieved in 1960 [106]. 5-Formyl-2-acetylthiophene *(26)* was obtained in this way. In this synthesis, the thiophene derivative was metalated by butyllithium exclusively in position 5 of the thiophene ring, as was shown by the oxidation of *(26)* to 5-acetyl-2-thiophenecarboxylic acid [106] and 2,5-thiophenedicarboxylic acid [96].



Some reactions of the acetals of 2-thiophenecarbaldehyde are illustrated in Scheme 2 [96, 107, 108].



Scheme 2

5-Propionyl-2-thiophenecarbaldehyde *(27)* was obtained, not only by the method shown in Scheme 2, but also by the action of dimethylformamide on the diethyl ketal of 5-lithium-2-propionylthiophene [96]. Compound *(27)* is crystalline, m.p. 101 °C, and can be oxidized to the carboxylic acid (proof of structure). On the other hand, a product obtained from 5-chloromethyl-2-propionylthiophene, which was thought to be *(27)*, is a liquid [94, 95].

The syntheses of unsymmetrical bifunctional thiophenes from the monoacetal of thiophene-2,5-dicarbaldehyde *(28)* [109] are particularly important. The acetal group in the monoacetal is not affected during the reduction of the free aldehyde group and its condensation with amines, hydroxylamine, compounds containing active methylene groups, *etc.* (see Section 3).

The Schiff bases *(30)* can be readily reduced to the amino acetals *(31)* by $NaBH_4$. Under the usual conditions these give the *N*-acyl derivatives *(32)*, which form the acylamino aldehydes *(33)* on careful hydrolysis. When *(28)* is heated with malonic ester, the sub-

[103] *Ja. L. Goldfarb* and *V. P. Litvinov*, Izvest. Akad. Nauk SSSR, Otdel. chim. Nauk *1963*, 352.

[104] *A. E. Tschitschibabin* and *S. A. Elgazin*, Ž. russ. fizikochim. Obščestva *46*, 39 (1914); Ber. dtsch. chem. Ges. *47*, 48 (1914).

[105] *A. E. Tschitschibabin* and *S. A. Elgazin*, Ž. russ. fizikochim. Obščestva *46*, 802 (1914).

[106] *Ja. L. Goldfarb* and *Ju. B. Volkenštein*, Izvest. Akad. Nauk SSSR, Otdel. chim. Nauk *1960*, 2238.

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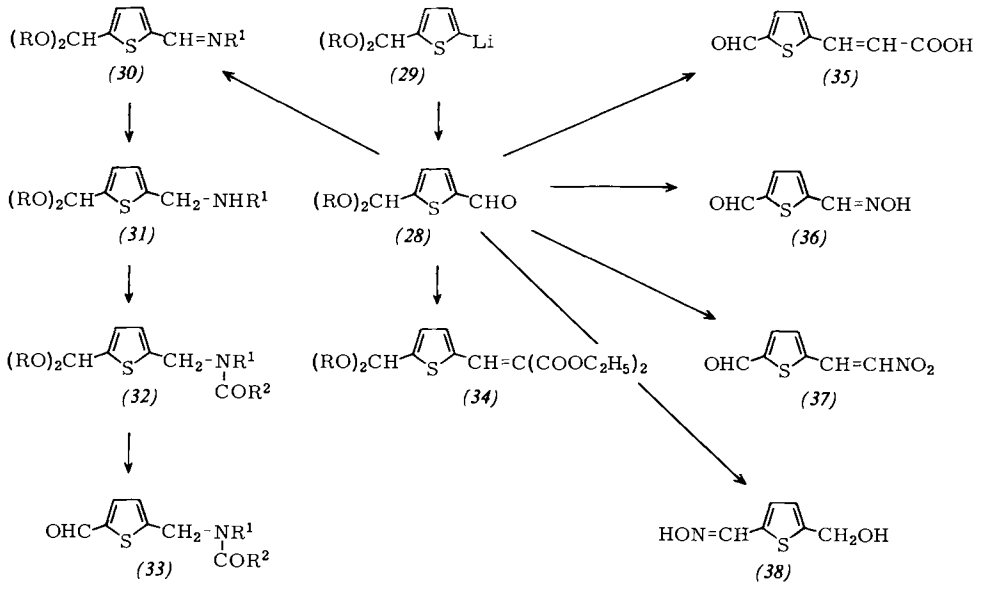
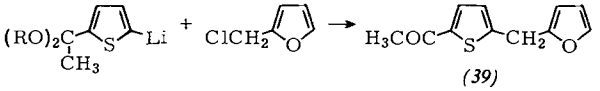
[108] *Ja. L. Goldfarb, B. P. Fabričnyi*, and *V. I. Rogovik*, Izvest. Akad. Nauk SSSR, Ser. chim. *1965*, 515.

[109] *V. I. Rogovik* and *Ja. L. Goldfarb*, Izvest. Akad. Nauk SSSR, Ser. chim. *1963*, 2178.



Scheme 3 $R = C_2H_5$; R^1 = n-C_6H_{13}, cyclo-C_6H_{11}, C_6H_5; $R^2 = CH_3$, C_6H_5

stituted thenylidenemalonic ester *(34)* is formed. The reactions of the monoacetal *(28)* with malonic acid, hydroxylamine, and nitromethane, followed by hydrolysis, lead to *(35)*, *(36)*, and *(37)* respectively. The oxime of the hydroxymethyl aldehyde *(38)* can be obtained by reduction of *(28)* to the alcohol. 5-Furfuryl-2-acetylthiophene *(39)* [110] has been synthesized by the reaction of the diethyl ketal of 5-lithium-2-acetylthiophene with 2-chloromethylfuran.

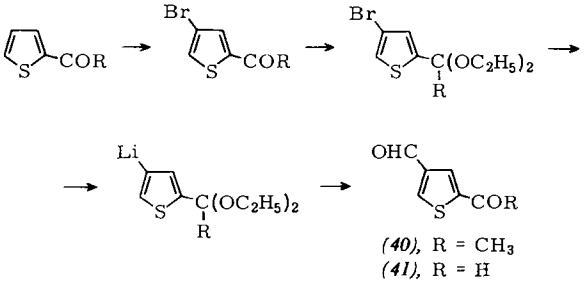


(39)

3.2. Syntheses of 2,4-Disubstitution Products

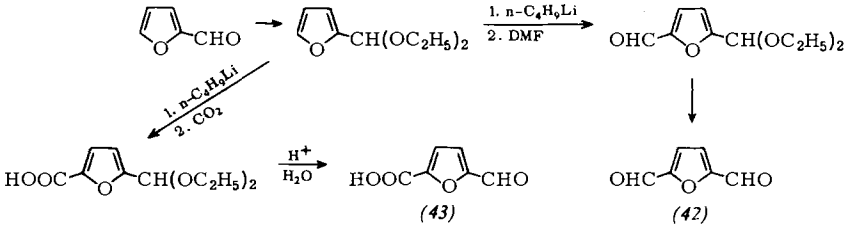
By combination of the two blocking methods and replacement of the β′-bromine atom in the thiophene acetal by lithium, we obtained 4-formyl-2-acetylthiophene *(40)* [106] and 2,4-thiophenedicarbaldehyde *(41)* [41].

Thus in the thienyl ketones, it is possible to direct bromine into the side chain (under normal conditions), into position 4 (by complex formation with an excess of aluminum chloride), or into position 5 (by bromination of the ketal).



(40), R = CH_3
(41), R = H

The blockage of a carbonyl group by acetalization also increases the range of methods available for the preparation of symmetrical and unsymmetrical bifunctional furan compounds. 2,5-Furandicarbaldehyde *(42)* and 5-formyl-2-furancarboxylic acid *(43)* were synthesized as early as 1962 [112].



(43) *(42)*

It should be finally recalled that the acetalization of the carbonyl group also permits the bromination of the thienyl ketones in position 5 [111] (see Section 2.1 [29]).

The compounds *(45)*–*(48)* in Scheme 4 have been prepared [113] from the acetal of 4,5-dibromofurfural *(44)*.

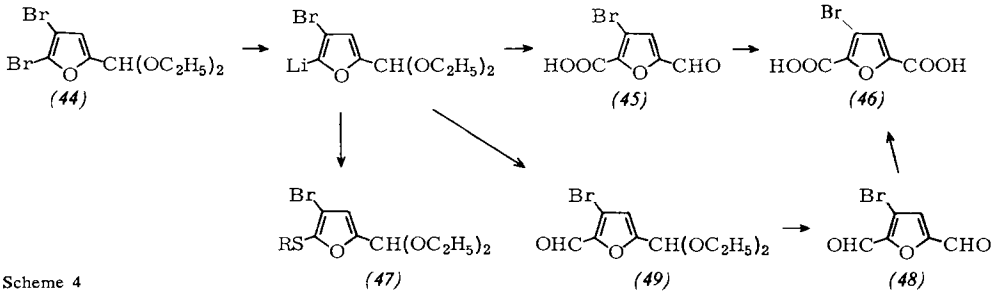
The monoacetal of 3-bromo-2,5-furandicarbaldehyde *(49)* is particularly important for the synthesis of unsymmetrical bifunctional compounds.

[110] *Ja. L. Goldfarb* and *Ja. L. Danjuševskij*, Izvest. Akad. Nauk SSSR, Otdel. chim. Nauk *1963*, 540.

[111] *V. I. Rogovik* and *Ja. L. Goldfarb*, Chim. geterocikličeskich Soedinenij *1965*, 657.

[112] *Ja. L. Goldfarb* and *V. I. Rogovik*, Author's license (USSR) 184877 (July 5, 1962).

[113] *L. D. Tarasova* and *Ja. L. Goldfarb*, Izvest. Akad. Nauk SSSR, Ser. chim. *1965*, 2013.

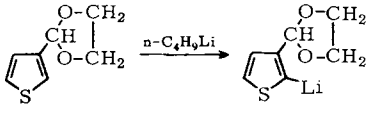


Scheme 4

3.3. Further Applications of Protection by Acetal Formation

The value of protection by acetal formation is also illustrated by the following examples. Whereas the synthesis published in 1967 for the preparation of 5-formyl-2-thiophenecarboxylic acid from 2-methylthiophene involves seven steps [114], we synthesized the acid in two steps from 2-thiophenecarbaldehyde. The first step is the acetalization, while the second includes metalation, reaction with CO_2, and hydrolysis of the acetal; the intermediates need not be isolated [109].

Gronowitz et al. [115] used the method of protection by acetal formation in the metalation of 3-thiophenecarbaldehyde with *n*-butyllithium; the adjacent free α position of the thiophene ring reacts in this case.



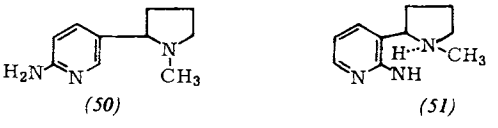
Pastour, *Savalle*, and *Emery* [116] obtained 2,3-thiophenedicarbaldehyde with the aid of this reaction. *Gronowitz* and *Bugge* [117] treated the acetals of 3-bromo-2-thiophenecarbaldehyde and of 4-bromo-3-thiophenecarbaldehyde with *n*-butyllithium and then with tributylboron to obtain 2- and 4-formyl-3-thiopheneboronic acids respectively. The method was recently used for the synthesis of organosilicon derivatives of 2-acetylthiophene and of 2-thiophenecarbaldehyde [118, 119], and the authors published their results as original work, though our findings had been published and abstracted some time before.

Similar investigations have also been reported in the furan series. In 1966 *Pastour* and *Plantard* independently synthesized 2,5-furandicarbaldehyde [120]. *Thames* and *Odom* [121] obtained 5-formyl-2-furancarboxylic acid by the acetalization method, which they also used in conjunction with metalation to obtain 5-benzoylfurfural, [5-D]-furfural, and some organosilicon derivatives of furfural. The method has recently been used for the synthesis of 2-formyl-3-furancarboxylic acid [122]. Finally, *Paulmier* and *Pastour* [123] have prepared 2,5-selenophenedicarbaldehyde and 5-formyl-2-selenophenecarboxylic acid by this method.

4. Conclusions

Two methods of blockage of the carbonyl group have been discussed, *i.e.* complex formation with aluminum chloride and acetalization. The primary purpose of blockage in this case is to provide the conditions necessary for the establishment of a new reaction center, but it should also protect the functional group against attack.

Blockage in this sense can obviously also be applied to other functional groups and be effected by processes other than acetalization and complex formation. The use of complexes involving the hetero atom and of chelates as intramolecularly blocked compounds would be particularly interesting. Compounds with an intramolecular hydrogen bond would also belong to this group. One example is the difference in the reactions of alkyl halides with the isomeric α-*(51)* and α'-aminonicotines *(50)* [124]. *(50)* is alkylated exclusively,



(50) *(51)*

or mainly, on the pyrrolidine nitrogen, whereas *(51)*, in which this nitrogen is involved in hydrogen bonding [125], reacts mainly at the pyridine nitrogen under comparable conditions.

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Translated by Express Translation Service, London.

[114] *V. N. Gogte, B. D. Tilak, K. N. Gudekar*, and *M. B. Sahasrabudhe*, Tetrahedron *23*, 2443 (1967).

[115] *S. Gronowitz, B. Gesterlom*, and *B. Matiasson*, Ark. Kemi *20*, 407 (1963).

[116] *P. Pastour, P. Savalle*, and *P. Emery*, C.R. hebd. Séances Acad. Sci. *260*, 6130 (1965).

[117] *S. Gronowitz* and *A. Bugge*, Acta chem. scand. *19*, 1271 (1965).

[118] *S. F. Thames* and *J. E. McCleskey*, J. heterocyclic Chem. *3*, 104 (1966).

[119] *S. F. Thames* and *J. E. McCleskey*, J. heterocyclic Chem. *4*, 146 (1967).

[120] *P. Pastour* and *C. Plantard*, C.R. hebd. Séances Acad. Sci. (C) *262*, 1539 (1966).

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[123] *C. Paulmier* and *P. Pastour*, Bull. Soc. chim. France *1966*, 4021.

[124] *Ja. L. Goldfarb* and *M. S. Kondakova*, Izvest. Akad. Nauk SSSR, Otdel. chim. Nauk *1950*, 418.

[125] *Ja. L. Goldfarb, M. S. Kondakova*, and *D. N. Šigorin*, Izvest. Akad. Nauk SSSR, Otdel. chim. Nauk *1956*, 336.

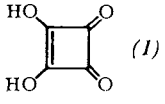
Cyclobutenediylium Dyes

BY H.-E. SPRENGER AND W. ZIEGENBEIN [*]

In agreement with the aromaticity and electrophilic behavior of squaric acid, a cyclobutenediyliumtetroxide ion is formulated as a limiting form of the squarate dianion. These views are confirmed by the structure of a series of new compounds that are readily obtainable from squaric acid or its derivatives, and most of which are deeply colored. The compounds contain the cyclobutenediyliumdioxide grouping as the chromophore, and form a new class of dyes, for which the name cyclobutenediylium dyes is proposed.

1. Introduction

Squaric acid *(1)* is a strong dibasic acid, which is thermally very stable and fairly stable toward oxidizing agents. The preparation and properties of its simple derivatives such as esters, amides, and halides are



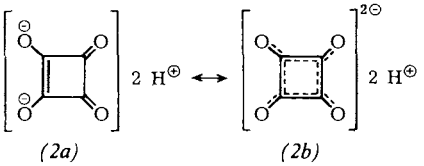
(1)

described in a recent review [11]. Condensations of squaric acid and its derivatives with nucleophilic compounds have recently been reported [2–6], and these reactions form the subject of the present article.

2. Limiting Structures of the Squarate Dianion

The readiness to react with nucleophiles points to limiting forms that would express the electrophilic reactivity of the squarate ion. Limiting structures of this nature have not previously been considered.

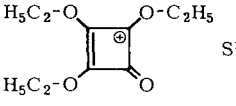
West et al. explained the aromatic character and the equivalence of the four oxygen atoms in the squaric acid molecule on the basis of resonance between *(2a)* and *(2b)* [7–9]:



(2a) *(2b)*

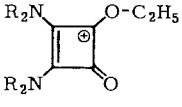
However, this formulation gives no indication of the electrophilic behavior of squaric acid. The resonance should therefore involve further limiting structures including carbonium ions. This is supported by some reactions of the esters and diamides of squaric acid [1].

Thus we have found that diethyl squarate can be smoothly ethylated with triethyloxonium hexachloroantimonate to give a colorless, salt-like, extremely hygroscopic product, to which the structure *(3)* can be assigned [10].



(3)

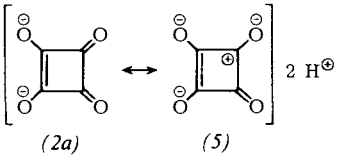
Diamides are converted in the same manner into salt-like, nonhygroscopic compounds *(4)*.



(4)

R_2N = Morpholino, Piperidino, Pyrrolidino

Ethylation to give *(3)* obviously depends on the polarization of a carbonyl group of the cyclobutenedione system in the diethyl squarate. Consideration of these observations would lead to the limiting forms *(2a)* and *(5)*.



(2a) *(5)*

However, structure *(5)* is in conflict with the aromatic properties of squaric acid, since only three of the oxygen atoms would be equivalent. We therefore propose a resonance between *(2a)* and the cyclo-

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[1] *G. Maahs* and *P. Hegenberg*, Angew. Chem. *78*, 927 (1966); Angew. Chem. internat. Edit. *5*, 888 (1966).

[2] *A. Treibs* and *K. Jacob*, Angew. Chem. *77*, 680 (1965); Angew. Chem. internat. Edit. *4*, 694 (1965).

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[5] *H.-E. Sprenger* and *W. Ziegenbein*, Angew. Chem. *78*, 937 (1966); Angew. Chem. internat. Edit. *5*, 894 (1966).

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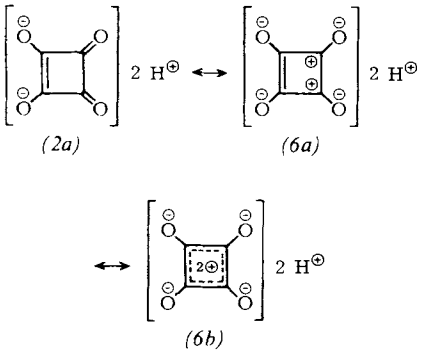
[8] *R. West* and *D. L. Powell*, J. Amer. chem. Soc. *85*, 2577 (1963).

[9] *M. Ito* and *R. West*, J. Amer. chem. Soc. *85*, 2580 (1963).

[10] *H.-E. Sprenger*, unpublished.

butenediyliumtetroxide limiting structures *(6a)* and *(6b)*, which may be thought of as resulting from the inclusion of both carbonyl groups of the squaric acid in the resonance system. These formulas express both the aromaticity and the electrophilicity of squaric acid.

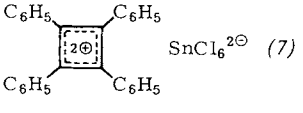


(2a) *(6a)* *(6b)*

Similar bonding and charge distributions occur in the anions of very stable inorganic acids. Thus the equivalence of the oxygen atoms in the phosphate, sulfate, and perchlorate ions can be explained by the participation of limiting structures in which the central atom carries one or more positive charges. These positive central atoms correspond to the doubly positive cyclobutenediylium skeleton of squaric acid.

The same cyclobutenediyliumtetroxide limiting structure of the squarate dianon follows from a comparison with cyanine dyes, which leads to contradictions, since the resonance in the cyanine dye molecule is best described by an alternating charge distribution along the C–C chain [11].

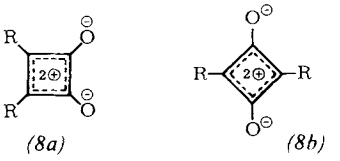
Finally, according to *Hückel*, a cyclobutene ring carrying two positive charges should be a homolog of ethylene, and should possess aromatic properties [12]. Cyclobutenediylium compounds have recently been prepared by *Freedman* and *Frantz jr.* [13]. Thus, the deep red tetraphenylcyclobutenediylium hexachlorostannate *(7)* is surprisingly stable in dry air and is relatively stable in general.



(7)

3. Condensations of Squaric Acid and its Derivatives

According to the views presented in Section 2, squaric acid and its esters should undergo condensations with nucleophilic compounds. This prediction has been confirmed by the synthesis of a number of new compounds, most of which are deeply colored. These compounds were prepared in our research laboratories [4–6], and independently by *Treibs* and *Jacob* [2,3], from squaric acid and nucleophilic compounds. The previously unknown chromophores in these dyes are the cyclobutenediyliumdioxide groups *(8a)* or *(8b)* [6].



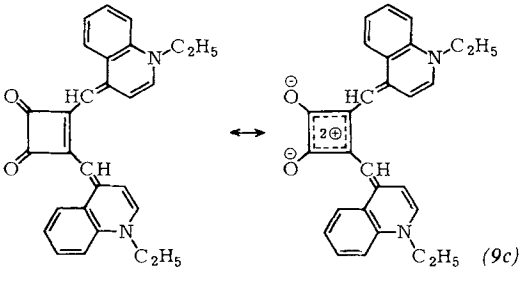
(8a) *(8b)*

Organic dyes are generally characterized by a polymethine structure with alternating charges [11]. This is not so in the compounds prepared by *Treibs* and by our team. On the contrary, instead of a single positive carbon atom in the cyanine chain, these dyes contain the cyclobutenediyliumdioxide group as a doubly positive charge center and are therefore to be considered as a new class of dyes.

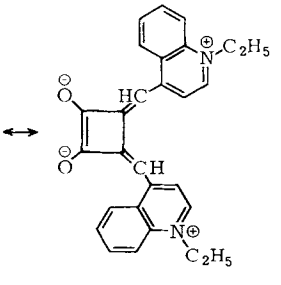
3.1. Condensations with Esters of Squaric Acid

We have found that squarates condense smoothly with compounds having acidic hydrogen atoms on carbon in alcoholic solution in the presence of sodium alkoxide. Pyridinium and benzothiazolium iodides bearing a methyl group in the 2- or 4-position, and an ethyl group on the N atom, were used as model compounds. These salts readily lose hydrogen iodide to form reactive bases, which react with esters of squaric acid to give colored products *(9)* that have been found to be derivatives of the unknown cyclobutenedione, the *o*-quinone of cyclobutadiene [6] (see Table 1).

Compounds *(9a)–(9e)* are not very soluble in alcohols or ethers, but dissolve more readily in high-boiling polar solvents such as dimethylformamide and benzonitrile. The deep color of all the new compounds can be explained by the contribution of a cyclobutenediylium limiting form to the resonance hybrid:



(9c)

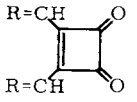


[11] *S. Dähne* and *D. Leupold*, Angew. Chem. *78*, 1029 (1966); Angew. Chem. internat. Edit. *5*, 984 (1966).

[12] *M. P. Cava* and *M. J. Mitchell* in: Cyclobutadiene and Related Compounds. Academic Press, New York, London 1967, p. 122.

[13] *H. H. Freedman* and *A. M. Frantz jr.*, J. Amer. chem. Soc. *84*, 4165 (1962).

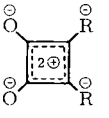
Table 1. Colored products *(9)* obtained from esters of squaric acid and *N*-ethyl nitrogen bases.



(9)

	R	M.p. (°C)	Yield (%)
(a)	*N*-Ethyl-1,4-dihydro-4-pyridylidene	328 (decomp.)	35
(b)	*N*-Ethyl-1,2-dihydro-2-pyridylidene	218 (decomp.)	16
(c)	*N*-Ethyl-1,4-dihydro-4-quinolylidene	257 (decomp.)	68
(d)	*N*-Ethyl-1,2-dihydro-2-quinolylidene	320	55
(e)	*N*-Ethyl-2,3-dihydro-2-benzothiazolylidene	274 (decomp.)	28

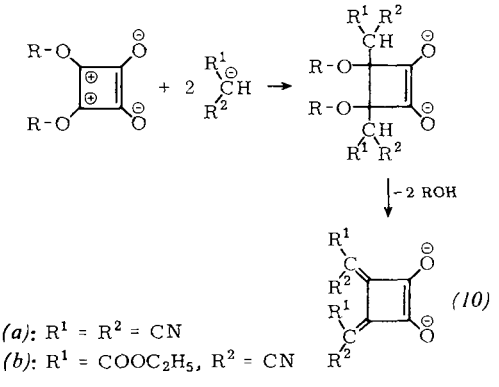
Esters of squaric acid react with compounds such as malononitrile in the presence of alkali metal alkoxide to form deep yellow salts *(10)* [6], which are soluble in water and remain unchanged on heating to 360 °C. The yields of *(10a)–(10c)* are 93, 89, and 97% respectively.



(10)

(a), $R^{\ominus} = {}^{\ominus}C(CN)_2$
(b), $R^{\ominus} = {}^{\ominus}C(COOC_2H_5)CN$
(c), $R^{\ominus} = {}^{\ominus}N{-}CN$

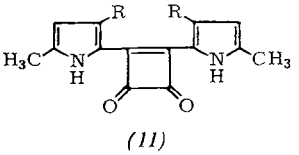
The smooth, ready formation of compounds *(10)* can be formulated as an addition of the nucleophile to the cyclobutenediyliumdioxide form of the squarate. The final product is then formed by elimination of alcohol. The reaction thus corresponds to an ester condensation.



(a): $R^1 = R^2 = CN$
(b): $R^1 = COOC_2H_5$, $R^2 = CN$

3.2. Condensations with Squaryl Diacetate

Treibs and *Jacob* [3] also obtained 1,2-derivatives of cyclobutenedione *(11a)* and *(11b)* (m.p.'s 245 °C and 205 °C; yields 45% and 19%) from squaryl diacetate and 2-methyl- or 2,4-dimethylpyrrole in acetic anhydride. 1,3-Derivatives of cyclobutenediyliumdioxide were also isolated as by-products.



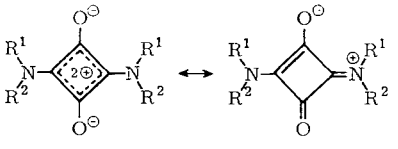
(11)

(a), R = H
(b), R = CH_3

3.3. Condensations with Squaric Acid

The reaction of squaric acid with excess secondary amines does not lead to diamides of squaric acid. Instead, colorless to pale yellow stable compounds *(12)* of high melting point are formed, presumably by way of hydrosquarates [10, 14]. These products form a new class of intramolecular salts, and are derived from 1,3-bisaminocyclobutenediyliumdioxides (see Table 2).

Table 2. Intramolecular salts *(12a)–(12d)* from squaric acid and secondary amines, and *(13a)–(13g)* from squaric acid and aromatic amines.



(12), (13)

	R^1	R^2	M.p. (°C)	Yield (%)
(12a)	$-(CH_2)_5-$		281–283	60
(12b)	$-(CH_2)_2-O-(CH_2)_2-$		> 340	72
(12c)	$(-CH_2)_4-$		287–293	60
(12d)	$-(CH_2)_2-NCH_3-(CH_2)_2-$		233–236	77
(13a)	C_6H_5	CH_3	192	48
(13b)	C_6H_5	H	> 360	87
(13c)	C_6H_5	C_6H_5	360 (decomp.)	66
(13d)	α-Naphthyl	H	340	85
(13e)	β-Naphthyl	H	313	63
(13f)	1-Anthraquinonyl	H	> 360	80
(13g)	2-Anthraquinonyl	H	353 (decomp.)	96

Similar condensation products *(13)* have been prepared from squaric acid and aromatic amines [14, 15] (see Table 2).

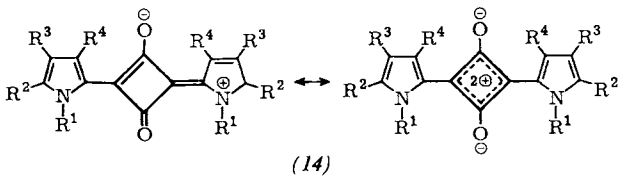
Compounds *(13)* were prepared by azeotropic removal of the water of reaction in butanol/benzene mixtures. These stable, high-melting substances are pale yellow to deep brown, depending on the nature of the aromatic substituent. Although not involved in the resonance, the aromatic group has a color-deepening effect. This leads one to assume that reaction occurs *ortho* or *para* to the amino group, as is the case with other reactions of anilines. However, condensation on the phenyl substituent of the amino group can be definitely ruled out on the basis of ^1H–NMR studies.

In the case of *N,N*-dialkyl aromatic amines or nucleophilic tertiary amines having an enamine character, on the other hand, condensation should occur on the substituents of the amino group. The products should be phenylogs or vinylogs of the 1,3-diaminocyclobutenediyliumdioxides described above. *Treibs* and *Jacob* actually obtained deep blue, high-melting 1,3-dipyrrolylcyclobutenediyliumdioxides *(14)* from squaric acid and reactive pyrroles; as expected, these products are vinylogs of 1,3-diaminocyclobutenediyliumdioxides [2, 3] (see Table 3).

[14] *G. Manecke* and *J. Gauger*, Tetrahedron Letters *1967*, 3509; *1968*, 1339.

[15] *H.-E. Sprenger*, German Pat. Appl. C 41650 IVb/120 (March 1, 1967), Chem. Werke Hüls.

Table 3. 1,3-Dipyrrolylcyclobutenediyliumdioxides *(14)*.

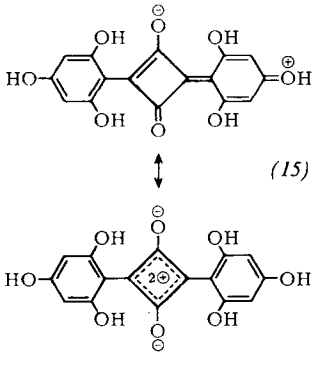


(14)

	R^1	R^2	R^3	R^4	M.p. (°C)	Yield (%)
(a)	H	CH_3	C_2H_5	CH_3	265	90
(b)	H	CH_3	H	CH_3	240–250	75
(c)	CH_3	CH_3	H	CH_3	242	79
(d)	H	CH_3	$CO_2C_2H_5$	CH_3	296	60
(e)	H	CH_3	$COCH_3$	CH_3	299	76

The condensation is carried out in ethanol or acetic acid. *Treibs* and *Jacob* assigned the IR band at 1640 cm^{-1} to a vinylogous carboxylate grouping. It appears to us that the spectroscopic findings agree more closely with the presence of a cyclobutenediylium moiety.

In a similar manner, these authors readily obtained compounds of the same type by reaction of nucleophilic phenols, *e.g.* phloroglucinol. The wine-red, very stable compound *(15)* melts at 340–345 °C, and is obtained in yields of 67%.

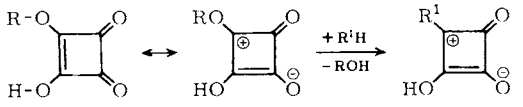


(15)

Independently of *Treibs*, we found that squaric acid reacts under surprisingly mild conditions with a number of classes of nucleophilic compounds in the absence of catalysts. Condensation takes place in a butanol/benzene mixture, so that the water formed can be removed azeotropically as the reaction proceeds. The resulting high-melting, extremely stable dyes, which are 1,3-derivatives of cyclobutenediyliumdioxide, are obtained as crystalline solids, usually in an analytically pure state, toward the end of the reaction or after cooling.

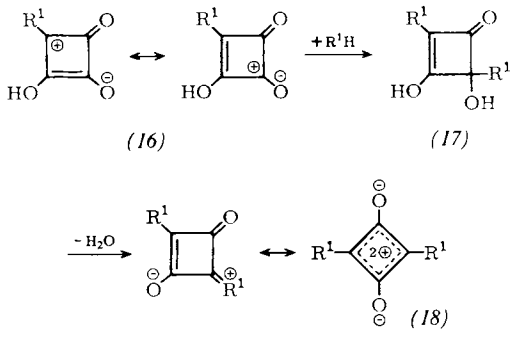
The dyes *(18)* are not very soluble in alcohols or ethers, but dissolve more readily in high-boiling polar solvents such as DMF, benzonitrile, or nitrobenzene. They dissolve in cold concentrated sulfuric acid, with lightening of the color, probably because of salt formation; however, they are reprecipitated on addition of water. The compounds are not very stable toward bases, and are generally decomposed with formation of brown products. Strong reducing agents, such as rongalite solutions, decolorize the dye solutions. A strong IR absorption band between 1500 and 1630 cm^{-1}, which we regard as evidence of a cyclobutenediyliumdioxide structure, is common to all compounds.

The formation of these dyes can be explained as follows. It is known from investigations by *Cohen et al.* that when squaric acid is heated in alcohols it forms a half-ester [16], which probably reacts with the nucleophilic compound R^1H, subsequent elimination of alcohol leading to the formation of the 1:1 reaction



(16)

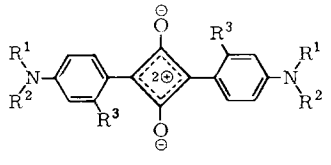
product *(16)* containing one electrophilic C atom [17]. A further molecule of nucleophile R^1H can add to this remaining electrophilic center; dehydration of *(17)* then yields the final product *(18)*.



(16) *(17)* *(18)*

To obtain phenylogs of the 1,3-diaminocyclobutenediyliumdioxides, we allowed squaric acid to react with *N,N*-dialkylanilines. Stable 1,3-bis(dialkylaminophenyl)cyclobutenediyliumdioxides *(18a)–(18e)* were formed in good yields [5] (see Table 4). In agreement with our concepts these products are deep blue. Furthermore, we condensed nucleophilic quinaldine, benzothiazole, and benzoselenazole bases with squaric acid to obtain vinylogous 1,3-diaminocyclobutenediyliumdioxides *(18f)*, *(18g)*, and *(18h)* [6] (m.p.'s 320 °C, 300 °C, and 286 °C; yields 31%, 80%, and 42%, resp.).

Table 4. Dyes with cyclobutenediyliumdioxide structure *(18a)–(18e)*.



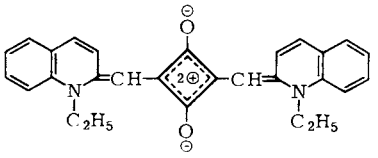
(18a)-(18e)

	R^1	R^2	R^3	M.p. (°C)	Yield (%)
(a)	CH_3	CH_3	H	276	60
(b)	$(CH_2)_2OH$	$(CH_2)_2OH$	H	230 (decomp.)	6
(c)	$-(CH_2)_2-O-(CH_2)_2-$		H	250	38
(d)	$CH_2-C_6H_5$	$CH_2-C_6H_5$	H	274–276 (decomp.)	27
(e)	CH_3	CH_3	OH	303 (decomp.)	98

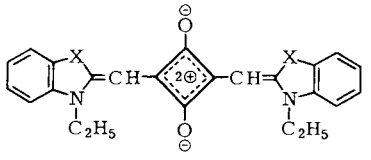
The deeply colored, thermally stable products can be distinguished from the corresponding 1,2 compounds, which can be obtained from squarate esters, by thin layer chromatography.

[16] *S. Cohen* and *S. G. Cohen*, J. Amer. chem. Soc. *88*, 1533 (1966).

[17] *A. Treibs*, private communication; see also *A. Treibs* and *K. Jacob*, Liebigs Ann. Chem. *712*, 123 (1968).

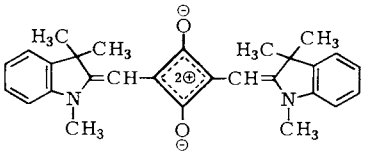


(18f)



(18g), X = S
(18h), X = Se

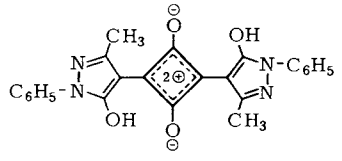
A similar vinylogous 1,3-diaminocyclobutenedioxide derivative *(18i)* was obtained from squaric acid and Fischer base[6] (m.p. 301.5 °C; yield 92%). The deep



(18i)

blue stable dye was obtained independently by *Treibs* and *Jacob*, though by a different route[3]. The identity of the two products was verified by thin layer chromatography.

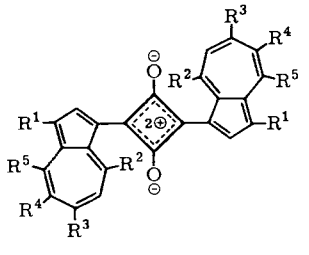
We also condensed 3-methyl-1-phenyl-5-pyrazolone with squaric acid. The product was a yellow-red dye *(18k)*, which is soluble in alcohols and crystallizes from the solutions as long needles[10] (m.p. 170 °C; yield 54%).



(18k)

Azulenes, which are nucleophilic in position 1 or 3, react similarly with squaric acid to give high yields of thermally stable, 1,3-cyclobutenediyliumdioxides *(18l)–(18n)* (see Table 5). These compounds are deep blue-green in solution, and separate out as green crystals with a metallic luster[4]. It is interesting to note that in this case a hydrocarbon is sufficiently nucleophilic to react.

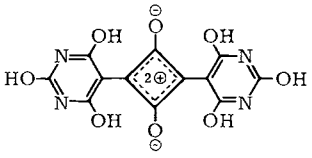
Table 5. Dyes with cyclobutenediylium structure *(18l)–(18n)*.



(18l)-(18n)

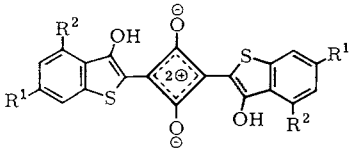
	R^1	R^2	R^3	R^4	R^5	M.p. (°C)	Yield (%)
(l)	H	H	H	H	H	240–245 (decomp.)	90
(m)	CH_3	CH_3	H	$CH(CH_3)_2$	H	245–250 (decomp.)	80
(n)	H	CH_3	CH_3	H	CH_3	> 350	90

An analogous product was obtained from barbituric acid and squaric acid. The deep red dye *(18o)* is insoluble in all common solvents[10] (m.p. 330 °C; yield 72%).



(18o)

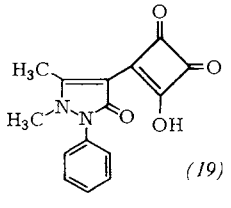
No dye is formed in the reaction of indoxyl with squaric acid. The investigation of the product obtained has not yet been completed[10]. On the other hand, 3-hydroxybenzothiophene gives deep violet, bronze-colored crystals *(18p)* (m.p. 290 °C; yield 12%). From 6-chloro-3-hydroxy-4-methylbenzothiophene the compound *(18q)* is obtained as bronze colored crystals [m.p. 326 °C (decomp.); yield 35%][10]. *(18p)* and



(18p), $R^1 = R^2 = H$
(18q), $R^1 = Cl$, $R^2 = CH_3$

(18q) are slightly soluble in dimethylformamide, but are otherwise insoluble in the usual solvents, even in concentrated sulfuric acid.

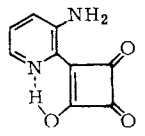
Mention should also be made of some other products obtained by reaction of squaric acid with nucleophiles. An attempt to condense antipyrine (which is nucleophilic in position 4) with squaric acid did not yield the expected 1,3-cyclobutenediyliumdioxide, since only one antipyrine molecule combined with squaric acid to form *(19)*[18] (m.p. 238 °C; yield 56%). The bright yellow crystalline product is formed on azeotropic removal of the water formed in the reaction.



(19)

3-Aminopyridine reacts likewise with squaric acid to give a deep yellow, sparingly soluble compound, for which we propose the structure *(20)*[10] [m.p. 324 °C (decomp.); yield 91%]. The deep yellow color points to ring condensation of the 3-aminopyridine with the squaric acid. Owing to the low solubility of the compound, its NMR spectrum could not be recorded.

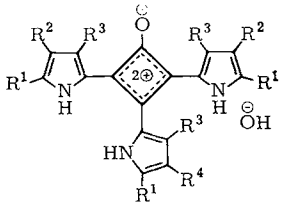
[18] *H.-E. Sprenger*, German Pat. Appl. C 39587 IVd/12p (July 12, 1966), Chem. Werke Hüls.



(20)

On condensation of squaric acid with ethyl 2,4-dimethyl-3-pyrrolecarboxylate *Treibs* and *Jacob* obtained equal quantities of the cyclobutenediyliumdioxide dye and a bright yellow compound to which they assigned the structure of a 3:1-condensation product *(21a)* [3] (see Table 6).

Table 6. Condensation products *(21a)*—*(21c)* from squaric acid and pyrrole derivatives.

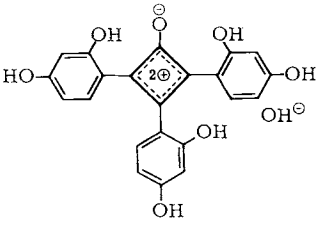


(21)

	R^1	R^2	R^3	R^4	M.p. (°C)	Yield (%)
(a)	CH_3	$CO_2C_2H_5$	CH_3	$CO_2C_2H_5$	130—135	15
(b)	CH_3	$CO_2C_2H_5$	CH_3	C_2H_5	185—188 (decomp.)	93 [a]
(c)	CH_3	$CO_2C_2H_5$	H	$CO_2C_2H_5$	266—268 (decomp.)	79

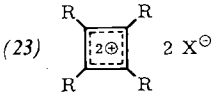
[a] Crude product.

However, the compounds are not very stable, since the third pyrrole ring is readily split off by electrophilic reagents, with regeneration of the 1,3-bispyrrolylcyclobutenediyliumdioxide. *Treibs* and *Jacob* also obtained a 3:1 condensation product from resorcinol and squaric acid under more vigorous conditions. As in the case of the pyrrole, however, the resulting compound *(22)* (m.p. 273–274 °C; yield 24%) is unstable, and readily loses resorcinol to form the 1,3-derivative [3].



(22)

It should in principle also be possible to prepare 1,2,3,4-tetrasubstituted cyclobutenediylium derivatives having the formula *(23)* from squaric acid and nucleophilic compounds.



(23)

Attempts to do so have been made both by *Treibs* [17] and by our own group, but so far without success.

We are very grateful to Prof. Becher of the Universität Münster and to Dr. Böhm-Gössl, Dr. Frenzel, and G. Peitscher of Chemische Werke Hüls AG for the recording and discussion of the spectra.

We thank the Management of the Company, and particularly Prof. H. Hellmann, for their support of this work and for permission to publish it.

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COMMUNICATIONS

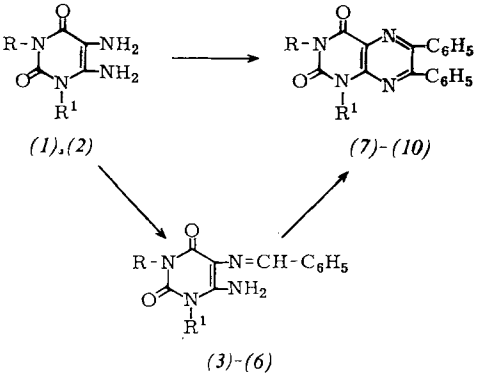
A New Pteridine Synthesis [**]

By *W. Pfleiderer* and *H.-U. Blank* [*]

Traube [1] reported that 7-benzyl-8-phenylpurines are obtained by the action of 2 molecular equivalents of benzaldehyde on 4,5-diaminopyrimidines. However, his 7-benzyl-8-phenyltheophylline was not identical with the substance obtained by us by cyclization of 4-benzylamino-5-benzylideneamino-1,3-dimethyluracil [2] or by benzylation of 8-phenyltheophylline.

We have found that purines are not formed on treatment of the 4,5-diaminopyrimidine *(1)* or *(2)* with 2 molecular equivalents of benzaldehyde or of the readily accessible 4-amino-5-benzylideneaminopyrimidines *(3)*—*(6)* with 1 molecular equivalent of benzaldehyde, in each case at 180 °C; instead, the 6,7-diphenylpteridine derivatives *(7)*—*(10)* are obtained. The reaction course is not completely homogeneous, but pteridines always form the main product and can be isolated by fractional crystallization.

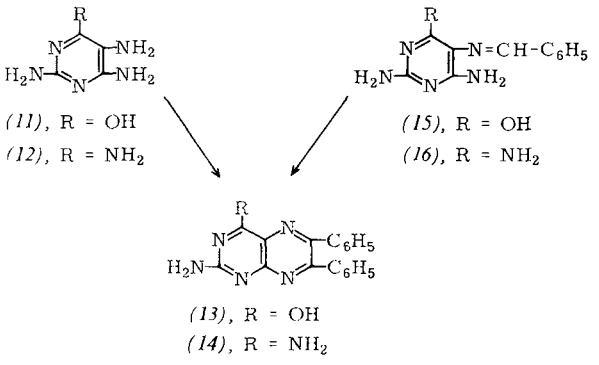
2,4,5-Triamino-6-pyrimidinol *(11)* or its 5-benzylidene derivative *(15)* similarly affords the 6,7-diphenylpterin *(13)* in 53% yield, but *(12)* or *(16)* undergoes an obscure reaction to afford a difficultly separable mixture of many products, in



(1),*(2)* *(7)*-*(10)* *(3)*-*(6)*

Starting Material	Time (h)	Product	R	R^1	Yield (%)	M.p. (°C)	Lit. — m.p. (°C)
(1)	3	*(7)*	CH_3	CH_3	33	227—232	231—232 [3]
(2)	4	*(8)*	H	CH_3	60	270—272	278—280 [4]
(3)	3	*(7)*	CH_3	CH_3	47	230—232	231—232 [3]
(4)	3	*(8)*	H	CH_3	65	276	278—280 [4]
(5)	4	*(9)*	CH_3	H	62	304—305	307 [5]
(6)	5	*(10)*	H	H	51	316—323	315—322 [6]

which the presence of 2,4-diamino-6,7-diphenylpteridine *(14)* could be detected and its identity proved only by chromatography.



(11), R = OH
(12), R = NH_2

(15), R = OH
(16), R = NH_2

(13), R = OH
(14), R = NH_2

It can be assumed that in the new pteridine synthesis 4-amino-5-benzylideneaminopyrimidines and then the 4,5-bis-benzylideneaminopyrimidines are first formed, and that the latter, which cannot be isolated, are stabilized by valence isomerization and subsequent dehydrogenation with formation of the pteridine ring system. This assumption is supported by the corresponding valence isomerizations of double Schiff's bases of 1,2-diamines[7].

1-Methyl-6,7-diphenyllumazine (8):

4,5-Diamino-3-methyluracil (0.8 g) *(2)* is heated with benzaldehyde (1.2 g) for 4 h at 180 °C. The mixture is then cooled, treated with ethanol (10 ml), set aside for a day, and subsequently filtered under suction; the crystalline mass recovered is then recrystallized from ethanol. Yield: 1.0 g of colorless needles.

3-Methyl-6,7-diphenyllumazine (9):

4-Amino-5-benzylideneamino-1-methyluracil (0.6 g) *(5)* is heated with benzaldehyde (0.4 g) for 4 h at 180 °C. The mixture is cooled, treated with ethanol (5 ml), set aside for 2 days, and filtered; the solid is then recrystallized from ethanol. Yield: 0.5 g of small colorless needles.

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[**] Part 35 of Pteridines. – Part 34: *W. Pfleiderer, J. W. Bunting, D. D. Perrin*, and *G. Nübel*, Chem. Ber. *101*, 1072 (1968).

[1] *W. Traube* and *W. Nithak*, Ber. dtsch. chem. Ges. *39*, 227 (1906).

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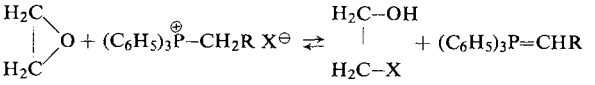
Wittig Reactions with the Aid of Ethylene Oxide

By *J. Buddrus*[*]

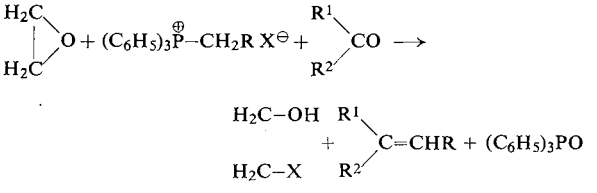
In the presence of some catalysts, epoxides behave as strong bases[1–3]. They remove hydrogen halide from haloforms, being converted in the process into halo-alcohols, while the dihalocarbene and olefins form α,α-dihalocyclopropanes. Soluble halides such as quaternary ammonium[1] and phosphonium[4] halides are suitable catalysts.

Epoxides also remove hydrogen halide from phosphonium salts. Ethylene oxide *(1)* and an alkyltriphenylphosphonium halide *(2)* enter into equilibrium with the 2-haloethanol *(3)* and the alkylidenetriphenylphosphorane *(4)*.

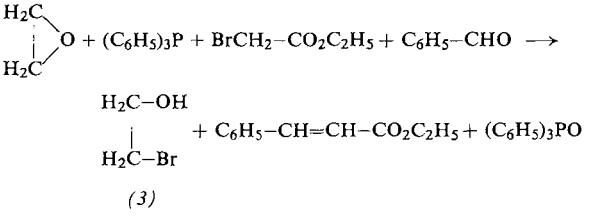


(1) *(2)* *(3)* *(4)*

The phosphorane *(4)* can be isolated in some cases (R = CO_2R'), and in others can be recognized by its color (R = C_6H_5, red). Conversely, the compounds *(3)* (X = Br) and *(4)* (R = C_6H_5) react to yield *(1)* and *(2)*. If at the beginning of the experiment an aldehyde or ketone is added that reacts with *(4)*, then there is complete conversion of *(1)* (or some other epoxide) and *(2)* into *(3)*, an olefinic compound, and triphenylphosphine oxide. Separate preparation of the phosphorane *(4)* is not necessary.



It is also often unnecessary to prepare the salts; triphenylphosphine, a halide R–CH_2–X (R = CO_2R', CH=CH_2, or C_6H_5), and *(1)* are allowed to react directly with the carbonyl compound. The oxide *(1)*, $(C_6H_5)_3P$, and ethyl bromoacetate react with benzaldehyde at 25 °C to give ethyl cinnamate (91%; *trans*:*cis* = 93:7), with crotonaldehyde at 25 °C



(3)

to give ethyl 2,4-hexadienoate (81%), and with cyclohexanone at 100 °C (sealed tube) to give ethyl cyclohexylideneacetate (68%). The oxide *(1)*, $(C_6H_5)_3P$, benzyl bromide, and propionaldehyde at 25 °C afford β-ethylstyrene (89.5%; *trans*:*cis* = 56:44). Benzyltriphenylphosphonium chloride and *(1)* react with cyclohexanone at 100 °C to give benzylidenecyclohexane (69%), but the weaker acid triphenylpropylphosphonium bromide reacts only at 150 °C with *(1)* and benzaldehyde, to yield β-ethylstyrene (74%; *trans*:*cis* = 40:60). The last example shows, incidentally, that ethylene oxide can replace even strong bases such as Li alkyls, which are used for formation of phosphoranes from phosphonium salts[5].

Experimental

$(C_6H_5)_3P$ (6.6 g, 0.025 mole), benzaldehyde (2.6 g, 0.025 mole), ethylene oxide (2.5 ml, 0.05 mole), and, with cooling, ethyl bromoacetate (4.2 g, 0.025 mole) are dissolved in methylene chloride (5 ml). The solution is allowed to stand overnight at room temperature and then distilled, whereupon 2-bromoethanol (2.45 g, 78%), b.p. 55 °C/17 torr, and ethyl cinnamate (4.0 g, 91%), b.p. 142–144 °C/17 torr, are collected

as distillate. The distillation residue of triphenylphosphine oxide solidifies (m.p. 150 °C, 97%, 6.75 g).

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[1] *J. Buddrus* and *F. Nerdel*, German Pat. 1198355 (Jan. 7, 1963); Chem. Zbl. *137*, 18-2333 (1966).

[2] *F. Nerdel* and *J. Buddrus*, Tetrahedron Letters *1965*, 3585.

[3] Nachr. Chem. Techn. *15*, 79 (1967).

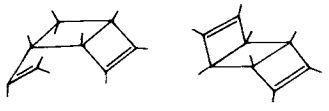
[4] *D. Klamann, M. Fligge, P. Weyerstahl, K. Ulm*, and *F. Nerdel*, Chemie-Ing.-Techn. *39*, 1024 (1967).

[5] For a summary, see *A. Maerker*, Org. Reactions *14*, 270 (1965).

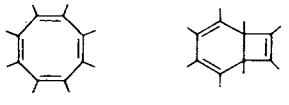
Octamethylsemibullvalene

By *R. Criegee* and *R. Askani*[*]

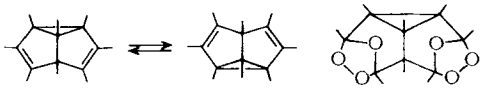
When any of the valence-isomeric hydrocarbons *(1)*, *(2)*, and *(3)* is heated in 1% Na ethoxide solution in ethanol at 240 °C a hydrocarbon $C_{16}H_{24}$ of m.p. 23 °C is formed to which the constitution *(4)* of an octamethylbicyclo[4.2.0]octatriene was previously provisionally assigned[1]. This constitution is incorrect and is to be replaced by that of octamethylsemibullvalene (octamethyltricyclo[3.3.0.$0^{2,8}$]octa-3,6-diene) *(5)*.



(1) *(2)*



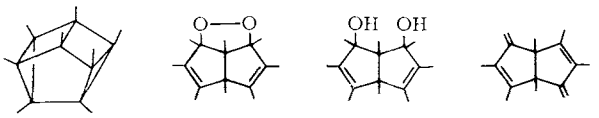
(3) *(4)*



(5) *(6)*

As a result of the extremely rapid valence isomerization of this system[2] the NMR spectrum is independent of temperature down to −100 °C; in pyridine/CCl_4 (9:1) it shows 3 singlets at τ = 8.52, 8.58, and 9.10 in the intensity ratio 1:2:1. The UV spectrum shows no maximum, only a shoulder at 240 nm, which requires additional assumptions on the basis of structure *(4)* but is at once intelligible on the basis of *(5)*. With tetracyanoethylene and azodicarboxylic ester the new hydrocarbon gives adducts that are different from those obtained from *(3)*, whereas those from *(3)* and *(4)* must be identical. The new hydrocarbon gives the crystalline diozonide *(6)*[3], whose NMR spectrum shows that, apart from the four CH_3 groups on the ozonide ring [τ = 8.41 (s), 8.43 (s)], all the methyl groups are attached to saturated C atoms [τ = 8.87 (s), and 8.90 (s)].

Thus, the hydrocarbon can contain only two double bonds, *i.e.* it must be tricyclic. The two double bonds present in *(5)* can add to each other photochemically (1% ethereal solution, 100 W low-pressure lamp, 0 °C, 12 h), affording the saturated hydrocarbon, octamethylpentacyclo[3.3.0.$0^{2,4}$.$0^{3,7}$.$0^{6,8}$]-octane *(7)* in 10–20% yield. M.p. 92 °C. NMR (CCl_4): τ = 8.92 (s), 9.13 (s), and 9.15(s) in the proportions 1:2:1.



(7) *(8)* *(9)* *(10)*

The change of formula *(4)* to *(5)* for the hydrocarbon requires that the structures of the products derived from it also be changed. Thus the peroxide (m.p. 78 °C), which is also formed in the dark, is now to be formulated as *(8)*, and the hydrocarbon of m.p. 55 °C obtained by way of the diol *(9)* or directly from *(5)* with silver nitrate is to be formulated as *(10)*. In accord with their different symmetries the H atoms of the bridgehead methyl groups in *(8)* show in the NMR spectrum two singlets lying close together (τ = 9.03 and 9.10), whereas *(10)* shows only one singlet (τ = 8.90). Following the unsubstituted parent[2] and a bis(trifluoromethyl) derivative[4], compound *(5)* is the third semibullvalene. In contrast to the other two it is not formed by a photoreaction and it is relatively easily accessible in gram quantities. The fourth semibullvalene (with eight methoxycarbonyl groups) was prepared by *J. C. Kauer* and *H. E. Simmons*[5]. Recently *L. A. Paquette* obtained an azasemibullvalene[6].

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[2] *H. E. Zimmermann* and *G. L. Grunewald*, J. Amer. chem. Soc. *88*, 183 (1966).

[3] We thank *H. Korber* for carrying out this experiment.

[4] *R. S. H. Liu*, J. Amer. chem. Soc. *90*, 215 (1968).

[5] *J. C. Kauer*, private communication.

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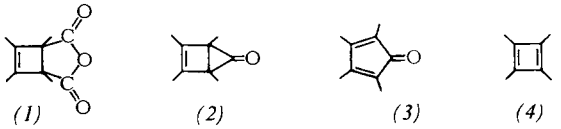
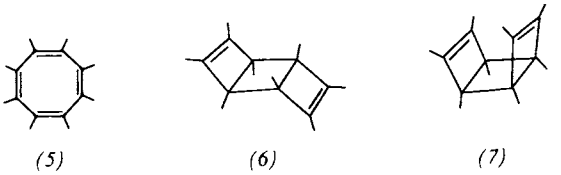
Photolysis of Tetramethylcyclobutenedicarboxylic Anhydride, a Possible Route to Tetramethylcyclobutadiene

By *G. Maier* and *U. Mende*[*]

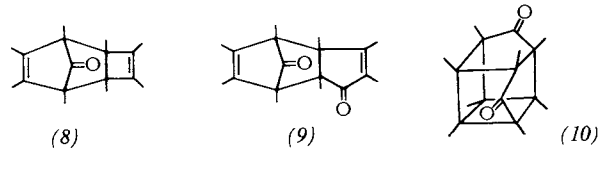
In connection with attempts to synthesize a compound with the ring skeleton of tetrahedrane we illuminated the anhydride *(1)* (Hanovia 450W high-pressure mercury lamp, Vycor filter, ether, 20 °C, 40 min). The following products were isolated by chromatography on silica gel:



(1) *(2)* *(3)* *(4)*



(5) *(6)* *(7)*



(8) *(9)* *(10)*

octamethylcyclooctatetraene *(5)* (5.3% yield), the dimers *(6)* (2.5%) and *(7)* (0.6%) of tetramethylcyclobutadiene *(4)*, hexamethylbenzene (0.7%), the peroxide (3%) and photoisomer (2%) of octamethylsemibullvalene[1], the ketone *(8)* (28%), the dimer *(9)* of tetramethylcyclopentadienone *(3)* (14%), and the cage diketone *(10)* (8.5%).

The structures of the new compounds, octamethyltricyclo-[4.2.1.$0^{2,5}$]nona-3,7-dien-9-one *(8)*, m.p. 192 °C, octamethyltricyclo[5.2.1.$0^{2,6}$]deca-4,8-diene-3,10-dione *(9)*, m.p. 190 °C, and octamethylpentacyclo[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{5,8}$]decane-4,10-dione *(10)*, m.p. 260 °C, are proved by elemental analysis, osmometrically determined molecular weights, and spectral data [NMR: CCl_4; *(8)*: 4 s at τ = 8.37, 8.63, 8.99, 9.12 (relative intensity 1:1:1:1); *(9)*: 2 m (J = 1 Hz) at 8.08, 8.42; 5s at 8.53, 8.80, 8.87, 8.99, 9.16 (1:1:2:1:1:1:1); *(10)*: 4 s at 9.08, 9.10, 9.15, 9.24 (1:1:1:1); IR: CCl_4; *(8)*: 1757; *(9)* 1765, 1690, 1640; *(10)*: 1745 cm^{-1}].

It is probably not dimerization of intermediate tetramethylcyclobutadiene that leads to compounds *(6)* and *(7)*; rather, the ketone *(8)* seems to be the effective intermediate. Irradiation of pre-isolated *(8)* gives the same hydrocarbons as are obtained from *(1)*, and the proportions in which the hydrocarbons are formed are the same. Apparently, removal of the CO bridge does not lead exclusively to octamethylbicyclo-[4.2.0]octatriene which could then give octamethylcyclooctatetraene *(5)* by valence isomerization or could be cleaved to hexamethylbenzene and butyne; instead, it provides to some extent a stereoselective formation of a new four-membered ring.

Control experiments showed that octamethylcyclooctatetraene *(5)* cannot be derived from *(6)* or *(7)*, but that octamethylsemibullvalene[1] and its photoisomer are to be considered as derived from *(5)*, which is formed from the ketone *(8)*. The cage diketone *(10)* is to be regarded as a photoproduct of *(9)*; the dimer *(9)* thus has the *endo*-configuration.

Formation of the ketone *(8)* is preferably considered as evidence for the occurrence of tetramethylcyclobutadiene *(4)* as intermediate product. We presume that first *(1)* is converted into *(2)*, that this then isomerizes to *(3)*, which in turn partly dimerizes to *(9)* and partly reacts with *(4)* [formed from *(2)* by loss of CO] to yield *(8)*. However, direct addition of *(2)* to *(3)* and formation of the ketone *(8)* from this adduct cannot be excluded[**].

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[1] *R. Criegee* and *R. Askani*, Angew. Chem. *80*, 531 (1968); Angew. Chem. internat. Edit. *7*, 537 (1968). A comprehensive review of the chemistry of cyclobutadiene is given by *M. P. Cava* and *M. J. Mitchell*: Cyclobutadiene and Related Compounds. Academic Press, New York 1967

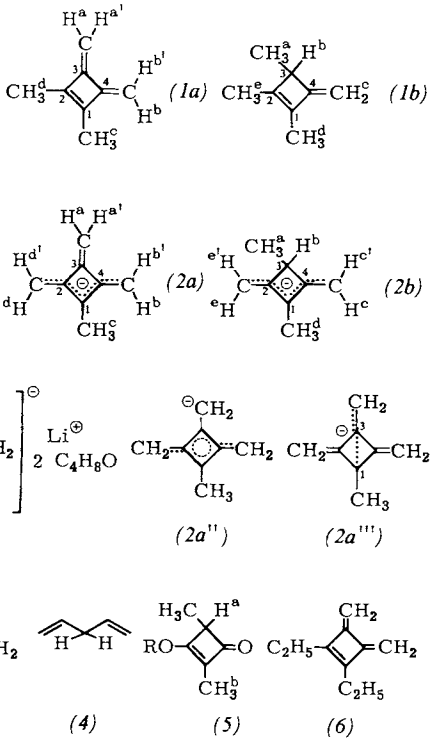
[**] Note added in proof (June 21, 1968): Meanwhile 3,4-dimethyl-3-cyclobutene-1,2-dicarboxylic anhydride has been irradiated. The products formed indicate that the main reaction is again the addition of 1,2-dimethylcyclobutadiene to 3,4-dimethylcyclopentadienone.

H. Prinzbach also photolyzed *(1)* and found ketones and octamethylcyclooctatetraene *(5)* (personal communication).

1-Methyl-2,3,4-trimethylenecyclobutenide Ion

By *D. Seebach* and *B. Graf* [*]

The first report about production of pentadienyllithium compounds in solution was published in 1967[1]. We were interested in whether we could prepare the anion *(2a)* derived from dimethyldimethylenecyclobutene *(1a)*[2], which would be a C_8 compound with seven coplanar sp^2-hybridized C atoms and a total of eight π-electrons. In the presence of strong bases would *(1a)* (free valence index on the *exo*-methylene C atom F = 0.86[3a]) give up a proton, add the base, or polymerize anionically? What influence would be exerted on or by the methylene group that does not participate[3b] in the pentadienyl system, perhaps through a resonance structure such as *(2a'')*? Would comparison of the anions *(2a)* and *(2b)* provide an indication of the often discussed[4] overlap between the p-orbitals of C-1 and C-3 (separation *ca.* 2 Å, calculated resonance integral $\beta_{1,3}$ = 0.76 eV) [as indicated in *(2a''')*]? Are reactions of the anion *(2a)* with electrophiles of value for preparation of substituted trienes *(3)*[5]?



Experience to date[1a] shows that butyllithium in THF gives pentadienyl anions only from 1,4-pentadienes *(4)*, and not from 1,3-pentadienes. However, crystals separate within 5 min of mixing butyllithium and *(1a)* (see Experimental); NMR spectroscopic studies in 1,2-dimethoxyethane (Fig. 1) show that these crystals are the lithium compound *(2a')* containing two molecules of THF. Integration of the THF signals and the signals of the anion gives a ratio of (2.0 ± 0.1):1. With respect to the starting material *(1a)* the signals of the protons H^c are shifted by 0.26, and those of H^a by about 0.55 ppm, towards higher field. The difference is considerable when one remembers that the CH_3^c group is bound directly to the central C atom of the pentadienyl system (the charge density

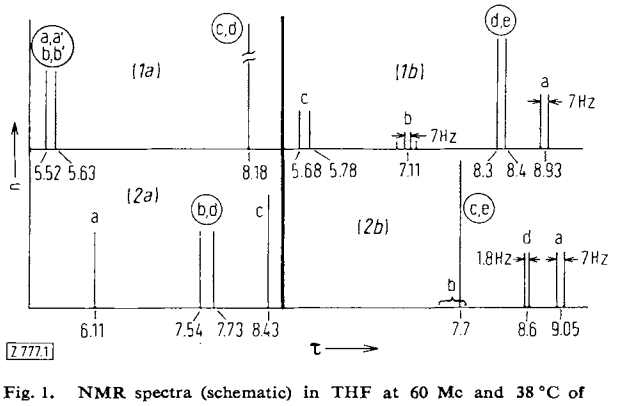


Fig. 1. NMR spectra (schematic) in THF at 60 Mc and 38 °C of compounds *(1a)*, *(1b)*, *(2a)*, and *(2b)* (n = number of protons, shifts in τ-units, standard THF (referred to TMS))[**].

is a maximum at the central and terminal C atoms), and that the distances from H^a and H^c to the terminal C atoms of this system are about the same. The protons H^b and H^d, and also $H^{b'}$ and $H^{d'}$ at the ends of the anion system, are identical; their chemical shift is not altered at 0 °C. Study of other pentadienyl anions[1b] showed that the signals of their protons of the type H^b and $H^{b'}$ coalesce below or up to 35 °C (Li ions are probably covalently bonded in the process)[1b,6]. Since *(2a)* shows two sharp signals even at 38 °C (half-width HW = 2.5 Hz) for these protons, this anion is more resistant to rotation than any other known pentadienyl anion[**].

Metalation of the diene *(1b)*[2a] to give *(2b)* occurs only above −30 °C. The NMR spectrum of the product proves the structure shown: here the four terminal protons H^c, $H^{c'}$, H^e, and $H^{e'}$ are identical at 38 °C (two signals at 0 °C[**]) as in all the pentadienyl anions studied to date. The signals of the protons H^d of the methyl group on C-1 are again shifted by about 0.25 ppm upfield; owing to the well-known coupling[7] [see *(5)*: J_{ab} = 2.5 Hz] with the single proton H^b on C-3 they appear as a sharp 1.8-Hz doublet (HW = 1.5 Hz). The signal of the protons H^a that appears as a doublet as in the starting material now occurs shifted by about 0.12 ppm upfield, although these protons are somewhat nearer to the negative charge than are the methylene protons H^a in the anion *(2a)*. This difference, and also the appreciably greater readiness of formation and the high rotational barrier of *(2a)*, might be be construed as arguments for participation of the resonance structures discussed above.

The methyl-ethyl-triene *(3)*, R = CH_3, is metalated exclusively on the methyl group. Treatment of the resulting lithium compound with methyl iodide affords compound *(6)*, b.p. 71–74 °C/25 torr, in 60% yield. The preparation of *(6)* and of the products *(3)* given in the Table, whose structures have been established by IR and NMR spectroscopy, demonstrate the preparative importance of the anions described here.

Table 1. Products *(3)* from the 1-methyl-2,3,4-trimethylenecyclobutenide ion *(2a)* and electrophiles.

Electrophile	*(3)*, R	Yield [a] (%)	B.p. (°C/torr)
$(CH_3)_3SiCl$	$(CH_3)_3Si$	80	90–92/18
CH_3I	CH_3	94 [b], 60 [c]	55–57/25
Ethylene oxide	$HOCH_2-CH_2$	40	63–64/0.1
Acetone	$(CH_3)_3C(OH)$	20	50/0.08
CH_3S-SCH_3	CH_3S	30	62–64/2

[a] Losses are considerable owing to the enormous tendency of the crude products to polymerize on distillation.
[b] By gas-chromatographic analysis of the reaction solution.
[c] Product isolated by distillation.

Experimental:

A solution of *n*-butyllithium (2 M in hexane, 20% excess) is added to a solution, stirred at −78 °C, of the triene *(1a)* (1.60 g) in THF (25 ml). Crystals begin to separate after 5 min, and after 5 h the red solution is sucked through a sinter disk. The crystals are recrystallized from THF/pentane at −40 to −78 °C and then washed with pentane. Adhering solvent is removed first at −40 °C, then at 25 °C/0.01 torr. All operations are conducted in an atmosphere of pure nitrogen. The yield of fine, pale yellow crystals of *(2a')* amounts to about 1 g. The substance becomes black immediately on exposure to air, or it ignites spontaneously. Dilute solutions in ethers are bright yellow, concentrated ones are red. *(2a')* decomposes in water to yield *(1a)*, LiOH, and THF; for reactions of *(2a)* molar amounts of *(1a)* and butyllithium are used and the reaction time increased.

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[1] a) *R. B. Bates, D. W. Gosselink*, and *J. A. Kaczynski*, Tetrahedron Letters *1967*, 199; b) 205.

[2] a) *R. Criegee et al.*, Chem. Ber. *96*, 2362 (1963); b) *G. W. Griffin* and *L. I. Peterson*, J. Amer. chem. Soc. *85*, 2268 (1963).

[3] a) *J. D. Roberts, A. Streitwieser*, and *C. M. Regan*, J. Amer. chem. Soc. *74*, 4579 (1952); b) *J. D. Roberts*: Molecular Orbital Calculations. Benjamin, New York 1962, p. 108.

[4] *J. D. Roberts et al.*, J. Amer. chem. Soc. *80*, 5507 (1958); *82*, 1793 (1960); *M. Simonetta* and *S. Carra*, Tetrahedron Letters *1965*, 913; *R. D. Brown* and *F. R. Burden*, Chem. Commun. *1966*, 448.

[5] For a recent review of the preparation of such systems see: *M. P. Cava* and *M. J. Mitchell*: Cyclobutadienes and Related Systems. Academic Press, New York 1967, pp. 157, 232.

[6] *E. Grovenstein et al.*, J. Amer. chem. Soc. *88*, 1275 (1966); *H. H. Freedman, V. R. Sandel*, and *B. P. Thill*, *ibid. 89*, 1762 (1967).

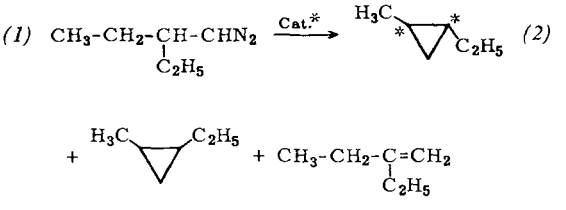
[**] Note added in proof (June 22, 1968): Measurement at 100 MHz shows: *(2a)*, −30 °C, 2 signals 20 Hz apart, temperature of coalescence +70 °C; *(2b)*, −30 °C, 2 signals 6 Hz apart, temperature of coalescence +25 °C.

[7] *D. Farnum et al.*, J. Amer. chem. Soc. *86*, 673 (1964); *87*, 5191 (1965); see also *J. D. Roberts et al.*, J. Amer. chem. Soc. *84*, 2935 (1962).

Asymmetric Induction in Intramolecular Reactions of Carbenoids

By *W. Kirmse* and *H. Arold*[*]

Alkylcarbenoids, which are intermediates in the α-elimination from haloalkanes[1] and in catalytic decomposition of diazoalkanes[2], give the same intramolecular insertion products as "free" alkylcarbenes. Carbenoids, however, show a higher selectivity in favor of secondary and tertiary C–H linkages[1,2] and larger isotope effects[3]. A possible explanation for the behavior of carbenoids is the participation of metal salts in the product-determining step of the reaction. We can now confirm that assumption by demonstrating an asymmetric induction on use of optically active catalysts.



Decomposition of 2-ethyl-1-diazobutane *(1)*[4] by silver salts of optically active acids gave optically active *trans*-1-ethyl-2-methylcyclopropane *(2)* (yield 20–30%) (see Table 1).

Table 1. Catalytic decomposition of 2-ethyl-1-diazobutane *(1)* by silver salts in *n*-pentane at 20 °C to yield *trans*-1-ethyl-2-methylcyclopropane *(2)*

Catalyst: silver salt of	*(2)*, $[\alpha]_{365}^{20}$
(*S*)-(+)-Alanine	+0.093
(*R*)-(−)-Alanine	−0.107
(*S*)-(+)-Camphor-1-sulfonic acid	+0.106
(*S*)-(+)-Ketopinic acid	+0.271
(*R*)-(+)-6,6'-Dinitro-2,2'-diphenic acid	+0.049

The (1 *R*, 2 *R*)-configuration is assigned to (−)-*trans*-1,2-dimethylcyclopropane, $[\alpha]_{365}^{20} = -125°$, because of its synthesis from (*S*)-(−)-2-methylbutan-1-ol[6]. (−)-*trans*-1-Ethyl-2-methylcyclopropane probably has the same configuration and a similar molar rotation. Catalytic decomposition of 2-methyl-1-diazobutane[7] by silver (+)-ketopinate (= (+)-7,7-dimethyl-2-oxonorbornane-1-carboxylate) afforded *trans*-1,2-dimethylcyclopropane with $[\alpha]_{365}^{0} = +0.27°$, in good agreement with the value for *trans*-1-ethyl-2-methylcyclopropane given in Table 1. The optical yield in this case, which is the most favorable so far, amounts to 0.22%.

Thermolysis of 2-ethyl-1-diazobutane *(1)* in (−)-α-methylbenzylamine or (−)-2-methylbutan-1-ol leads to inactive cy-

Table 2. Thermolysis of 2-ethyl-1-diazobutane *(1)*, to *trans*-1-ethyl-2-methylcyclopropane *(2)*.

Solvent	Temp. (°C)	*(2)*, $[\alpha]_{365}^{20}$
(*S*)-(−)-α-Methylbenzylamine	170	±0.002
(*S*)-(−)-α-Methylbenzylamine + $AgNO_3$	80	+0.039
(*R*)-(+)-α-Methylbenzylamine + $AgNO_3$	80	−0.057
(*S*)-(−)-2-Methylbutan-1-ol	120	±0.002
(*S*)-Ethyl (−)-lactate	145	−0.040
(*R*)-Dibutyl (+)-tartrate	170	+0.082

clopropane derivatives (no asymmetric induction by optically active solvent). Yet on addition of silver ions to the α-methylbenzylamine asymmetric induction is again observed (Table 2).

Weak proton donors (alcohols with acidifying substituents) recall the picture of a carbenoid reaction[2]. Presumably the proton can play the role of a metal ion in carbenoid catalysis. In accord with this hypothesis we obtained optically active *trans*-ethyl-2-methylcyclopropane on thermolysis of 2-ethyl-1-diazobutane in (*S*)-ethyl (−)-lactate or (*R*)-dibutyl (+)-tartrate. Carbonium ions $R'CH_2^{\oplus}$ cannot occur in these reactions. The catalyzing proton must retain a relation to the carbene-carbon as well as to the asymmetric alkoxide ion.

Because of the low optical yields, the above reactions are not well suited for asymmetric synthesis of cyclopropane derivatives. But they show unequivocally the participation of the catalyst in the product-determining step of intramolecular reactions of carbenoids[8].

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[1] *W. Kirmse* and *G. Wächtershäuser*, Tetrahedron *22*, 73 (1966).

[2] *W. Kirmse* and *K. Horn*, Chem. Ber. *100*, 2698 (1967).

[3] *W. Kirmse*, *H. D. v. Scholz*, and *H. Arold*, Liebigs Ann. Chem. *711*, 22 (1968).

[4] Prepared from the lithium salt of 2-ethylbutanal tosylhydrazone, m.p. 104 °C, by dry pyrolysis in a vacuum at 80–125 °C [5].

[5] *G. M. Kaufman*, *J. A. Smith*, *G. G. van der Strouw*, and *H. Shechter*, J. Amer. chem. Soc. *87*, 935 (1965).

[6] *W. v. E. Doering* and *W. Kirmse*, Tetrahedron *11*, 272 (1960).

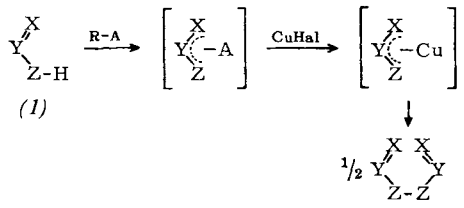
[7] 2-Methyl-1-diazobutane is not suitable for series of experiments because of its poor accessibility and the difficulty of separating its reaction products; cf. *W. Kirmse* and *G. Wächtershäuser*, Tetrahedron *22*, 63 (1966).

[8] For similar results on carbenoid addition of diazoacetic ester to styrene see *H. Nozaki*, *S. Moriuti*, *H. Takaya*, and *R. Noyori*, Tetrahedron Letters *1966*, 5239.

Dimerization of Oxaallyl, Azaallyl, Oxaphosphaallyl, and Oxathiaallyl Groups by Way of Organocopper Compounds[1]

By *Th. Kauffmann*, *G. Beissner*, *H. Berg*, *E. Köppelmann*, *J. Legler*, and *M. Schönfelder*[*]

Compounds of type *(1)* are formally derived from allyl compounds by replacement of allyl-carbon atoms by hetero atoms and may thus be termed heteroallyl compounds. In several cases they can be dehydrodimerized in accord with the following scheme[2,3]:

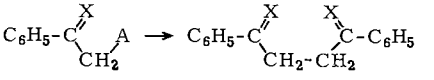


(A = alkali metal; Cu = Cu^{I} or Cu^{II})

Dehydrodimerization of heteroarylated alkanes[4] is a particular case of this reaction principle.

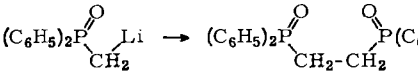
Continuing these investigations we have now observed dimerization of the 1-oxaallyl group on treatment of *(2)*[5,6] with one molar equivalent of CuCl in ether at 35 °C. The yield of dimerization product *(3)* of only 11% for this case increases to 42% if the 1-azaallyl compound *(4)* is used and dimerization (treatment with CuI in ether at 35 °C) is followed by hydrolysis with 2 N HCl[7]; compound *(4)* is formed by the action of $NaNH_2$ on acetophenone anil in ether at 35 °C.

Yields are still better [52% for *(7)*, 84% for *(9)*] in the analogous reaction (treatment with CuCl at −60 to +20 °C, then with O_2 at 20–65 °C; solvent tetrahydrofuran) of *(6)* and *(8)*, which were obtained on treatment of the corresponding ketazines with lithium diisopropylamide in tetrahydrofuran at 10 °C. The dehydrodimerization of ketazines thus disclosed may open a convenient route to long-chain azapolyenes.



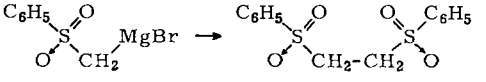
(2), X = O; A = Na
(3), X = O
(4), X = N-C_6H_5; A = Na
(5), X = N-C_6H_5
(6), X = N-N=C(C_6H_5)CH_3; A = Li
(7), X = N-N=C(C_6H_5)CH_3
(8), X = N-N=C(C_6H_5)$_2$; A = Li
(9), X = N-N=C(C_6H_5)$_2$

The 1-oxa-2-phosphaallyl group of *(10)*[8] can be dimerized, giving *(11)* (43%), by treatment with 1 molar equivalent of CuCl at −40 to +20 °C in tetrahydrofuran and subsequently with O_2 at 20 °C.



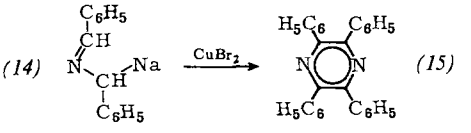
(10) *(11)*

The 1-oxa-2-thiaallyl group of compound *(12)*[9], which arises on reaction of phenylmagnesium bromide with methyl phenyl sulfone in benzene at 20 °C, was dimerized on treatment with 1 molar equivalent of CuCl at −68 to +20 °C in ether/benzene/tetrahydrofuran (*ca.* 1:3:4), yielding *(13)* (20–25%).



(12) *(13)*

Surprisingly, the 2-azaallyl group of *(14)*, which can be dimerized by use of CuI[3], was cyclized on treatment with 1 molar equivalent of $CuBr_2$ in ether at 35 °C, affording *(15)* in 18% yield (presumably not optimal).



(14) *(15)*

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[1] Activation of Organic Compounds by Introduction of Transition Metal Atoms. Part 5. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. — Part 4: *Th. Kauffmann* and *D. Berger*, Chem. Ber., in press.

[2] *Th. Kauffmann, J. Albrecht, D. Berger*, and *J. Legler*, Angew. Chem. *79*, 620 (1967); Angew. Chem. internat. Edit. *6*, 633 (1967).

[3] *Th. Kauffmann, G. Beissner, E. Köppelmann, D. Kuhlmann, A. Schott*, and *H. Schrecken*, Angew. Chem. *80*, 117 (1968); Angew. Chem. internat. Edit. *7*, 131 (1968).

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[5] *L. Claisen*, Ber. dtsch. chem. Ges. *38*, 697 (1905).

[6] It is considered unnecessary to formulate the individual metal compounds realistically here. Yields quoted refer to the metal-free compound brought into reaction.

[7] The dianil *(5)*, which was detected indirectly, was not isolated.

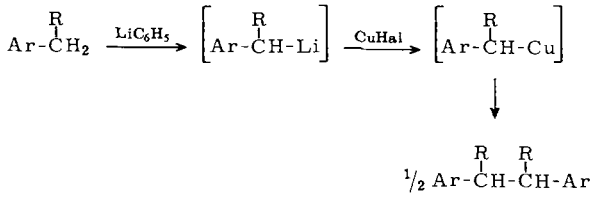
[8] *L. Horner, H. Hoffmann*, and *V. G. Toscano*, Chem. Ber. *95*, 536 (1962).

[9] *L. Field*, J. Amer. chem. Soc. *74*, 3919 (1952).

Dehydrodimerization of Heteroarylated Alkanes by Way of Organocopper Compounds[1]

By *Th. Kauffmann, D. Kuhlmann, W. Sahm*, and *H. Schrecken*[*]

We recently reported the dehydrodimerization of 2-methylpyridine (78% yield)[2]. Analogously the heteroarylated alkanes listed in the Table can be converted into the corresponding dehydrodimers according to the scheme indicated. Since the yields are mostly satisfactory this seems to be a useful method for preparation of bis(heteroaryl)ethanes and thus of bis(heteroaryl)ethylenes and -acetylenes.

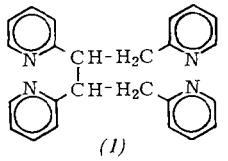


Ar	R	CuHal	Dehydrodimers, yield (%)
2-Pyridyl [a]	CH_3	CuCl	63
	C_6H_5		65
6-Methyl-2-pyridyl [a]	H	$CuCl(CuBr_2)$	71 (77)
4-Pyridyl [a]	H	CuCl	54
	CH_3		40
	C_2H_5		34
	C_6H_5		65
2-Quinolyl [b]	H	CuCl(CuBr)	67 (69)
4-Quinolyl [b]	H	CuCl	58
2-Phenyl-4-quinolyl [b]	H	CuCl	74
3-Methyl-2-quinoxalinyl [b]	H	$CuCl(CuBr_2)$	61 (65)

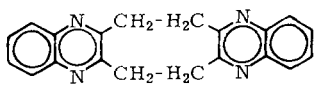
[a] Reaction in tetrahydrofuran/diethyl ether (*ca.* 1:1).
[b] Reaction in dimethoxyethane/diethyl ether (*ca.* 1:1). To obtain a higher boiling point the diethyl ether was distilled off on decomposition of the organocopper compounds.

For preparation of the necessary lithium compounds the heteroarylated alkanes were treated with 1 to 1.1 molar equivalents of phenyllithium in the solvents listed, at −10 to 0 °C under N_2. Then 1 molar equivalent of CuCl or $CuBr_2$ was added at −60 to −40 °C and the mixture was warmed slowly to 60 to 80 °C, whereupon the organocopper compounds (brown or red; not isolated) which were formed as intermediates decomposed with precipitation of elemental copper or of CuBr according to whether CuCl or $CuBr_2$ had been used.

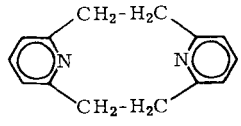
It is remarkable that the compounds formed by this process are mostly susceptible to further reactions of the same type. For instance, the dehydrodimer of 2-methylpyridine[2] can be converted into the two isomers of constitution *(1)* (yield 73%; ratio racemic:*meso*-form = *ca.* 1:1), and the product from 2,3-dimethylquinoxaline (see Table) can be converted into the pentacyclic compound *(2)* (yield 25%) if the dilution method is used. On the other hand, attempts to convert the dehydrodimer of 2,6-dimethylpyridine (see Table) into the known compound *(3)*[3] failed.



(1)



(2)



(3)

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[1] Activation of Organic Compounds by Introduction of Transition Metal Atoms. Part 6. This work was supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie. – Part 5: *Th. Kauffmann, G. Beissner, H. Berg, E. Köppelmann, J. Legler*, and *M. Schönfelder*, Angew. Chem. *80*, 565 (1968); Angew. Chem. internat. Edit. *7*, 540 (1968).

[2] *Th. Kauffmann, G. Beissner, E. Köppelmann, D. Kuhlmann, A. Schott*, and *H. Schrecken*, Angew. Chem. *80*, 117 (1968); Angew. Chem. internat. Edit. *7*, 131 (1968).

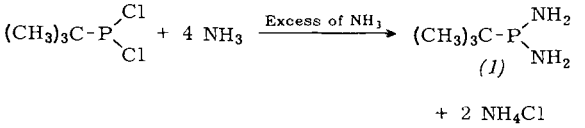
[3] *W. Baker, K. M. Buggle, J. F. W. McOmie*, and *D. A. M. Watkins*, J. chem. Soc. (London) *1958*, 3594.

Diamino-*tert*-butylphosphine. – Synthesis and Conversion into *N*-Silylated Aminophosphine Imines with Non-equivalent Replaceability of the Hydrogen Atoms

By *O. J. Scherer* and *P. Klusmann*[*]

Alkyl diaminophosphines and diaminoarylphosphines[1] have not been described previously, and phosphorodiamidous acid derivatives[2] are polymeric substances.

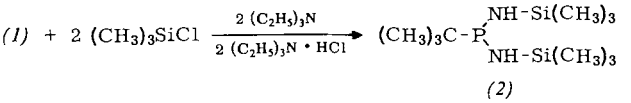
Ammonolysis of *tert*-butyldichlorophosphine[3] in ether at −50 °C gives the diamino-*tert*-butylphosphine *(1)* in *ca.* 60% yield.



(1)

+ 2 NH_4Cl

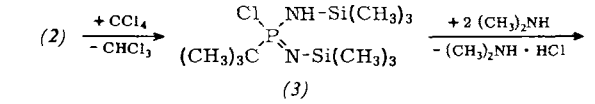
(1): colorless crystals, subliming at 75–85 °C/12 torr, extremely sensitive to oxygen and hydrolysis, m.p. 77–79 °C, readily soluble in ether or benzene. ^1H-NMR: $J^{31}PCCH$ = 12.5 Hz (δNH_2, broad signal, observable only on integration). Treatment of *(1)* with chlorotrimethylsilane gives *tert*-butylbis(trimethylsilylamino)phosphine *(2)* in 70% yield.



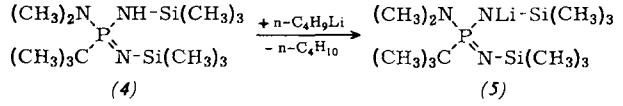
(2)

(2): b.p. 51–55 °C/0.1 torr, $J^{31}PCCH$ = 12.7 Hz, $J^{31}PNSiCH$ = 0.75 Hz, very sensitive to oxygen and hydrolysis, readily soluble in ether or benzene. Reaction of compound *(2)* with

CCl_4 gives *P-tert*-butyl-*P*-chloro-*N*-(trimethylsilyl)-*P*-(trimethylsilylamino)phosphine imine *(3)*[4], which with dimethylamine affords compound *(4)*. This can be metalated by *n*-butyllithium, affording the lithium amide derivative *(5)* in good yield.



(3)



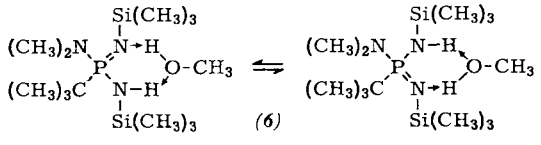
(4) *(5)*

(3): b.p. 55–59 °C/0.1 torr, m.p. 11–12 °C, $J^{31}PCCH$ = 20.4 Hz, yield 70%.

(4): b.p. 54–58 °C/0.1 torr, m.p. −26 °C, $^{31}JPCCH$ = 16.3 Hz, $J^{31}PNCH$ = 9.1 Hz, yield 70%.

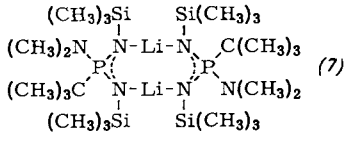
(5): m.p. 137–140 °C, sublimes at 190–200 °C/0.1 torr, $J^{31}PCCH$ = 14.9 Hz, $J^{31}PNCH$ = 8.8 Hz.

Although the ^1H–NMR spectrum of *(3)* shows two sharp signals even at *ca.* 60 °C (pure substance or dilute solution), for the non-equivalent trimethylsilyl groups, compound *(4)* (pure substance or in 10% solution in CCl_4 or benzene) at +35 °C gives only one, slightly broadened signal. If the benzene solution of *(4)* is diluted approximately tenfold, two trimethylsilyl signals appear (separation *ca.* 9 Hz), which combine to a single one on warming or on addition of *ca.* 5 mg of methanol (alcoholysis is observable only at higher concentration). This finding is best interpreted by assuming that in *(4)* transfer of the proton (that becomes stationary on strong dilution) is effected *(a)* intermolecularly within one molecule [cf. formula *(7)*; in the IR spectrum, *(4)* gives no indication (strong dilution) of bonding by fixed hydrogen bridges] and *(b)* by the alcohol molecule as in *(6)*.



(6)

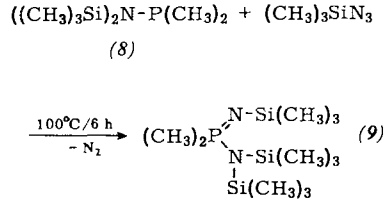
In contrast to the monomeric *(4)*, the "lithium salt" *(5)*, which is readily soluble in ether, CCl_4, or benzene, is dimeric in the last-mentioned solvent (cryoscopic determination). The ^1H–NMR spectrum of *(5)* shows only one sharp signal for the trimethylsilyl groups (even on strong dilution). These facts are best accounted for by the suggested formula *(7)*.



(7)

Attempts to convert *(3)* into a "phosphine diimine" by elimination of HCl and to substitute *(5)* by chlorotrimethylsilane were unsuccessful.

If impure dimethylbis[(trimethylsilyl)amino]phosphine *(8)*[5] [prepared from $((CH_3)_3Si)_2NNa$ and $(CH_3)_2PCl$] is treated with trimethylsilyl azide, the thrice-silylated aminophosphine



(8) *(9)*

imine *(9)*, b.p. 70–74 °C/0.1 torr, m.p. 4–6 °C, is obtained in 10% yield.

As in metalorganic amidines[6] the non-equivalent trimethylsilyl groups of *(9)* appear in the ^1H–NMR spectrum at 35 °C only as a single, broadened signal, which splits into two signals at *ca.* −20 °C (separation ≈ 20 Hz in $CDCl_3$; area ratio 2:1).

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[1] Cf. $C_6H_5P(NHR)_2$ compounds: *A. P. Lane, D. A. Morton-Blake*, and *D. S. Payne*, J. chem. Soc. (London) *A 1967*, 1492.

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Preparation of Single Crystals of Chromium Thiospinels by Means of Transport Reactions

By *H. D. Lutz* and *Cs. von Lovász* [*]

Nitsche et al.[1] prepared single crystals of thiospinels – in particular of indium and gallium thiospinels – by using iodine as transport agent in transport reactions. Single crystals of chromium thiospinel, which we required for electrical studies of thiospinel semiconductors[2], cannot be prepared in this way since, in contrast to chromium chloride, chromium sulfides are not transported by halogens – apparently the entropy of reaction of the corresponding gas-phase reaction is negative.

Chromium sulfides and chromium thiospinels can, however, be transported by anhydrous aluminum chloride:

$$Cr_2S_{3(s)} + 4\,AlCl_{3(g)} \underset{T'}{\overset{T}{\rightleftharpoons}} 4\,AlCl_{(g)} + 2\,CrCl_{4(g)} + 3/2\,S_{2(g)}$$

We obtained the following chromium thiospinels as black octahedra (sides of length 1 mm) as well as various modifications of chromium sulfide such as Cr_2S_3 as hexagonal leaflets of 10 mm size:

$MnCr_2S_4$ 1000→900 °C
$ZnCr_2S_4$ 1000→850 °C
$CdCr_2S_4$ 1000→800 °C

$FeCr_2S_4$, $CoCr_2S_4$, $CuCr_2S_4$, and $HgCr_2S_4$ could not be transported by $AlCl_3$.

2 g of the substance was transferred, together with 0.2 g of anhydrous $AlCl_3$, to a 10 cm long, evacuated quartz ampoule in a dry box and then heated for about 80 hours in a temperature gradient oven.

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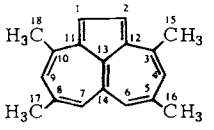
[2] *H. D. Lutz* and *K. Grendel*, Z. anorg. allg. Chem. *337*, 30 (1965).

Crystal Structure and Molecular Structure of 3,5,8,10-Tetramethylaceheptylene

By *E. Carstensen-Oeser* and *G. Habermehl*[*] [**]

3,5,8,10-Tetramethylaceheptylene, $C_{18}H_{18}$ *(1)*, a hydrocarbon with a 14 π electron system, was prepared by *Hafner et al.*[1] and has been subjected to quantum-mechanical study[2]. To test the quantum-mechanical conclusions about molecular geometry we carried out an X-ray crystal structure analysis.



(1)

3,5,8,10-Tetramethylaceheptylene forms monoclinic crystals from benzene but orthorhombic ones from light petroleum. The lattice constants of the monoclinic modification are $a = 8.43 \pm 0.03$ Å, $b = 13.24 \pm 0.03$ Å, $c = 12.44 \pm 0.03$ Å, $\beta = 107.7 \pm 0.1°$. The space group is $P\,2_1/c$; the unit cell contains four molecules. The orthorhombic form gave the following crystallographic results: $a = 17.27 \pm 0.03$ Å, $b = 10.98 \pm 0.03$ Å, $c = 7.00 \pm 0.03$ Å; space group $Pna\,2_1$, with four molecules in the unit cell.

We have first worked with the orthorhombic structure. Analysis of the monoclinic modification is in progress.

Measurement of the intensities of 865 symmetry-independent reflections of the layers *hk* 0 to *hk* 4 was carried out on an automatic Weissenberg diffractometer with punched-tape control, system Stoe-Güttinger. We determined the sign of 66 reflections by *Sayre, Cochran,* and *Zachariasen*'s method[3]. A Fourier synthesis with the *E* values of these 66 reflections as coefficients could be interpreted unambiguously. Refinement was effected by further Fourier and difference Fourier syntheses, as well as by the method of least squares. Finally we reached an *R* factor of 7.6%. Anisotropic thermal motion was taken into account for the carbon atoms in these calculations.

The calculations show that the molecule is completely planar except for the hydrogen atoms of the methyl groups. Bond distances and bond angles can be read from Figures 1 and 2. The values agree well with the bond lengths calculated for the parent aceheptylene by *Ali* and *Coulson*[2] using the MO method and by *DasGupta* and *Ali*[2] using the Pople SCF method. *Coulson*'s relation[4] was used for calculations between bond order and bond length.

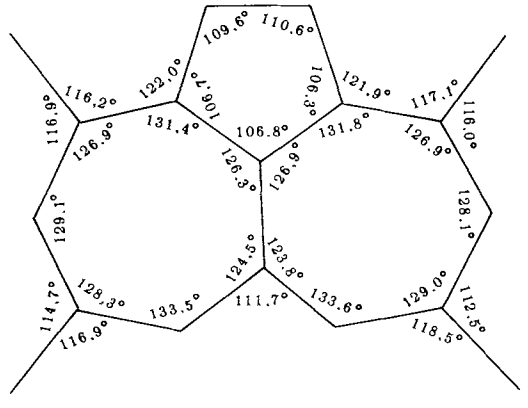


Fig. 1. Bond distances in 3,5,8,10-tetramethylaceheptylene; max. error, ±0.008 Å.

Fig. 2. Bond angles in 3,5,8,10-tetramethylaceheptylene; max. error, ± 1°.

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[**] We wish to thank Dipl.-Ing. *O. Ermer* of the Organisch-chemisches Laboratorium der ETH Zürich for the program used in the calculation of the *E*-values and the Deutsche Forschungsgemeinschaft for support of our work.

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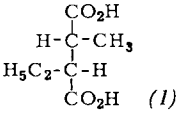
The Absolute Configuration of (−)-*threo*-2-Ethyl-3-methylsuccinic Acid[1]

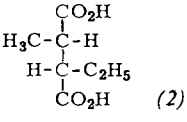
By *H. Brockmann jr.* and *D. Müller-Enoch*[*]

By comparison of the molar optical rotations of anhydrides of mono- and di-alkyl-substituted succinic anhydrides the (2*R*, 3*R*)-configuration was recently[2] assigned to (+)-*threo*-2-ethyl-3-methylsuccinic acid *(1)*, and thus the absolute configuration of bacteriochlorophyll was determined. We have now proved the (2*S*, 3*S*)-configuration of (−)-*threo*-2-ethyl-3-methylsuccinic acid *(2)* by a chemical method, in that we converted *(2)* by total reduction into (3*S*)-(−)-2,3-dimethylpentane *(5)*, whose absolute configuration is known[3].

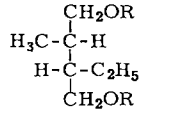
Compound *(2)* [m.p. 66–68 °C, $[\alpha]_D^{20} = -17.8°$ ($c = 2.5$, in water), corresponding to 68% optical purity] was reduced by lithium aluminum hydride in ether to the diol *(3)*, which was converted by *p*-toluenesulfonyl chloride in pyridine at 0 °C into the ditosylate *(4)*; the yield was 53% calculated on *(2)*. Crystallization of *(4)* gave several fractions, with various optical activities, $[\alpha]_D^{20} = -2.1°$ to $-2.9°$, and various melting points (56 to 60 °C). A partly oily preparation with $[\alpha]_D^{20} = -3.2°$ ($c = 2.5$, in chloroform) was used for further reduction. It was treated with lithium aluminum hydride in di-*n*-



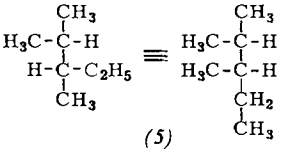
(1)



(2)



(3), R = H
(4), R = $SO_2C_6H_4$-p-CH_3



(5)

butyl ether and, after decomposition of the excess of hydride with sulfuric acid, the product *(5)* was distilled off together with some solvent. By extraction with conc. sulfuric acid and distillation over sodium we obtained a 37% yield of the hydrocarbon *(5)*, b.p. 87 °C and $[\alpha]_D^{20} = -7.8°$ (c = 2.5, in chloroform), which had a faint smell of petrol.

In comparison with the rotation $[\alpha]_D^{20} = -11.4°$ given by *Freudenberg*[3] for the optically pure hydrocarbon our value indicates an optical activity of 68%. The purity of *(5)* was proved by its mass spectrum: $M^+ = 100$, $(M-15)^+$, $(M-29)^+$, $(M-43)^+$.

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[2] *H. Brockmann jr.*, Angew. Chem. *80*, 234 (1968); Angew. Chem. internat. Edit. *7*, 222 (1968). Inadvertently an incorrect value was given in this paper for the $[\alpha]_D^{20}$ value of bis(*p*-bromophenacyl) (+)-*threo*-2-ethyl-3-methylsuccinate. The correct rotations at various wavelengths are: $[\alpha]_D^{20} = -36.5 \pm 3°$, $[\alpha]_{578}^{20} = -38.5° \pm 3°$, $[\alpha]_{546}^{20} = -49.5 \pm 3°$, $[\alpha]_{436}^{20} = -87 \pm 4°$ (c = 1.3, in chloroform).

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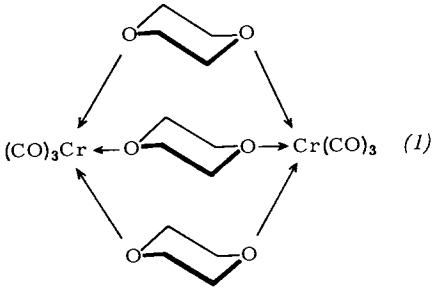
A Binuclear Chromium Complex with Dioxane as Bridging Ligand

By *H. Werner* and *E. Deckelmann*[*]

Recently we reported the synthesis of hexaalkylborazole-tricarbonylchromium compounds, the first representatives of borazole-transition metal complexes. These are most profitably obtained by starting with $(CH_3CN)_3Cr(CO)_3$ or analogous compounds of the type *cis*-$A_3Cr(CO)_3$ (A = amine)[1,2]. The choice of solvent is decisive for success in this method of preparation; dioxane has so far proved most suitable for this purpose. Measurements of absorption in the visible region indicated at once that in the reaction of tris-(amine)tricarbonylchromium compounds with hexaalkylborazoles the dioxane clearly acts, not merely as solvent, but also as coordination partner.

We have now confirmed this assumption by isolating the binuclear complex $(C_4H_8O_2)_3Cr_2(CO)_6$ *(1)*. This orange, diamagnetic substance is extremely sensitive to air and glows on exposure to even traces of oxygen; as expected, it does not sublime and it decomposes slowly even at room temperature. Darkening is observed from 90 °C if the material is heated rapidly under nitrogen in a sealed tube. In the region of the CO stretching vibrations, the IR spectrum (in KBr) shows two strong bands of relative intensities 1:2 at 1919 and 1763 cm^{-1}, thus confirming the existence of a $Cr(CO)_3$ group. Absorptions at 1455, 1370, 1289, 1252, 1119, 1103, 1047, 879, and 866 cm^{-1} are ascribed to the coordinately bonded dioxane molecules (cf. free dioxane[3]: 1451, 1366, 1292, 1255, 1124, 1085, 1049, and 879 cm^{-1}). The presence of $C_4H_8O_2$ ligands is also proved by the mass spectrum[4].



(1)

In the NMR spectrum of *(1)* (in deuterioacetone) a sharp signal is observed at $\tau \approx 6.45$ (referred to tetramethylsilane as internal standard), which is hardly shifted in comparison with that for free dioxane ($\tau = 6.44$). However, in this connection a very rapid exchange between solvent molecules and the dioxane ligands in solution cannot be excluded; this would explain why it has not yet been possible to recover the dioxane complex from its solution in acetone or deuterioacetone; moreover, on addition of acetonitrile to *(1)* an extremely rapid exchange of ligands occurs, with quantitative formation of $(CH_3CN)_3Cr(CO)_3$.

The binuclear nature of the complex is shown by elemental analysis and determination of the molecular weight, and on the basis of the above results we assume structure *(1)* with three dioxane molecules as bridging ligands. The weak donor character of the ether oxygen atoms is probably mainly responsible for the low stability of the compound. On the other hand, its extreme reactivity, shown in the synthesis of the hexaalkylborazole-tricarbonylchromium compounds, makes it predestined as a starting material for the preparation of other $Cr(CO)_3$ complexes. In this connection it may be noted that very recently tris(dimethylamino)borane-tricarbonyltungsten was obtained by reaction of $(CH_3CN)_3W(CO)_3$ with $B[N(CH_3)_2]_3$ in dioxane[5]. It can be assumed that here also a carbonyldioxanetungsten complex analogous to *(1)* is formed as intermediate and that this then reacts rapidly with the tris(dimethylamino)borane by ligand exchange.

Experimental:

1 g of $(CH_3CN)_3Cr(CO)_3$ was treated with two successive portions, each 50 ml, of dioxane in a two-necked flask under nitrogen, and the solution was evaporated almost to dryness in vacuum at a bath temperature of *ca.* 15 °C. The resulting crystalline mass was made into a slurry with a little dioxane and filtered rapidly through a G 3 fritted filter. The orange solid thus isolated was washed several times with a few ml of cold dioxane, then with ether, and was finally dried under a high vacuum. The yield was 75%.

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Hammett Constants of Phosphorus-containing Groups Determined from Nuclear Magnetic Resonance Spectra of *para*-Phosphorus-substituted Toluenes[1]

By *G. P. Schiemenz*[*]

Earlier[2] we found Hammett constants of *ca.* +1 for substituents $-\overset{\oplus}{P}RAr_2$ on the aromatic ring. Onium-phosphorus is thus disclosed as a stronger electron acceptor than positive nitrogen[3,4]. In view of the electronegativity series N > P

this finding could not be explained as an inductive effect alone.

By proton magnetic resonance spectroscopy of anilinium salts *Fraenkel*[5] showed that the inductive effect of the 'onium atom is almost wholly abolished by ion-pair formation. We found, also by nuclear magnetic resonance spectroscopy, that triarylmethylphosphonium salts in chloroform associate to contact ion pairs, in which the anionic charge is localized on the phosphorus[6]. Thus, Hammett constants, determined in the same medium and by the same method, should provide information about the non-inductive portions of the electronic effect of 'onium phosphorus.

For compounds $X-C_6H_4-Y-H$ the position of the nuclear resonance signal of $-Y-H$ is often linearly dependent on the Hammett constants σ of X ($-Y-H$ = CHO[7], OH[8], or NH_2[9]), so that σ values for new substituents X can be determined from δ ($-Y-H$). In this way we obtained "satisfactory"[3] correlation for *para*-substituted toluenes ($-Y-H$ = CH_3) in $CDCl_3$ between δ and σ[3] of groups X that contain no free electron pair [X = NO_2, SO_2CH_3, CN, $COOC_2H_5$, $COCH_3$, COC_6H_5, CHO, C_6H_5, H, $Si(CH_3)_3$, $CH(CH_3)_2$, CH_3, $C(CH_3)_3$; equation (1)][10]. The experimental points for 16 toluenes whose substituents X do carry a free electron pair all lie below the best straight line [X = F, Cl, Br, I, NH_2, $NHCH_3$, $N(CH_3)_2$, NHCHO, $NHCOCH_3$, $NHCOC_6H_5$, OH, OCH_3, OC_2H_5, OC_6H_5, SH, SCH_3][10]. Thus new substituent constants can be calculated from equation (1), although for groups with free electron pairs these are only minimal values.

$$\delta = 0.142 \cdot \sigma + 2.332 \qquad (1)$$

$r = 0.960$, for δ $s = \pm 0.016$ ppm, for σ $s = \pm 0.11$ σ unit

In this way we determined σ_{para} values for 28 groups X that contain phosphorus or, for comparison, sulfur or nitrogen (Table 1). For all phosphonium groups σ_{para} is again about 1; σ_{para} is larger when electron-donating methyl groups are replaced by electron-attracting aryl groups. The three sulfur-containing groups also have Hammett constants near 1, whereas, in agreement with earlier results[2], phosphinyl- and thiophosphinyl-phosphorus usually behaves as a moderately strong electron-acceptor (in two cases σ_{para} does not differ significantly from 0).

Table 1. Chemical shifts δ (ppm) of the NMR signals of the CH_3 protons in *p*-$X-C_6H_4CH_3$ [*ca.* 0.9 mole of *p*-$CH_3C_6H_4$ group/1000 g of $CDCl_3$; $(CH_3)_4Si$ as internal standard] and Hammett constants of the substituents X.

X [a]	δ [b]	σ [c]	σ_I [d]	σ_M [d]
$-PCl_2$	2.425	>+0.65		
$-P(OH)_2$	2.383	>+0.37		
$-P(CH_3)_2$	2.329	>−0.02		
$>PCH_3$	2.321	>−0.09		
$-P(C_6H_5)_2$	2.275	>−0.41		
$>PC_6H_5$	2.308	>−0.16		
>P−	2.308	>−0.16		
$-SO_2Cl$	2.504	+1.22		
$-SO_3CH_3$	2.463	+0.90		
$-SO_3C_2H_5$	2.458	+0.90		
>NH	2.292	>−0.26		
$-N(C_6H_5)_2$	2.279	>−0.37		
$>NC_6H_5$	2.283	>−0.34		
>N−	2.296	>−0.26		
$>P(O)CH_3$	2.379	+0.34		
$>P(O)C_2H_5$	2.367	+0.23		
$-P(O)(C_6H_5)_2$	2.342	+0.05	+0.27	(<0)
$>P(O)C_6H_5$	2.375	+0.30	+0.27	+0.03
>P(O)−	2.375	+0.30	+0.27	+0.03
$-P(S)(C_6H_5)_2$	2.342	+0.05	+0.25	(<0)
$>P(S)C_6H_5$	2.375	+0.30	+0.25	+0.05
>P(S)−	2.367	+0.23	+0.25	−0.02
$>P^{\oplus}(CH_3)_2$ $I^{\ominus}$	2.454	+0.86	+0.65	+0.21
$-P^{\oplus}(CH_3)(C_6H_5)_2$ $I^{\ominus}$	2.500	+1.18	+0.71	+0.47
$>P^{\oplus}(CH_3)C_6H_5$ $I^{\ominus}$	2.492	+1.11	+0.71	+0.40
$>P^{\oplus}(CH_3)-$ $I^{\ominus}$	2.500	+1.18	+0.71	+0.47
$>P^{\oplus}(C_2H_5)-$ $I^{\ominus}$	2.508	+1.25	+0.71	+0.54
$>P^{\oplus}(C_6H_5)-$ $I^{\ominus}$	2.558	+1.61	+0.76	+0.85

[a] Multivalent groups carry a corresponding number of *p*-$CH_3C_6H_4$ groups. [b] Third decimal place estimated. [c] Calculated according to eq. (1). [d] Approximate values.

Martin and *Griffin*[11] determined Taft constants σ^* of some phosphorus-containing groups, some of which are so similar to our substituents that the inductive portion σ_I of their Hammett constants can be determined from σ^* by *Taft*'s method[12] (see Table 1). Using the relation $\sigma = \sigma_I + \sigma_M$ then affords for phosphonium-phosphorus a mesomeric contribution σ_M that greatly exceeds that of the ethoxycarbonyl group ($\sigma_M^{COOC_2H_5} = +0.20$[12]). 'Onium-phosphorus thus behaves as a strong (−M)-substituent, whereas in the chalcogenides phosphorus gives no indication of a (−M)-effect.

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Hammett Constants of Phosphorus-containing Groups Determined from Nuclear Magnetic Resonance Spectra of *meta*- and *ortho*-Phosphorus-substituted Toluenes[1]

By *G. P. Schiemenz* [*]

We found[2] phosphorus Hammett constants $\sigma > 1$ for *para*-tolyl-substituted phosphonium salts $Ar_2\overset{\oplus}{P}(CH_3)C_6H_4CH_3$-*p* $I^{\ominus}$ although, because of formation of contact ion pairs, there should be no good grounds for an inductive effect. We wished to use the same method to test applicability of this remarkable finding to the *meta*- and *ortho*-isomers.

Exner's equation[3]

$$\sigma_{para} - \sigma_{meta} = 0.12 \cdot \sigma_{para}$$

should apply to the *meta*-compounds, *i.e.* σ_{meta} of 'onium phosphorus should be somewhat smaller than σ_{para} but still around +1. Eleven phosphorus-free *meta*-substituted toluenes *m*-$X-C_6H_4CH_3$ without an electron pair on X [X = NO_2, CN, CHO, $COOC_2H_5$, $COOCH_3$, COOH, $COCH_3$, $CH=CH-C_6H_5$, H, CH_3, or $C(CH_3)_3$] gave a markedly poorer correlation in the plot of $\delta(CH_3)/\sigma_{meta}$ of X than did the *para*-compounds; the best linear relation [equation (1)], with $r = 0.850$, is according to *Jaffé*[4] less than "satisfactory"

and thus gives only approximate σ_{meta}-values for new substituents; in view of this low accuracy it must be considered as almost identical with the corresponding relation for the *para*-series. The points for substituents carrying a free electron pair (X = F, Cl, Br, I, OH, OCH_3, NH_2, $NHCOC_6H_5$) again lie under the best straight line, so that equation (1) gives only minimal values for such groups. For all the substituents studied, σ_{meta} is somewhat lower than σ_{para}, but for 'onium-phosphorus it has the expected value of *ca.* +1. (It should be noted that in compounds containing several tolyl groups the part of the molecule considered as substituent in one $CH_3C_6H_4$ group is not quite the same in the *para*- as in the *meta*-series.)

$$\delta = 0.135 \cdot \sigma_{meta} + 2.338 \quad (1)$$

$r = 0.850$, for δ $s = \pm 0.024$ ppm, for σ $s = \pm 0.15$ σ unit

$$\delta = 0.323 \cdot \sigma_{ortho} + 2.321 \quad (2)$$

$r = 0.996$, for δ $s = \pm 0.018$ ppm, for σ $s = \pm 0.05$ σ unit

For anilines $X-C_6H_4NH_2$ *Lynch, Macdonald,* and *Webb*[5] found an excellent correlation between $\delta(NH_2)$ and σ of X, into which the *ortho*-substituted compounds fit if σ_{ortho} is put equal to σ_{para}. In analogy to this, eleven toluenes o-$X-C_6H_4CH_3$ with or without free electron pairs on X, including o-$CH_3C_6H_4SO_2Cl$ (with the σ-value evaluated from the NMR spectrum of the *para*-isomer[2]) give an "excellent"[4] regression line [equation (2), X = SO_2Cl, NO_2, CN, I, Br, Cl, H, CH_3, OCH_3, OH, NH_2] which, however, is not followed by any C=O compound (X = $NHCOCH_3$, $OCOCH_3$, COOH, $COOC_2H_5$; such substituents were not investigated in the aniline series[5]). Unlike the case for the anilines, the line for the *ortho*-compounds is steeper than those for the *para*- and *meta*-compounds. For phosphine-, phosphine-oxide-, and phosphine-sulfide-phosphorus, equation (2) leads to positive Hammett constants in good accord with σ_{para}-values determined previously[6] from the pK values of *para*-phosphorus-substituted benzoic acids. However, σ is unexpectedly small for 'onium-phosphorus. *ortho*-Tolylphosphonium salts do not differ from their *para*- and *meta*-isomers in ion pair association but do in a staggering of the tolyl groups[7] as in tri-*ortho*-tolylphosphine[8]. Thus a steric hindrance to mesomerism may express itself in the low δ values.

Table 1. Chemical shifts δ (ppm) of the NMR signals of the CH_3 protons of *m*- and *o*-$X-C_6H_4CH_3$ [*ca.* 0.9 mole of $CH_3C_6H_4$ group/1000 g of $CDCl_3$; $(CH_3)_4Si$ as internal standard] and Hammett constants of the substituents X.

X [a]	*m*-$X-C_6H_4CH_3$		*o*-$X-C_6H_4CH_3$	
	δ [b]	σ_{meta}	δ [b]	σ_{ortho}
$-P(C_6H_5)_2$	2.242	>−0.72	2.385	+0.20
$>PC_6H_5$	2.279	>−0.43	2.394	+0.23
>P−	2.308	>−0.21	2.402	+0.25
$-P(O)(C_6H_5)_2$	2.325	−0.09	2.454	+0.41
$>P(O)C_6H_5$	2.354	+0.13	2.521	+0.61
>P(O)−	2.358	+0.17	2.521	+0.61
$-P(S)(C_6H_5)_2$	2.296	−0.32	2.392	+0.22
$>P(S)C_6H_5$	2.350	+0.09	2.475	+0.47
>P(S)−	2.367	+0.20	2.390	+0.21
$-P^{\oplus}(CH_3)(C_6H_5)_2$ $I^{\ominus}$	2.492	+1.13	2.325	+0.01
$>P^{\oplus}(CH_3)C_6H_5$ $I^{\ominus}$	2.483	+1.09	2.392	+0.22
$>P^{\oplus}(CH_3)-$ $I^{\ominus}$	2.492	+1.13	2.421	+0.31
$-N(C_6H_5)_2$	2.208	>−0.94	2.029	−0.89
$>NC_6H_5$	2.238	>−0.72		
>N−	2.250	>−0.65		
>NH	2.292	>−0.35		

[a] Multivalent groups carry a corresponding number of $CH_3C_6H_4$ groups.
[b] The third decimal place is estimated.

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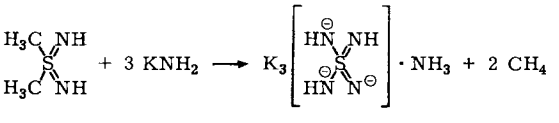
Diaminosulfur Diimide, the Aza Analog of Sulfuric Acid[1]

By *R. Appel* and *B. Ross*[*]

The aza analogs of sulfuric acid and sulfur trioxide have hitherto been missing from the series of isoelectronic oxygen and nitrogen compounds of sulfur. We have now found that a tripotassium salt of diaminosulfur diimide can be prepared by treating *S,S*-dimethylsulfur diimide (sulfodiimine)[2,3] with potassium amide in liquid ammonia. When the reaction is effected above 60 °C in an autoclave two methyl groups are removed quantitatively as methane and replaced by amino groups. Diaminosulfur diimide is then precipitated as its colorless potassium salt *(1)* in small crystals:



(1)

The structure of the tetraazasulfate *(1)* follows from its synthesis, elemental composition, and hydrolysis in a stream of moist nitrogen; in the last-mentioned reaction, three molar equivalents of ammonia are removed and sulfamide is formed:

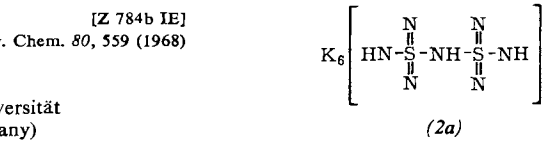
$$K_3[SN_4H_3]\cdot NH_3 + 5\,H_2O \rightarrow O_2S(NH_2)_2 + 3\,KOH + 3\,NH_3$$
(1)

The additional NH_3 in compound *(1)* is very probably present as crystal ammonia and not bound as an ammonium ion. It cannot be exchanged for K^+ by means of an excess of potassium amide, and of the two characteristic IR bands of the NH_4^+ ion[4] at 3340–3030 cm^{-1} and 1480–1390 cm^{-1} only the strong NH stretching vibration at 3220 cm^{-1} is present.

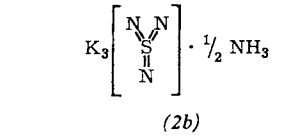
When heated in a stream of dry N_2 to 100 °C, compound *(1)* loses 1.5 moles of NH_3 per mole, and is converted into a yellow highly explosive powder, which is also crystalline; this can be reconverted into *(1)* by liquid ammonia:

$$2\,K_3[SN_4H_3]\cdot NH_3 \underset{\text{liquid } NH_3}{\overset{-3NH_3\,(100\,^\circ C)}{\rightleftharpoons}} K_6[S_2N_6]\cdot NH_3$$
(1) *(2)*

Whether compound *(2)* is potassium di(tetraazasulfate) *(2a)* or the potassium salt of sulfur triimide *(2b)* cannot yet be decided.



(2a)



(2b)

Experimental:

S,S-Dimethylsulfur diimide (4 g) and KNH_2 (8 g) in liquid NH_3 as solvent are heated to 80–100 °C for 10 h in a steel autoclave fitted with a glass lining. The reaction product is washed free of potassium amide with liquid NH_3 under inert conditions. Diaminosulfur diimide *(1)* can be stored indefinitely under nitrogen; it detonates on shock and on contact with water.

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Structure of the Principal Aglycon of Horse Chestnut Saponin[1]

By *W. Hoppe, A. Gieren*, and *N. Brodherr*[*]
also *R. Tschesche* and *G. Wulff*[**]

The seeds of the horse chestnut (*Aesculus hippocastanum* L.) contain a mixture of saponins known as aescin, whose chemical structure has not previously been fully clarified. In particular, the positions of the ester groups were not clear because the acyl groups are readily removed or undergo migration[2]. We have now succeeded in obtaining an aglycon with unchanged ester groups and clarifying its structure by X-ray analysis.

On mild extraction of chestnuts with 2-propanol and subsequent separation on Sephadex an aescin was obtained that was as "genuine" as possible. The sugars were removed from this by hydrolysis with snail enzyme (from *Helix pomatia*), this yielding a mixture made up of esters of barringtogenol C and of protoaescigenin. The principal constituent, a pure protoaescigenin diester *(1a)*, was thence obtained by chromatography on silica gel; it had m.p. 241–252 °C (from benzene), $[\alpha]_D^{20} = +25.6°$ (chloroform). Alkaline cleavage of this product *(1a)* converts it into protoaescigenin and two molar equivalents of acids (acetic acid, tiglic acid, angelic acid, α-methylbutyric acid, and isobutyric acid in the ratio 8:6:4:1:1). The main product *(1b)* of the diester *(1a)* should contain 1 equivalent of acetic acid and 1 equivalent of tiglic acid (angelic acid).

For the three-dimensional X-ray analysis we used monoclinic crystals of *(1a)* obtained from benzene. Crystallographic data are: $a = 22.18_6$ Å, $b = 14.14_5$ Å, $c = 6.82_5$ Å, $\gamma = 69.0_7°$, $d_{obs} = 1.18$ g·cm^{-3}. The space group is $P\,2_1$. The asymmetric unit contains one molecule of $C_{37}H_{58}O_8$ and one of C_6H_6 ($d_{calc} = 1.18$ g·cm^{-3}). All the reflections with $\theta \geqslant 70°$ were measured with Cu–K_α radiation on our single-crystal diffractometer ($\theta/2\theta$ scan, 5-point measurement). Of 4142 independent reflections, only 562 were unobserved ($J < 2\sigma J$).

We were able to locate 15 structurally connected atoms by a combination of the convolution molecule method, group refinement[3a], and the determination of signs in the centrosymmetrical projection by triple product methods[3b]. The complete structure was solved ($R = 27\%$) by several weighted[3c] Fourier syntheses. Refinement by the method of least squares (full matrix) required overlapping cycles because of the large number of parameters. Difficulties arose through the strongly librating benzene and the disorder in the region of the 21-acyl group; these were largely overcome by difference Fourier syntheses, and the isotropic refinement closed with $R = 18.1\%$. On anisotropic calculation the R value then decreased to 10.1%. In the last cycle the change in the parameters was on average 0.12 of the respective standard deviation. We are continuing the refinement of the structure. In one difference Fourier synthesis we have found most of the expected hydrogen atoms.

Figure 1 shows the molecular structure. The constitution and configuration of protoaescigenin agree with the recently revised data in the literature[7]. The acetyl group is on C-22, and the unsaturated acyl group (mostly tigloyl) is on C-21.

The conformation of the ring system is determined mainly by the interactions of the axial substituents. Ring D is flattened by sp^2 hybridization at C-13 and by the α-axial substituents on C-14, C-16, and C-18, which diverge from one another.

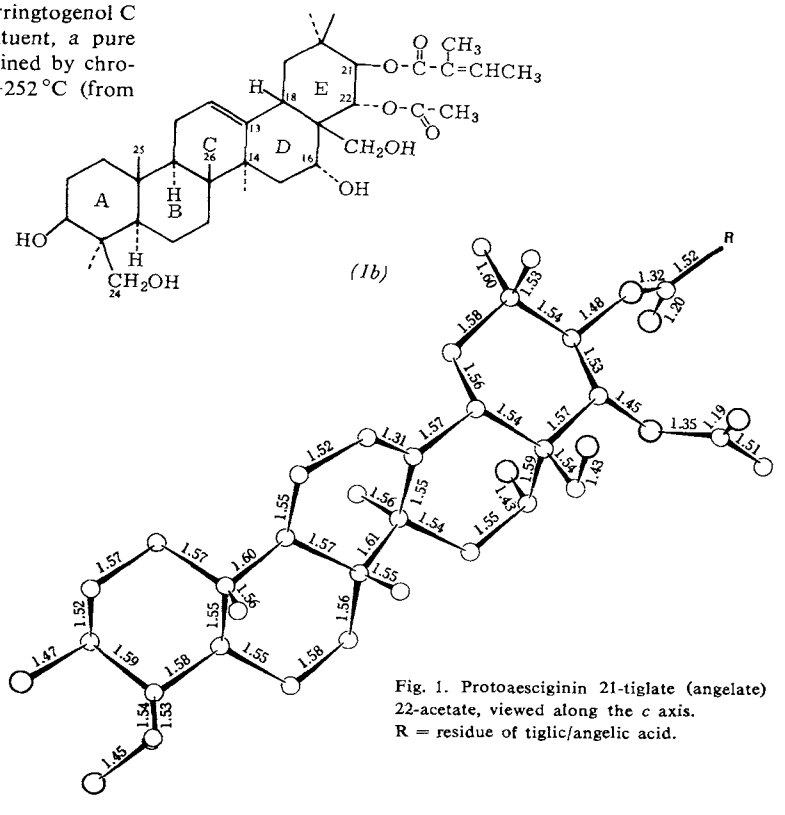

Fig. 1. Protoaesciginin 21-tiglate (angelate) 22-acetate, viewed along the *c* axis.
R = residue of tiglic/angelic acid.

As a consequence the *cis*-decalin system D/E also flattens out appreciably. Rings A, B, and C have a form that minimizes mutual repulsions of atoms C-24, C-25, and C-26. Apart from solving the special problems concerning the aglycon of aescin these results lay the foundation for the stereochemistry of various triterpenes that have recently been correlated chemically with protoaescigenin.

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[3a] We thank Dr. *Ch. Scheringer*, Aachen, for provision of his new program [4].

[3b] We thank *S. Hechtfischer*, München, for help in use of his program for the triple product method [5].

[3c] Our own modification of a program following *Sim*'s method [6].

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First Synthesis of a Thioacylium Cation

By *E. Lindner* and *H.-G. Karmann* [*]

In principle acylium salts are accessible in two ways, namely by treatment of acyl fluorides with BF_3 [1] or MF_5 [2] (M = P, As, or Sb) or by reaction of the anhydrous complexes $Ag[MF_6]$ with acyl chlorides or bromides in polar, aprotic solvents [2, 3]. However, since the corresponding thio compounds have been unknown, except for the perfluorinated thioacyl fluorides and chlorides [4] that polymerize rapidly, our initial investigations concerned the behavior of C_6H_5CSCl *(1)*, a compound that has long been accessible, with $Ag[SbF_6]$ *(2)* in dry, liquid SO_2. Thiobenzoylium hexafluoroantimonate(v) *(3)* is thereby obtained if stoichiometric amounts of *(1)* and *(2)* are used at −40 °C:

$$\underset{(1)}{C_6H_5CSCl} + \underset{(2)}{Ag[SbF_6]} \xrightarrow{-40\,^\circ C} \underset{(3)}{[C_6H_5CS][SbF_6]} + AgCl$$

The thio complex *(3)* is extremely hygroscopic but remarkably stable at room temperature; it dissolves very readily in liquid SO_2 with a deep reddish-brown color but with decomposition in other polar solvents such as acetone or alcohols. The ionic nature of *(3)*, whose composition is proved by elemental analysis, could be proved by measurement of the concentration- and temperature-dependent conductivity in liquid SO_2 (equivalent conductivity at −50 °C: $v = 376.5$ l·mole^{-1}; $\mu = 80.9\ \Omega^{-1}\cdot cm^2\cdot mole^{-1}$). Further, the IR spectrum proves that *(3)* exists as an ion pair: in comparison with *(1)*, whose ν(C−S) vibration appears at 1250 cm^{-1}, the band for the C−S stretching vibration of the $[C_6H_5CS]^+$ cation *(3)* is shifted to shorter wavelengths [1332 (vs) cm^{-1}]. The satellite of varying intensity (w−m) at 1355 cm^{-1} is probably to be ascribed to decomposition that must have occurred after the thin film of substance had been placed on the AgCl window for the measurement. The IR-active, three-fold degenerate SbF_6 stretching vibration of the species T_{1u} absorbs, as expected, at 673 (vs) cm^{-1}. The $[C_6H_5CS]^+$ cation can thus be said to exist mainly in two mesomeric limiting forms, which have approximately equal importance

$$H_5C_6\text{-}C{\equiv}\overset{\oplus}{S}: \longleftrightarrow H_5C_6\text{-}\overset{\oplus}{C}{=}S:$$

so that the mean bond order for C−S is 2.5. Further limiting forms are obtained by including the benzene nucleus in the mesomerism. Stabilization of the cation *(3)* thus follows from delocalization of the positive charge.

A purely chemical proof that a thiobenzoylium cation occurs in compound *(3)* was also obtained. When *(3)* is treated with anhydrous benzene at temperatures higher than 6 °C and the reaction mixture is worked up as for Friedel-Crafts syntheses, thiobenzophenone *(4)* is obtained:

$$\underset{(3)}{[C_6H_5CS][SbF_6]} + C_6H_6 \rightarrow \underset{(4)}{(C_6H_5)_2CS} + H[SbF_6]$$

The product can be identified by IR spectroscopy [ν(C−S) = 1226 cm^{-1}], as well as by preparation of the 2,4-dinitrophenylhydrazone, m.p. 238 °C. Already hydrolyzed *(4)* was purified chromatographically and worked up to give benzophenone [ν(C−O) = 1666 cm^{-1}; m.p. 48 °C], the total yield being *ca.* 20%.

This reaction may constitute the first synthesis of a thioketone by the Friedel-Crafts method.

Experimental:

Thiobenzoylium hexafluoroantimonate(v) *(3)*: Very pure $AgSbF_6$ *(2)* (3.44 g, 10 mmole) is dissolved in liquid SO_2 (*ca.* 100 ml) and treated at −40 °C with a solution of $C_6H_5CSCl_2$ *(1)* (1.56 g, 10 mmole) also in liquid SO_2 (*ca.* 100 ml) and the mixture is stirred vigorously for 3 h. After filtration, the solvent is removed at −50 °C under high vacuum. The yield is almost quantitative.

Thiobenzophenone *(4)* and benzophenone: An excess of benzene is added to *(3)* (3.5 g, 10 mmole) and the reaction mixture is allowed to stand for about 2 days. The mixture is then shaken rapidly with acidified ice water and the deep blue organic phase is separated off and dried as quickly as possible. After the benzene has been removed under vacuum, a blue-violet product can be separated off, which proves to be thiobenzophenone *(4)*, m.p. 50 °C. If the remaining crude product is dissolved in ether and hydrolyzed with water for a few hours, benzophenone is obtained. Neutral Al_2O_3 ("Woelm") was used for chromatographic purification of the product.

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^{13}C-Experiments on Carbon Skeleton Rearrangements: Automerization of Naphthalene

By *H. A. Staab* and *M. Haenel* [*]

In investigations of rearrangements of organic compounds using ^{14}C-tracers, localizing the label requires most frequently a series of degradative reactions which might give rise to errors. On the other hand, labeling with ^{13}C which has a nuclear magnetic moment permits the non-degradative determination of the label in the intact molecule on the basis of (a) the ^{13}C−NMR spectra, (b) the ^{13}C satellites of ^1H−NMR

spectra, and (c) the ^{13}C hyperfine structure of ESR spectra (with compounds which can be converted into radicals).

Balaban and *Fărcaşiu*[1] recently deduced from activity determinations on degradation products that treatment of [1–^{14}C]-naphthalene with aluminum chloride in benzene for 2 hours at 60 °C leads to complete rearrangement of the carbon skeleton and thus to a statistical scrambling of the ^{14}C label over all ten positions of naphthalene. Because of the far reaching consequences of this result we have tried to detect this "automerization" directly in ^{13}C-labeled naphthalene by the three resonance methods mentioned above.

By analogy with known methods[2], [1–^{13}C]-naphthalene was prepared by the following route: Treatment of the Grignard compound of 1-bromo-3-phenylpropane with [^{13}C]-carbon dioxide (from barium [^{13}C]carbonate; 50.9% enriched) yielded [1–^{13}C]-4-phenylbutyric acid, which was cyclized to [1–^{13}C]-1-tetralone; Clemmensen reduction and catalytic dehydrogenation of the [1–^{13}C]-tetralin afforded [1–^{13}C]-naphthalene (yield 55% based on barium [^{13}C]carbonate). The ^{13}C enrichment was determined mass spectrometrically to be 50.6%. The selective α-labeling follows from the intensities of the ^{13}C satellites of the ^{1}H–NMR spectrum considering the known assignments of the proton resonance signals[3]; it is further confirmed by the analysis of the ESR spectrum of the radical ion obtained with potassium in 1,2-dimethoxyethane[4].

The automerization experiments were carried out with 2 g quantities of [1–^{13}C]-naphthalene in benzene using aluminum chloride according to the method proposed by *Balaban* and *Fărcaşiu*[1]; the yields of re-isolated and purified naphthalene were of the same order as those obtained in the above authors' experiments (45%).

The ^{13}C–NMR spectra[5] were identical before and after the automerization experiment. Intensity ratios and splitting pattern of the ^{13}C satellites in the ^{1}H–NMR spectrum (100 MHz) were in complete agreement with those of the starting material. That a statistical distribution of ^{13}C labeling on the α, β, and γ positions did *not* in fact occur followed also from the ESR spectrum of the radical anion, which, likewise, was unchanged after the automerization experiment: no decrease in intensity in the lines attributed to the ^{13}C coupling at the α-position was noticeable; the β and γ ^{13}C satellites appear only in intensities corresponding to the natural ^{13}C abundance.

A degree of automerization of the order of 5% would have been clearly detected by these methods. Thus, investigations with the non-degradative ^{13}C method do not confirm the results in the literature[1] on the automerization of naphthalene[6].

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[1] *A. T. Balaban* and *D. Fărcaşiu*, J. Amer. chem. Soc. *89*, 1958 (1967); Tetrahedron Letters *1968*, 1273.

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[5] We are grateful to Dipl.-Chem. *U. Jentschura*, Berlin, for the ^{13}C–NMR spectra. Particular thanks are also due to Prof. *K. H. Hausser*, Heidelberg, for valuable discussions.

[6] Note added in proof (July 2, 1968): According to a personal communication dated June 20, 1968, *A. T. Balaban* and coworkers have also independently come to the conclusion that previous data concerning the automerization of naphthalene can no longer be considered valid.

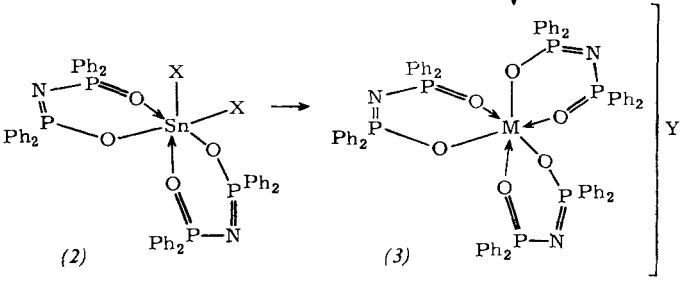
Tris(imidodiphosphinato) Cationic Complexes of Silicon, Germanium, and Tin[1]

By *A. Schmidpeter* and *K. Stoll*[*]

Whereas cyclic phosphazenes and siloxanes have long been known, rings containing both such units have not yet been prepared. Compounds *(3)*, M = Si, Y = Cl, or Br, which contain the ring system of a 1,3,5,4,6,2-dioxazadiphosphasiline, are formed on treatment of bis(diphenylphosphinyl)-imine *(1)* with $SiCl_4$ or $SiBr_4$. Three halogen atoms are always replaced independently of the proportions of the reactants and of the conditions. The remaining halogen is ionically bound; it is built into complex halogen anions without change in the IR spectrum and is exchanged for nitrate on reaction with $AgNO_3$. The tricyclic structure of the cation follows from the equivalence of all the phosphorus atoms that is detected in the ^{31}P–NMR spectrum; three edges of the central SiO_6 octahedron each carry a phosphazene bridge, and 12 phenyl groups form the periphery of the ion.

$$HN(Ph_2PO)_2 + MX_4 \quad (M = Si, Ge)$$

(1)



(2) *(3)*

(2a), X = Cl
(2b), X = Br
(2c), X = I

(3), M = Si, Y = Cl (decomp. 250 °C)
Br$_3$ (yellowish-orange, m.p. 360 °C decomp.)
SbCl$_6$ (m.p. 355 °C decomp.)
CuCl$_3$ (red, m.p. 305 °C decomp.)
NO$_3$ (m.p. 250 °C)

M = Ge, Y = Cl (m.p. 264 °C)
SbCl$_6$ (m.p. 315 °C decomp.)
CuCl$_3$ (pink, m.p. 320 °C decomp.)

M = Sn, Y = Cl (m.p. 178 °C)
I (m.p. 380 °C)
ICl$_2$ (orange, m.p. 279 °C)
I$_3$ (brown, m.p. 365 °C decomp.)
I$_{8/2}$ (black, m.p. 370 °C decomp.)
Br$_3$ (yellowish-orange, m.p. 284 °C)
SbCl$_6$ (m.p. 270 °C)
CuCl$_3$ (red, m.p. 322 °C decomp.)
HgI$_3$ (pale yellow, m.p. 360 °C decomp.)
NO$_3$ (m.p. 332 °C)
ClO$_4$ (m.p. 400 °C decomp.)
MnO$_4$ (violet)
OH (m.p. 188 °C)

$GeCl_4$ reacts like the silicon halides in boiling tetrachloroethane, but there is no reaction at 25 °C. Reaction of *(1)* with $SnCl_4$ or $SnBr_4$ is different[2]; in these cases adducts are first formed that disproportionate readily to the bis(imidodiphosphinato)tin dihalides *(2)*; the third imidodiphosphinate group can be introduced into *(2a)* only by means of $Na[N(Ph_2PO)_2]$ at elevated temperature. Reaction of *(2a)* with $AgNO_3$ results in further disproportionation and gives tris(imidodiphosphinato)tin nitrate *(3)*, M = Sn, Y = NO_3.

The tris(imidodiphosphinato)tin cation is formed remarkably easily from *(2c)* either on heating or under the action of basic reagents such as $NaOCH_3$ or of electrophiles such as I_2, CH_3I, HgI_2, or $AgNO_3$. Its preferential formation corresponds to a high stability; the iodide *(3)*, M = Sn, Y = I, is

not attacked by boiling sodium methoxide solution (but is attacked by NH_3) and is merely converted into the perchlorate by an excess of anhydrous $HClO_4$.

The hydrophobicity and the considerable size resulting from their structure render these cations excellently suited for extraction of weakly hydrated anions from the aqueous phase. When shaken with *(3)*, M = Sn, Y = NO_3, in CH_2Cl_2 an aqueous solution of $KMnO_4$ is completely decolorized. Addition of ether to the methylene dichloride solution then precipitates the permanganate *(3)*, M = Sn, Y = MnO_4, as violet crystals. Cations with M = Si or Ge behave similarly but are slowly hydrolyzed in the process. The size of the cation may be responsible for the fact that with an excess of iodine *(3)*, M = Sn, Y = I, gives, not only a triiodide, but also an octaiodide corresponding to Cs_2I_8 [3].

Shielding of the phosphorus in *(3)* decreases with increase in the acceptor capacity of the central atom:

(3), Y = Cl, M =	Si	Ge	Sn
$\delta^{31}P$	−29.4	−31.3	−35.7 ppm ref. to 85% H_3PO_4

The resonance signals are shifted strongly downfield from those for the imidodiphosphinate anion (−12.7 ppm [4]); they lie in the same region as that of the dimethylated cation $[N(Ph_2POCH_3)_2]^+$ (−35.0 ppm [4]), thus indicating strong involvement of the ligands.

Experimental:

(3), M = Si, Ge: A suspension of compound *(1)* (12.5 g) in 100 ml of a suitable solvent (CH_2Cl_2 for M = Si, s-$C_2H_2Cl_4$ for M = Ge) is treated with 0.01 mole of MX_4, X = Cl, Br. HX is liberated and clear solution results on standing or after several hours' refluxing, respectively. Compounds *(3)*, Y = X, crystallize out quantitatively from this solution on addition of ether.

(3), M = Sn: Compound *(2)* (X = Cl, I [2]) and $AgNO_3$ is each dissolved in acetonitrile in a molar ratio of 1:2. The hot solutions are combined, precipitated AgX is filtered off, and the filtrate is evaporated to dryness. The residue is dissolved in CH_2Cl_2 and addition of ether to the resulting solution causes crystallization of *(3)*, X = NO_3.

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CONFERENCE REPORTS

Redox Behavior of the Latent Image in Silver Halide Films

By *E. A. Frei* [*]

According to the "silver nucleus theory" latent image specks in photographic silver halide films are small centers consisting of silver atoms. This being so, the question arises: Is the latent image silver more noble or less noble than metallic silver, or are the two equivalent?

To provide an answer, photographic films were treated for ~ 24 h with buffered solutions at variable redox potentials and at a fixed silver equilibrium potential. After development the degrees of blackening were compared with a control (no redox treatment). In such a system only the redox potential can be measured directly with a Pt electrode. The potential measured with a Ag electrode is not an equilibrium potential since a mixed potential is set up at this electrode. The silver equilibrium potential can, however, be measured directly in the special circumstance where the silver potential and the redox potential are equal. It was thus possible to determine the effect of the ions used for buffering on the silver equilibrium potential.

By measuring the redox potential of a Pt electrode coated with gelatine in comparison with an ordinary Pt electrode it was shown that there is no Donnan potential between the swollen gelatine phase and the pure electrolyte solution.

Surprisingly, appreciably more negative redox potentials were obtained in the gelatine phase shortly after its immersion in the buffered solution than existed in the surrounding solution. This temporary depression of the potential shows that in the initial stage of the redox treatment the gelatine phase is more strongly reducing than the pure electrolyte phase, and this was particularly marked for formalin-hardened films.

A series of commercial films (including one with gold-sensitized emulsion) was studied. One that was successively fixed, treated with redox buffers, and physically developed gave the same results as a chemically developed film.

1. For all the emulsions except the gold-sensitized one, no latent image can any longer be developed after redox treatment in a solution whose redox potential equals the silver equilibrium potential.

2. Latent image nuclei formed by longer illumination at correspondingly weaker light intensities exhibit increased stability; also they are partly developed by redox solutions that completely bleach the latent image formed by short exposure.

3. The results with the gold-sensitized emulsion agree with those reported by *Bourdon* and *Bonnerot* [1] and by *Matejec* and *Moisar* [2]: the nuclei were bleached only at redox potentials that were more positive than the silver equilibrium potential.

4. The results described in 1 and 2 can be understood on *Reinders'* [3] and *Hillson's* [4] assumption that the free enthalpy of the latent image is greater than that of massive silver. The difference in free enthalpies lies between 0.04 and 0.07 eV according to the amount of illumination. The stability of the latent image nucleus against external influences, which is surprising in view of its size, can be explained thermodynamically if we assume that the latent image nucleus contains not only silver atoms but also impurities in the form of the components of the sensitivity centers. In this way the free surface enthalpy of the nuclei is strongly reduced and the nuclei themselves are thus protected against external attack.

Photographic Colloquium at Zürich (Switzerland), February 8, 1968 [VB 151 IE]
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[1] *J. Bourdon* and *A. Bonnerot*, Sci. Ind. photogr. *30*, 205 (1959).

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[3] *W. Reinders*, J. physic. Chem. *38*, 783 (1934).

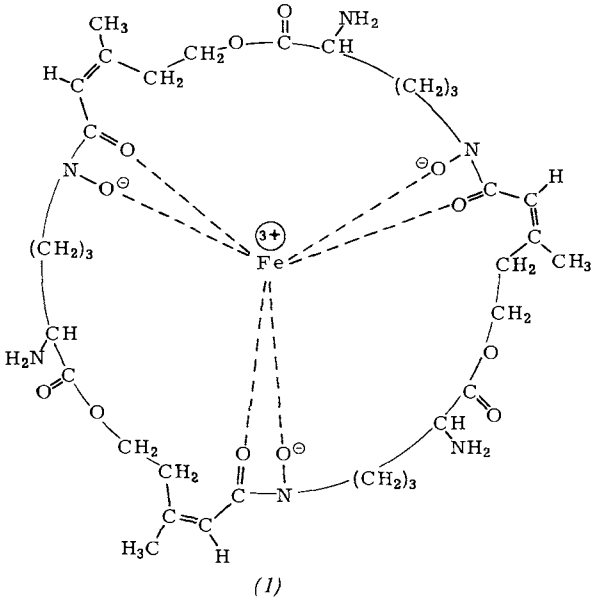
[4] *P. J. Hillson*, J. photogr. Sci. *6*, 97 (1958).

New Sideramins from Molds

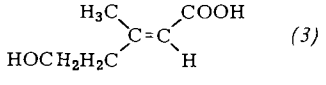
By *H. Diekmann* [*]

Along with known sideramins, other hydroxamic acids have been found [1] in mold cultures (*Fusarium* spp., *Penicillium* spp.) grown with a deficiency of iron, and after their extraction and purification their structures have been elucidated. Fusigen *(1)* is the iron(III) complex of a basic hydrophilic trihydroxamic acid, in which three molecules of fusarinin are joined together in a ring by means of ester groups [2]. Hydrolysis of fusigen under mild conditions gives first an open-chain trihydroxamic acid (fusigen B), and then fusarinin and a dihydroxamic acid (fusigen C) by cleavage of a further ester group. The instability of the hydroxamic acid grouping in fusarinin eventually has the result that *cis*-5-hydroxy-3-methyl-2-pentenoic acid *(2)* can be extracted from the cultures [3].

Other sideramins that have not yet been isolated contain *trans*-5-hydroxy-3-methyl-2-pentenoic acid *(3)* and are related to coprogen. This acid *(3)* occurs to the extent of about 10 mg/l in cultures of some molds (*Penicillium variabile*, *Spicaria* spp., *Neurospora crassa*, *Myrothecium roridum*, *Myrothecium verrucaria*, *Fusarium* spp.) and can be prepared in good yield by isomerization of *(2)*. After purification by Craig distribution and chromatography on silica gel (solvent: chloroform/ethanol/formic acid, 94.5:5:0.5, v/v), the acid *(3)* was crystallized as its *N,N'*-dibenzylethylenediammonium salt (m.p. 64 °C). UV, IR, and NMR spectra, and also thin-layer chromatography, prove its structure.



(1)



(3)

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German version: Angew. Chem. *80*, 569 (1968)

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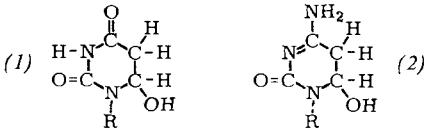
Investigations of the Chemical Causes of Biological Irradiation Damage

By *E. Fahr* [*]

The action of UV radiation on nucleic acids and their components involves, in the main, two photochemical reactions: formation of so-called "reversible irradiation products" and dimerization of pyrimidine bases to "dimeric pyrimidines".

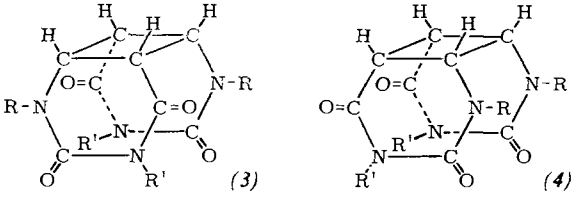
We have isolated the reversible irradiation products of uracil, uridine, and uridylic acids and have proved their structures to be *(1a–e)* by independent syntheses. By an analogous route we have proved that the very unstable reversible radiation products of cytosine, cytidine, and cytidylic acid have structures *(2a–c)*. Their radiation products *(2)* pass into *(1)* by deamination in a dark reaction. The photochemical formation of 5,6-dihydro-6-hydroxycytosine derivatives *(2)* in the DNA and their subsequent deamination to *(1)* are likely to be the cause of the mutations induced by UV radiation.



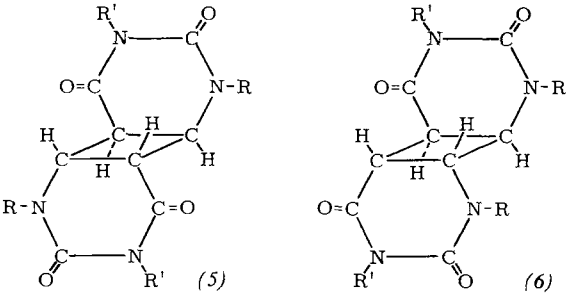
(1) *(2)*

(a): R = H
(b): R = Ribosyl
(c): R = Ribosyl-2'(3')-phosphate
(d): R = Ribosyl-5'-phosphate
(e): R = Ribosyl-5'-triphosphate

By degradation to cyclobutane derivatives we have shown that structure *(4a)* applies to the dimeric uracil that is formed on UV irradiation in an ice matrix. The *trans*-dimeric uracil *(5a)* was synthesized chemically.



(3) *(4)*



(5) *(6)*

(a): R = R' = H
(b): R = Ribosyl, R' = H
(c): R = R' = CH_3

Also the four possible dimeric dimethyluracils *(3c)–(6c)* have been prepared, as well as other dimers.

When we studied the action of ionizing radiation (radiation dose *ca.* 500000 rad/min) on aqueous degassed solutions of nucleic acid components we obtained a large number of radiation products. Pyrimidine components were attacked mainly by H atoms and/or OH radicals at the C=C double bond. Irradiation of cytosine, cytidine, and cytidylic acid showed that the mutations caused by ionizing radiations probably arise owing to the following processes: attack by H atoms and OH radicals on the C=C bond of the cytosine

part of the DNA with formation of derivatives of structure *(2)* and then deamination to *(1)*.

UV mutations and mutations induced by ionizing radiation can thus be interpreted by means of the same primary irradiation product.

Lecture at Saarbrücken (Germany) on February 9, 1968 [VB 152 IE]
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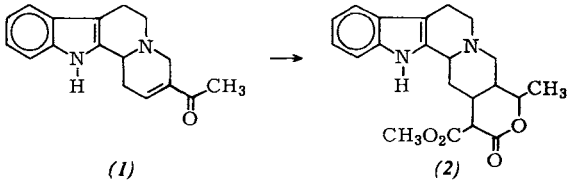
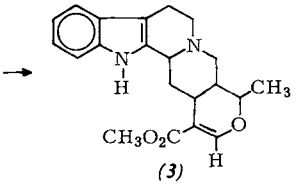
Synthesis and Configuration of Heterocyclic Indole Derivatives. The Stereoselective Total Synthesis of DL-Akuammigine and DL-Tetrahydroalstonine

By *E. Winterfeldt* [*]

The α,β-unsaturated ketone *(1)* is useful for synthesis of heterocyclic indole alkaloids of type *(3)*. Michael addition of malonic ester and subsequent reduction by $BH_4^{\ominus}$ affords the lactones of type *(2)*, which can be converted into *(3)* by reduction and loss of water [1].

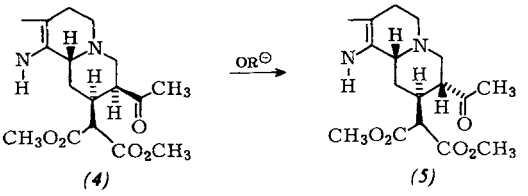


(1) *(2)*



(3)

In the stereoselective preparation of *(2)* the Michael addition to *(1)* occurs with simultaneous formation of a *cis*-quinolizidine system. Compound *(4)*, with the axial acetyl group, is the product obtained under kinetic control and on treatment with alkali affords the thermodynamically favored product *(5)* containing equatorial substituents.

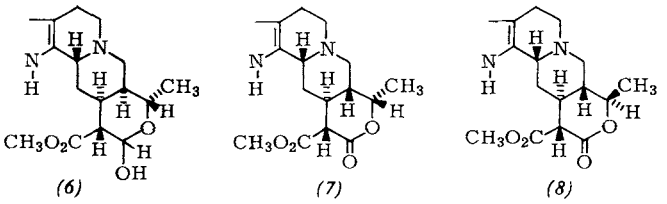


(4) *(5)*

Under thermodynamic control, compound *(5)* is thus obtained stereospecifically.

The keto group can also be reduced stereospecifically. Compound *(4)* reacts with $BH_4^{\ominus}$ to give exclusively *(6)*, whereas compound *(5)* with $BH_4^{\ominus}$ in the cold gives mainly *(7)* but with $Li[AlH_2(OR)_2]$ in tetrahydrofuran gives mainly *(8)*. The configurations follow from the IR and NMR data.

Reduction and dehydration of the sterically homogeneous lactones gives compounds of type *(3)* with the *cis*-quinolizidine system which are convertible into *trans*-quinolizidines by dehydrogenation [with $Pb(OAc)_4$] and subsequent reduction with $BH_4^{\ominus}$. In this way compound *(4)* yields DL-akuammigine stereospecifically and then DL-tetrahydroalstonine by reversal of configuration at C-3.



(6) *(7)* *(8)*

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[1] Cf. *E. Winterfeldt* and *H. Radunz*, Angew. Chem. *79*, 1023 (1967); Angew. Chem. internat. Edit. *6*, 1003 (1967).

Mechanism of the Oxo Synthesis

By *J. Falbe* [*]

Although the oxo reaction (conversion of olefins into aldehydes by CO/H_2) was discovered by *O. Roelen* in 1938 [1] and the annual world capacity of such plants will exceed 1.5×10^6 tons in 1968, the mechanism of the reaction is not yet fully clarified.

Many proposed mechanisms had to be discarded because they could not be brought into accord with the equation set up by *G. Natta et al.* [2] for the kinetics of the reaction:

$$d[\text{Aldehyde}]/dt = k[\text{Olefin}][\text{Co}][p_{H_2}]/[p_{CO}].$$

A reaction route by way of carbonium ions had to be rejected because the carbon chain was not isomerized in the reaction.

A reaction involving radicals is also unlikely because reaction is not hindered by radical-trapping agents such as iodine and sterically hindered phenols.

A scheme proposed by *R. F. Heck et al.* [3] is largely in accord with the kinetics of the oxo reaction:

$$HCo(CO)_4 \rightleftharpoons HCo(CO)_3 + CO \qquad (1)$$

$$HCo(CO)_3 + H_2C{=}CH_2 \longrightarrow H_2C{=}CH_2 \quad (2)$$
$$\downarrow$$
$$HCo(CO)_3$$

$$H_2C{=}CH_2 \rightleftharpoons H_3C{-}CH_2{-}Co(CO)_3 \qquad (3)$$
$$\downarrow$$
$$HCo(CO)_3$$

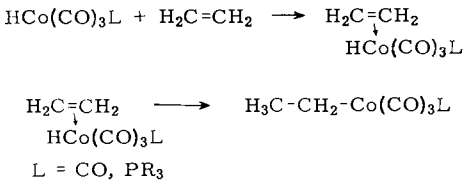
$$H_3C{-}CH_2{-}Co(CO)_3 \underset{-CO}{\overset{+CO}{\rightleftharpoons}} H_3C{-}CH_2{-}Co(CO)_4 \qquad (4)$$

$$H_3C{-}CH_2{-}Co(CO)_4 \rightleftharpoons H_3C{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}Co(CO)_3 \qquad (5)$$

$$H_3C{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}Co(CO)_3 + H_2$$
$$\longrightarrow H_3C{-}CH_2{-}CHO + HCo(CO)_3 \qquad (6)$$

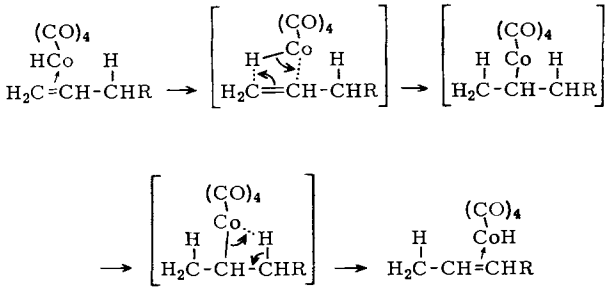
However, all attempts to detect tricarbonylhydridocobalt or alkyltricarbonylcobalt compounds under the conditions of the oxo reaction have failed. Recent investigations also indicate that a course involving (1)–(3) is doubtful since the oxo reaction occurs also at high pressure where the equilibrium in (1) should lie wholly to the left-hand side; against this mechanism is also the fact that the reaction can be carried out in the presence of complexes of the type $HCo(CO)_3PR_3$ in which the metal-carbon bond is so strong that loss of CO and formation of a coordinatively unsaturated carbonyl under the conditions of the reaction seem unlikely.

Equations (7) and (8) are therefore proposed as alternatives to (1)–(4).

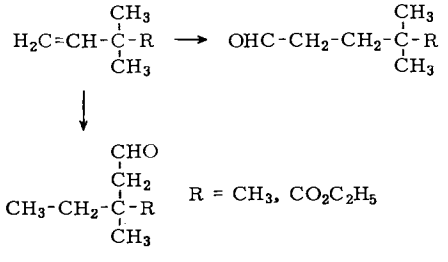


The π-complex formulated in (7) may occur as dsp^3-hybrid in the form of a trigonal bipyramid, in which the hydrogen is bonded as hydride ion in the outer sphere and cobalt has formally a single positive charge. The Co-alkyl compound pictured in (8) may also be a trigonal-bipyramidal dsp^3-hybrid.

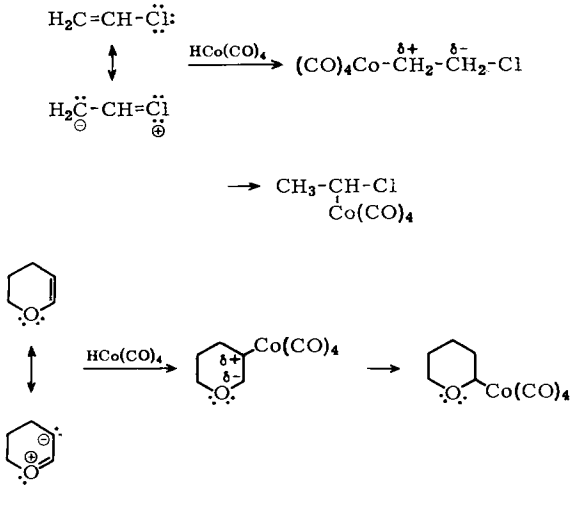
One of the factors promoting conversion of the alkyl into the acyl compound (equation 5) is to be found in the decrease in steric hindrance on the conversion dsp^3 (trigonal bipyramid) → sp^3 (tetrahedral). The mechanism proposed also agrees well with the isomerizations of Co-alkyl and -acyl compounds experimentally established as occurring during the oxo reaction, whereby according to *Orchin et al.* [4] a hydrogen shift from the allyl position occurs.



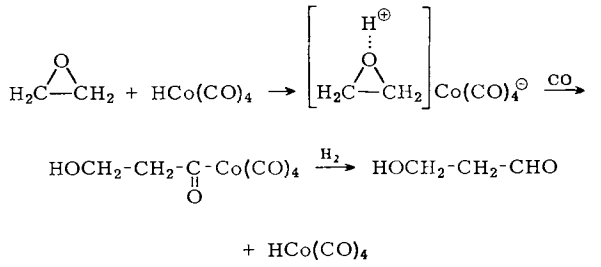
Compounds that do not possess hydrogen in the allyl position do not isomerize.



With vinyl chloride and dihydropyran the primary addition of cobalt to the C=C double bond and the subsequent isomerization occur in different directions:



In most of the known oxo reactions tetracarbonylhydridocobalt reacts as the hydride; it may react as protonic acid in the oxo reaction of epoxides.



Lecture at Berlin on February 12, 1968 [VB 154 IE]
German version: Angew. Chem. *80*, 568 (1968)

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[1] *O. Roelen*, DRP 849548 (1938), Chem. Zbl. *1953*, 927; US-Pat. 2327060 (1943); Chem. Abstr. *38*, 550 (1944); Belg. Pat. 436625 (1939); Chem. Zbl. *1941* I, 1354; French Pat. 860289 (1939), Chem. Zbl. *1941* II, 536; *O. Roelen*, Angew. Chem. *A 60*, 213 (1948); *O. Roelen*, in *K. Ziegler*: Naturforschung und Medizin in Deutschland, Vol. 36, Präparative organische Chemie, Part I. p. 157. Dieterich'sche Verlagsbuchhandlung, Wiesbaden 1948.

[2] *G. Natta, R. Ercoli*, and *S. Castellano*, Chim. e Ind. (Milano) *37*, 6 (1955).

[3] *D. S. Breslow* and *R. F. Heck*, Chem. and Ind. *1960*, 467; *R. F. Heck* and *D. S. Breslow*, J. Amer. chem. Soc. *83*, 4023 (1961).

[4] *L. Karapinka* and *M. Orchin*, J. org. Chemistry *26*, 4187 (1961).

Photolysis and Radiolysis of Carbon Monoxide in the Gaseous, Liquid, and Solid State at 298 °K, 77 °K, and 20.4 °K

By *W. Groth* [*]

In the gas phase CO is excited by light quanta (Kr or Xe resonance wave lengths, I line at 2062 Å, Hg sensitization) or γ-rays first to the $a^3\Pi$-state and then reacts with CO in the ground state to give CO_2 and C_3O_2. Excitation of the $A^1\Pi$ state and of triplet states of CO by the Kr and Xe resonance wavelengths can be detected by fluorescence studies.

Pure liquid CO is not decomposed by the 2062 Å I line. In CO–CH_4 mixtures ethane and acetaldehyde are formed by way of excited CO molecules.

In the γ-radiolysis of CO at 298 °K addition of noble gases shows that ionic reactions do not occur but that electronically excited CO molecules play an important part in the primary process. The dependence of $G(CO_2)$ on the pressure can also be explained by means of excited CO molecules which can pass into another excited state.

Radiolysis of pure liquid CO at 77 °K gives CO_2 with $G(CO_2)$ of 0.22, but no C_3O_2 is formed. In CO-CH_4 mixtures there are formed, besides CO_2 and C_3O_2, also aldehydes, ketene, ethane, and acetylene, whose mode of formation has been clarified by use of isotope techniques. In mixtures of CO and O_2 there are formed in the liquid phase (77 °K) CO_2, C_3O_2, and O_3, but in the solid phase (20.4 °K) only CO_2 and O_3. The dependence of the G values for CO_2, C_3O_2, and O_3 are explained for the liquid phase by assuming various excited states of CO ($A^1\Pi$, higher triplet states, $a^3\Pi$), and for the solid phase by assuming intermediate formation of CO_3.

Lecture at Göttingen (Germany) on February 15, 1968 [VB 155 IE]
German version: Angew. Chem. *80*, 538 (1968)

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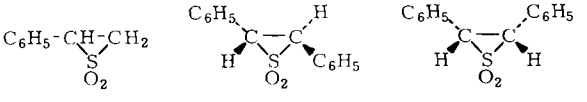
Twelve-membered polyether rings, namely 1,4,7,10-tetraoxacyclododecanes, cyclic tetramers of olefin oxides, have been obtained by *R. J. Kern* from propylene oxide, epichlorohydrin, and 2-ethylethylene oxide by treatment with BF_3 or triethyloxonium tetrafluoroborate, $(C_2H_5)_3OBF_4$, in CCl_4 or CH_2Cl_2. Conversion amounted to 30–40 %. Larger rings and a cyclic dimer were found in smaller amounts; no cyclic trimer was formed. Of the 23 geometric isomers of propylene oxide tetramer, *R. J. Katnik* and *J. Schaefer* detected 22 by gas chromatography, and by NMR and mass spectroscopy. / J. org. Chemistry *33*, 384, 388 (1968) / –Ma. [Rd 854 IE]

Aminotransferase activity of thermally prepared polylysine *(1)* has been observed by *G. Krampitz, S. Baars-Diehl, W. Hass*, and *T. Nakashima*. *(1)* catalyzes the transfer of amino groups of urea to α-oxoglutaric acid in the presence of Cu ions (pH optimum: 7.0). The transamination follows Michaelis-Menten kinetics. Depolymerization of *(1)* causes loss of the aminotransferase activity. The results contribute to clarification of the way in which the first enzymes may have been formed under prebiological conditions. / Experientia *24*, 140 (1968) / –Ma. [Rd 849 IE]

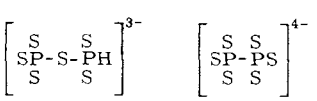
Decomposition of the thiirane 1,1-dioxides (episulfones) *(1)–(3)* at room temperature was studied by *F. G. Bordwell, J. M. Williams Jr., E. B. Hoyt Jr.*, and *B. B. Jarvis*. These compounds decompose in a first order reaction to styrene or stilbene and SO_2. The rate of decomposition depends greatly on the ionizing power of the solvent. The solvolytic decomposition of *(2)* and *(3)* is stereospecific. In the presence



(1) *(2)* *(3)*

of methoxide (faster decomposition), however, *trans*-stilbene is formed from both *(2)* and *(3)*. Deuterium-exchange experiments showed that *(3)* first rearranges to *(2)* and that this finally decomposes slowly by reaction with the methoxide ion. The reaction is held to proceed by way of diradicals. / J. Amer. chem. Soc. *90*, 429 (1968) / –Kr. [Rd 841 IE]

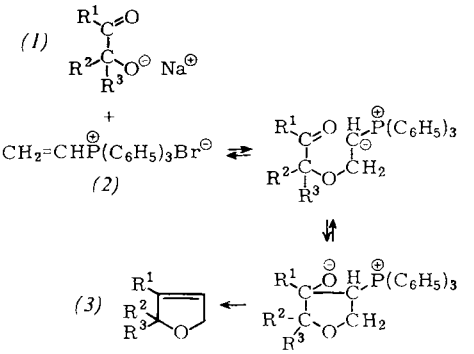
Sodium hexathiohypophosphate, $Na_4P_2S_6 \cdot 6H_2O$, a salt of a new acid of phosphorus has been prepared by *H. Falius* by the dropwise addition of PCl_3 to a solution of Na_2S in an open vessel (colorless, birefringent monoclinic crystals; a = 20.3, b = 7.1, c = 23.3 Å; $\alpha = \beta = \gamma = 90°$). Of the two possible structures *(1a)* or *(1b)* of the anion, only *(1b)* is



(1a) *(1b)*

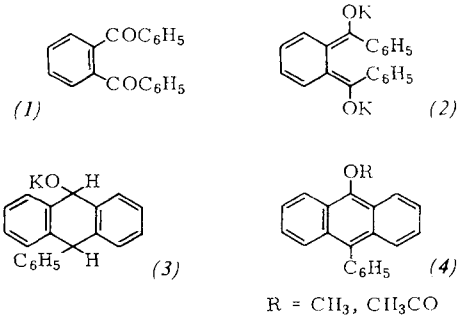
compatible with the facts that sulfur-free hypophosphate is formed with H_2O_2/NaOH, and diphosphate(v) with Br_2/$NaHCO_3$. In agreement with this, the NMR spectrum contains only one signal. The ion is very stable in aqueous solution; it forms colored precipitates with a number of heavy metals. / Z. anorg. allg. Chem. *356*, 189 (1968) / –Kr. [Rd 871 IE]

A general synthesis of 2,5-dihydrofurans *(3)* has been provided by *E. E. Schweizer* and *J. G. Liehr*. The sodium salt of an α-hydroxy ketone *(1)* is treated in DMF with triphenylvinyl-



phosphonium bromide *(2)* at room temperature or with heating, and the mixture is decomposed with water. The yields depend markedly on the purity of the starting materials. / J. org. Chemistry *33*, 583 (1968) / –Ma. [Rd 846 IE]

Formation of anthracene derivatives on treatment of *o*-dibenzoylbenzene *(1)* with potassium in the absence of air was noted by *B. J. Herold* and *H. E. Faustino*. Decomposition of the reaction mixture with CH_3I or acetyl chloride gave the compounds *(4)* in *ca.* 50 % yield. The reaction presumably involves reduction by the metal and intramolecular addition to



(1) *(2)* *(3)* *(4)*

R = CH_3, CH_3CO

the quinone methide *(2)* and to the intermediate *(3)*, whence *(4)* is formed by elimination. 9,10-Dimethoxy- and 9,10-diacetoxy-anthracene were formed as by-products by loss of a phenyl group as phenylpotassium. / Tetrahedron Letters *1968*, 467 / –Ma. [Rd 852 IE]

A carbon atom at the center of a Ru_6-octahedron has been located in $Ru_6C(CO)_{14}C_6H_3(CH_3)_3$ by X-ray crystallography. *R. Mason* and *W. R. Robinson* found that the edge length of the Ru_6C cluster (Ru–Ru distance) is 2.88 Å. In the Ru_6-octahedron, which is only slightly deformed, the Ru–C distance is 2.04 Å, the maximum deviation being 0.16 Å (σ = 0.04 Å). The coordination number of all the Ru atoms is 8 [4 Ru, 1 C, 3 CO, or $C_6H_3(CH_3)_3$ as nearest neighbors]. One CO group is in a bridging position. Of the combination of six d_{z^2} orbitals of the Ru atom, those with A_{1g} and T_{1u} symmetry can overlap with the s and p orbitals of the central C atom. / Chem. Commun. *1968*, 468 / –HB. [Rd 859 IE]

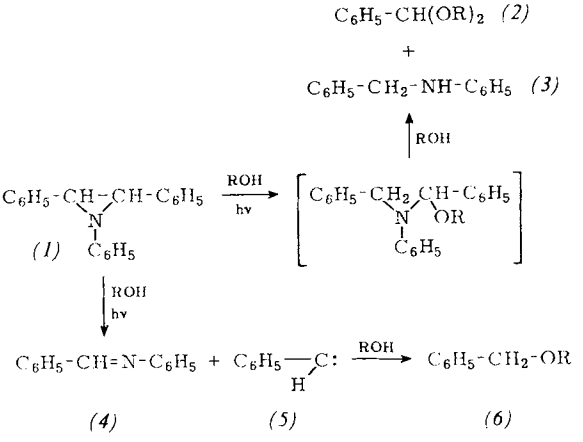
$OsOF_5$, the first compound with heptavalent Os, has been prepared by *N. Bartlett* and *N. K. Jha* as the main product (> 90 %) of the fluorination of OsO_2 at 250 °C. It is also

formed, alongside OsF_6, in the reaction of osmium with a F_2/O_2 mixture. $OsOF_5$ is a volatile, emerald green crystalline substance, orthorhombic below 32.5 °C and cubic above 32.5 °C; it is characterized by m.p. 59.2 °C and b.p. 100.6 °C, and has a temperature-independent magnetic moment of 1.47 BM (Θ = 6 °K). The vibrational spectrum is similar to those of $ReOF_5$ and IOF_5, and suggests a C_{4v} symmetry in the vapor phase. X-ray crystallographic analysis by *N. Bartlett* and *J. Trotter* indicates for the orthorhombic phase a distorted octahedral symmetry of $OsOF_5$ with the following distances: OsO 1.74, *trans*-OsF 1.72, *equatorial*-OsF 1.76 (2x), and 1.80 Å (2x) (± 0.03 Å for all). The unpaired electron of Os is antibonding; it is presumably located in the plane perpendicular to the OsO axis and is responsible for the weakening of the equatorial OsF bonds. / J. chem. Soc. (London) *A 1968*, 536; 543 / –HB. [Rd 860 IE]

Electrical properties of linear polyacetylene $(CH{\equiv}CH)_n$ have been investigated by *D. J. Berets* and *D. S. Smith*. Because of the special precautions taken during the polymerization, the product contained only 0.7 % of oxygen. The electrical resistivity, measured on tablets with a pore volume of about 7 %, increased from $\rho_{min} = 7.5{\times}10^5\ \Omega$ cm with the oxygen content. The thermoelectric EMF, the sign of which indicates that polyacetylene is a p-type semiconductor, also increased. On the other hand, the activation energy for the conduction is independent of the oxygen content. The resistivity is lowered by adsorbed electron acceptors (BF_3, BCl_3), while it is increased by about three orders of magnitude when electron donors (NH_3, CH_3NH_2) are introduced. However, they cause no change in the spin density measured by the ESR spectroscopic method ($3.8{\times}10^{18}\ cm^{-3}$). The deviations from earlier values for the resistivity are ascribed to differences in the degree of crystallinity, a property that is clearly as important for good conduction as is chemical purity. / Trans. Faraday Soc. *64*, 823 (1968) / –Hz. [Rd 864 IE]

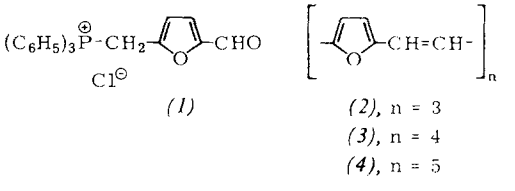
Energies of bonding electron states in simple molecules (here methane and ethane) have been measured by *K. Hamrin et al.* by a method which they call electron spectroscopy for chemical analysis (ESCA). Electrons are knocked out of the sample gas by monochromatic soft X-rays or very far-UV rays, and the kinetic energy of the electrons is measured in a spectrometer. The bonding energy is given by the difference between the energy of the radiation and the kinetic energy of the electrons. The X-rays used here (AlK_α and MgK_α) made it possible to determine the bonding energies of core electrons and valence electrons. The bonding energies of core electrons (C-1s) in methane and ethane is 290 eV. In methane, the valency electrons occupy two levels of type a_1 (two electrons with bonding energy of 23.1 eV) and the type t_2 (six electrons with bonding energy of 13.6 eV) of the tetrahedral group T_d. In ethane, there are five levels with the bonding energies of 23.9, 20.3, 14.7, and 10.7 eV. The last energy belongs to two molecular states characterized by accidental degeneracy. / Chem. Physics Letters *1*, 613 (1968) /–Hz. [Rd 865 IE]

The photochemistry of 1,2,3-triphenylaziridine *(1)* has been investigated by *H. Nozaki, S. Fujita,* and *R. Noyori*. UV irradiation (λ_{max} = 239 nm) of alcoholic solutions causes a new type of alcoholic cleavage of the aziridine ring: it leads



to benzaldehyde acetals *(2)* and *N*-benzylaniline *(3)*. In competition therewith, fragmentation affords benzylideneaniline *(4)* and phenylcarbene *(5)*, the latter being trapped by alcohols as alkyl benzyl ethers *(6)*. Photolysis in cyclohexene leads to 1,3-cycloaddition that provides octahydro-1,2,3-triphenylisoindole *(7)* as a mixture of two stereoisomers. / Tetrahedron *24*, 2193 (1968) / –Ma. [Rd 847 IE]

A synthesis of annulene polyoxides from saccharose is described by *J. A. Elix*. 5-(Chloromethyl)furfuraldehyde, which is readily accessible from saccharose by means of HCl, gives the phosphonium salt *(1)*, m.p. 228–230 °C, when treated with triphenylphosphine in benzene. Slow addition of $LiOC_2H_5$ to a solution of this salt in DMF leads to a Wittig reaction providing, presumably by way of an ylide, a mixture whence the following annulene polyoxides can be isolated by chromatography on Al_2O_3: 1,4:7,10:13,16-triepoxy[18]-annulene *(2)*, red plates, 0.07 % yield; two isomers of 1,4:7,10:13,16:19,22-tetraepoxy[24]annulene *(3)*, m.p. 216–217 °C, dark-violet prisms, 0.7 %, and m.p. 269–270 °C,



violet prisms, 0.8 %, severally; two isomers of 1,4:7,10:13,16:19,22:25,28-pentaepoxy[30]annulene *(4)*, m.p. 218 to 220 °C, deep red to black prisms, 0.4 %, and m.p. 192 to 194 °C, deep red needles, 0.15 %, severally. / Chem. Commun. *1968*, 343 / –Ma. [Rd 848 IE]

BOOK REVIEWS

Hoppe-Seyler/Thierfelder, Handbuch der physiologisch- und pathologisch-chemischen Analyse, für Ärzte, Biologen und Chemiker. (Hoppe-Seyler/Thierfelder, Handbook of Physiological and Pathological Chemical Analysis for Physicians, Biologists and Chemists). Edited by *K. Lang* and *E. Lehnartz* with the collaboration of *O. Hoffmann-Ostenhof* and *G. Siebert*. Volume 6: Enzyme, Part C. Springer-Verlag, Berlin-Heidelberg-New York 1966, 10th Edit., xii, 998 pp., 63 figures, DM 396.–.

The present Part C concludes the Enzyme part of "Hoppe-Seyler/Thierfelder" and completes the 10th edition of this work after 13 years of instalments [*]. A quarter of the volume is occupied by the index of the three parts, and another quarter is devoted to exopeptidases. The remaining half of the volume treats lyases, isomerases, ligases, and the so far undiscussed hydrolases.

[*] Cf. Angew. Chem. *79*, 876 (1967); Angew. Chem. internat. Edit. *6*, 893 (1967).

The appearance of the extensive cumulative index at last permits the work to be used to the full, as in the past a thorough knowledge of enzyme chemistry was sometimes needed to find one's way through the haphazardly classified material. The index contains several references to compounds which appear in the text under different names and the reader is expected to know that he will have to consult "adenylic acid" for full information about AMP after studying "adenosine monophosphate" and "adenosine phosphate". The coenzyme of numerous dehydrogenases is found both under "NAD" and "DPN". Once again two camps – the adherents to modern and to old nomenclature – are found in a book where uniformity is so desirable. Finally, depending on whether the contributions happen to be English or German, there are references to the same enzyme as *e.g.* "pancreatic carboxypeptidase" and "pancreas carboxypeptidase". Surprisingly, the action of amethopterin (and the same holds for aminopterin) on deoxyribonuclease is recorded, but not the much more significant action on the folic acid-dependent enzymes (*e.g.* Part B, p. 196).

The contents of the third part are assembled in a similar way to those of the first two. In some instances literature references extending to very recent times are included, in others (*e.g.* aconitase, carboanhydrase, thiamine pyrophosphate-containing enzymes) only those to the end of the fifties. Both encyclopedic articles and short contributions restricted to descriptions of methods are found side by side. The absence of an article on catalases or peroxidases is regrettable.

Handbooks such as this quickly become dated, especially, if some of the contributions are already out of date on the day of publication. Will it be wise to bring out a new edition soon? The reviewer thinks not, unless the structure of the handbook is fundamentally altered. Articles more than 100 pages in length will make it increasingly difficult to find qualified authors who will deliver on time manuscripts incorporating the latest advances. A large number of short articles would surely be entirely adequate for a book of enzyme methods. The editors would then have to coordinate the contributions and edit them systematically. The "Methods in Enzymology" should serve as a model. If each enzyme were treated by one author, it would be possible to go one step further in a future edition to keep the handbook abreast of new developments. Law books have for some time been issued in the form of loose-leaf editions, so that parts can be replaced as required. This arrangement seems eminently suited for a handbook on enzymology and should be imitated.

H. Sund [NB 705 IE]

Grundlagen der Tribochemie (Fundamentals of Tribochemistry). By *P.-A. Thiessen, K. Meyer,* and *G. Heinicke.* Abhandlungen der Deutschen Akademie der Wissenschaften zu Berlin, Kl. f. Chemie, Geologie und Biologie, 1966, No. 1. Akademie-Verlag, Berlin. 1967, 1st Edit., 194 pp., 159 figures, 24 tables, cloth, DM 33.–.

The book is divided into three monographs: Physicochemical investigations of tribomechanical processes (*Thiessen*), Energetically excited states in tribomechanical processes (*Meyer*), Physicochemical investigations of tribochemical processes (*Heinicke*); the common introduction is by *P.-A. Thiessen.*

The first contribution presents an excellent and concise survey of the phenomena caused by tribomechanical processes. Starting from the investigations by *Smekal* and *Bowden* on microplasticity and friction in solids, the magma-plasma model is taken as the basis, by virtue of its being subject to least contradiction. It is shown that the various associated phenomena of tribomechanical processes, such as detaching of lattice structural units, generation and migration of dislocations, material transfer, luminescence phenomena, charge transfer, emission of electrons, and increase in chemical reactivity are in accord with the requirements of this model.

The second contribution deals at length with fractureless mechanical deformation and the induced electrical phenomena. In the last contribution the chemical reactions that occur during mechanical processing are discussed in detail. The present book gives a good survey of a field which, scientifically, is still in its infancy, and which is in urgent need of further experimental and theoretical investigation. At the same time, the significance of these investigations for technology becomes evident. *I. N. Stranski* [NB 698 IE]

Praktikum der qualitativen Analyse (Practical Handbook of Qualitative Analysis). By *M. Becke-Goehring* and *J. Weiss.* Theodor Steinkopff. Dresden 1967. 1st Edit., x, 122 pages, 10 figures, DM 10.70.

"Praktikum der qualitativen Analyse" is the continuation of the successful "Kurze Anleitung zur qualitativen Analyse" (Short Introduction to Qualitative Analysis) by *Medicus/Goehring,* which ran to 28 editions. The concise presentation is retained in the present revised edition.

The individual elements and their characteristic reactions are discussed in the sequence of the classical methods of analytical separation. Special organic reagents are not dealt with apart from a few exceptions.

The separation processes for cations and anions are compiled in tabulated form. Supplementary chapters on the individual groups indicate peculiarities and possible sources of error. Evidently, it was decided to retain macro-scale analysis even within the framework of this small volume, so that only a few short paragraphs are devoted to semimicro methods. Separate discussion of some rarer elements makes the separation schemes clearer. On the other hand, the presentation is too condensed for the undergraduate majoring in chemistry, who will also have to turn to larger, more comprehensive works. This is all the more true as the theoretical basis has been almost entirely ignored.

Because of the clear presentation and well arranged content, the book can be recommended especially to those for whom chemistry is a subsidiary subject. *E. Blasius* [NB 700 IE]

The Industrial Chemistry of the Lanthanons, Yttrium, Thorium, and Uranium. By *R. J. Callow,* Pergamon Press, Oxford-London-Edinburgh 1967. 1st Edit. vii, 248 pp., several figures, 60 s.

An introductory historical survey is followed by nine chapters that are devoted to the production and technical applications of these elements as well as a discussion of analytical methods and the purity of commercial compounds and workable ores. A brief concluding chapter deals with problems associated with the radioactivity of thorium and uranium – understandably tailored to a British viewpoint. The individual chapters are well written and in general offer a clear presentation of the subject. Those dealing with the preparation, separation, and purification of the elements are particularly valuable, and reveal the depth of the author's knowledge of the field. The excellent flow sheets of the individual processes make a substantial contribution to the ease of comprehension. In the reviewer's opinion the chapter on the applications of the elements is a little skimped, not only in the selection but also in the detail. For example, no mention is made of the use of europium compounds as lasers, while that of thorium and uranium for nuclear energy is dismissed in an entirely inadequate and in some respects out-of-date section under the heading "Some possible applications". In the chapter on analysis the currently very important activation analysis for uranium is restricted to the sentence "neutron activation is applicable in some cases but necessary facilities are not generally available". Revision of certain chapters, particularly 8 and 9, would considerably enhance the value of this intrinsically satisfactory and instructive book. The author should not only discuss the fields that he himself considers important – as he states in the preface – but also devote to those problems in which he may be less interested the same care and thoroughness as he does, for instance, to Chapters 4 to 6. *C. Keller* [NB 716 IE]

Structure of High-Resolution NMR Spectra. By *P. L. Corio*. Academic Press, New York-London 1966. 1st Edit., xii, 548 pages, numerous illustrations, $ 15.00.

NMR spectroscopy is another subject that has today reached the stage where a detailed treatment is possible only by a separate study of its various aspects. *P. L. Corio*'s rendering of the particularly important field of mathematical fundamentals of high-resolution spectra is therefore most welcome.

The first four chapters (127 pages) describe the physical principles of NMR spectroscopy and the quantum-mechanical treatment of single and multiple spin systems. The five chapters (320 pages) forming the main part of the book embrace the theory of spectra, the analysis of spin systems with two groups of magnetically equivalent nuclei, the perturbation and moment theory, the analysis of symmetrical spin systems, and the treatment of multiple quantum transitions, double resonance, and spin-echo experiments. These descriptions are complemented by numerous illustrations of spectra of the highest experimental quality. A 100-page appendix contains mathematical expositions and numerical data for certain spin systems (A_2B, A_3B, A_4B, A_2B_2, A_3B_2). The author is undoubtedly right in stating in the introduction that his book is mathematical in character, and the chemist who has limited knowledge of quantum mechanics is likely to find it difficult to use the generally formulated relationships to solve his specific problems. Because of its formal approach and because it makes no mention of *e.g.* computer analysis, the book is less a practical guide than an all-embracing and thorough derivation of the mathematical laws of the spectra. It is therefore recommended as a reference and guide to the NMR spectroscopist for all problems encountered in this field. The detailed treatment of systems with magnetically equivalent nuclei and the tracing of higher spin systems back to simple subspectra is in many instances of general interest.

H. Günther [NB 708 IE]

Heteroatom Ring Systems and Polymers. By *H. R. Allcock*. Academic Press, New York-London 1967. 1st Edit., xi, 401 pages, $ 16.50

Heteroatom-containing molecules with linear, branched, or cyclic structures, particularly polymers consisting of such compounds which contain silicon, phosphorus, boron, and aluminum as structural units in addition to carbon, oxygen, sulfur, and nitrogen, have been the subject of discussion in many publications during recent years. Rapid development in this field has been promoted *inter alia* by a demand from the aerospace industry for novel materials possessing remarkable properties.

The author is not so much concerned with reproducing the available material in a fully comprehensive manner – such an ambition could not in any case be fulfilled in 400 pages of print – but rather aims at a systematic comparison between the heterocycles in respect of similarities, for instance interaction of the "delocalized" π-electrons and the "localized" σ-electrons (of aromatic character). This systematic treatment of similarities embraces the relationship between molecular structures, π-bonds, and steric hindrance in the specific hetero ring systems with examples selected from the thermodynamics of polymerization, depolymerization, and oligomerization of the heteroatom systems.

Chapters 1–4 are devoted to general and theoretical fundamentals, and in particular Chapter 2 discusses the atomic structure and the theory of the chemical bond.

The author deserves the reader's gratitude for proposing and using a uniform nomenclature in the field. The IUPAC committee on nomenclature should adopt these proposals if order is to be restored. (For example, there are five names for the trimer of phosphorus nitrochloride, $(NPCl_2)_3$.) A further welcome feature is the detailed survey of the possible synthetic routes to cyclic heteroatom compounds, giving 281 literature references and some valuable hints. The presentation of polymers is limited to addition polymerization reactions; polycondensations and other mechanisms leading to heteropolymers are not mentioned.

The reader is offered a large number of literature references, particularly following Chapters 5 and 8, and well prepared author and subject indexes. Having regard to the rapid expansion of this field (especially in the USA) any survey, and particularly one that deals with fundamentals, is welcome. It is to be hoped that supplementary volumes will be published to keep the work up-to-date.

A. Gumboldt [NB 710 IE]

The Chemistry of Non-Aqueous Solvents. Edited by *J. J. Lagowski*. Vol. II of the series "Acidic and Basic Solvents". Academic Press, New York-London 1967. 1st Edit. xv, 398 pp., $ 18.50.

In recent years the interest shown by chemists in reactions in non-aqueous ionizing solvents has increased sharply, because in these solvents novel reactions are possible that are observed neither in water nor in simple organic solvents. The latest work on progress in the chemistry of non-aqueous solvents has been edited by *J. J. Lagowski* and comprises several volumes.

The first volume deals with the physicochemical behavior of non-aqueous solvents (acid-base concepts, solvation, electrode potential) and with the experimental methods involved in dealing with low-boiling and high-melting non-aqueous solvents. The present, second volume is devoted to the chemistry of acid and basic solvents: halohydric acids (*F. Klanberg, M. Kilpatrick*, and *G. Jones*), sulfuric acid, nitric acid (*W. H. Lee*), organic acid amides (*J. W. Vaughn*), and liquid ammonia (*J. J. Lagowski* and *G. A. Moczygemba*).

The articles describe the preparation of the anhydrous solvents, their physicochemical properties are considered in some detail, and selected chemical reactions in these solvents are presented. An additional chapter, going beyond the scope of the present volume, describes the physical properties of solutions of metals in non-aqueous solvents (*J. C. Thompson*) in which solvated electrons are formed by ionization of the metals in question. Naturally, solutions of the alkali metals in ammonia are pre-eminent. A deficiency does exist in that there is little mention of the versatile chemical reactions of metal solutions (addition of electrons to aromatic systems, Birch reactions, *etc.*), which are of special interest to the organic chemist.

The text is supported by a wealth of tabulated data and illustrations. A total of 1200 references provides a good coverage of the principal original work, at least up to 1964; only three of the seven contributions include more recent literature.

The book's clear, concise, and readable text, written by competent authors, merits a wide distribution among all who are interested in any way in non-aqueous solvents.

U. Schindewolf [NB 691 IE]

Solvated Electron. Advances in Chemistry Series No. 50. Edited by *R. F. Gould*. American Chemical Society Publications, Washington 1965. 1st Edit., viii, 304 pp., numerous figures and tables, cloth, $ 8.00.

Since the discovery only a few years back that solvated electrons play an important role as intermediates in radiation-chemical processes in aqueous and water-like systems, this simplest and most reactive particle in chemistry (it was first observed in ammonia 100 years ago and some of its properties were described 50 years ago) has become the subject of extensive study. The present book, which consists of 21 papers read at a symposium in Atlantic City, reviews the present state of knowledge about solvated electrons.

Three of the lectures are theoretical in nature and are devoted to the description of the quantum mechanics of solvated

electrons and of electron transfer processes. Seven contributions deal with the structure, electrical and optical properties, and the kinetics of solvated electrons in solutions of metals in amines or liquid ammonia. The remaining lectures describe the formation of solvated electrons by radiation-chemical and photochemical processes, their reactions and physical properties in liquid and in frozen aqueous or alcoholic systems.

It becomes clear from the lectures that we are far from understanding the physics of solvated electrons, though many of their properties are known; the name is a term of convenience to describe particles whose structure is yet unknown. However, the chemistry of the particle has retained fewer secrets; several hundred reactions have been studied, their rates measured, and in many cases even the short-lived intermediates have been identified.

The contributions are highly readable, and are often supplemented by graphs and tables. A glance through the literature references reveals that next to no German contributions are listed. Unhappily, this reflects the facts. The solutions of metal in ammonia containing solvated electrons, as well as the direct proof of the existence of solvated electrons produced by radiation-chemical means, were first described in German periodicals, but have scarcely been mentioned in them since.

The symposium report was available little more than three months after the meeting. Both the editor and the publisher deserve commendation on this account, but unfortunately the speed of setting up the material in print has prevented the discussions from being included in the publication.

U. Schindewolf [NB 690 IE]

Handbook of Industrial Toxicology. By *E. R. Plunkett*, Chemical Publishing Company, Inc., New York, 1st Edit., 1966, viii, 448 pages, $ 16.50.

The author has attempted to bring to the attention of "chemists, managers, doctors, medical students, nurses, and poison control centers" the hazards to health posed by the chemicals, drugs, and insecticides which he regards as the most important. In addition to the usual alphabetical classification (Abrin to Zirconium) synonyms, appearance, possible occupational exposure, threshold limit values, toxicity (absorption, pathology, symptoms of poisoning, diagnosis, suggested treatment) and measures to prevent poisoning are given.

Unhappily, this laudable attempt has misfired completely. Even the selection of the substances is startling: does the occurrence of abrin in Buddhist rosaries justify its inclusion in this book? The only drugs mentioned in the book are resorcinol, salicylic acid, and tamarind.

It is untrue that yellow phosphorus is still used in matches, let alone in fertilizers. Dichloroacetic acid and trichloroacetic acid are listed as synonyms of acetic acid. Acetic acid is stated to produce black skin and hyperkeratosis; no mention of its hemolytic effect is made. According to the book practically all substances have a "sensitizing" action and one is practically as dangerous as another. For many substances the threshold limit values are taken from a scarcely reliable list compiled by ICI in 1952 (acetophenone = 20 ppm; acetylene = 5000 ppm). The difference in toxicity between acetone and acetone cyanhydrin can be no more than suspected from the value of 1000 ppm given as the threshold limit for acetone, and the absence of a figure for the cyanhydrin. Not a word to tell us that the cyanhydrin acts practically like prussic acid; it is even claimed to produce a "depression of the central nervous system" and a "cytotoxic anoxia".

Under toxic substances such as allyl alcohol no mention is made of the typical liver-damaging action. By contrast, the relatively harmless amyl acetate is accused of precisely this, as well as of causing renal damage. Aniline is stated to depress the cardiac action, the smooth musculature and the central nervous system, and occasionally to produce intravascular hemolysis. Tetrafluoroethylene – "a colorless, flammable gas" – is equated with Teflon and its decomposition products, and so on and so forth.

The three pages of bibliography list the well-known, excellent English-language textbooks and reference works on toxicology. Had the author consulted these books, this inaccurate, useless compilation would not have seen the light of day, and it would not now be necessary to warn the reader against it. The well-intentioned attempt by the author shows that it is necessary to possess toxicological and chemical knowledge to compile the essential information, even using good textbooks. In this task the present author has, regrettably, failed. One can only marvel at his audacity in wanting to write such a compendium, and one that is even described as a handbook, without being sure of the facts. *H. Oettel* [NB 695 IE]

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Isomerizations in Cyclobutenes[**]

BY R. CRIEGEE[*]

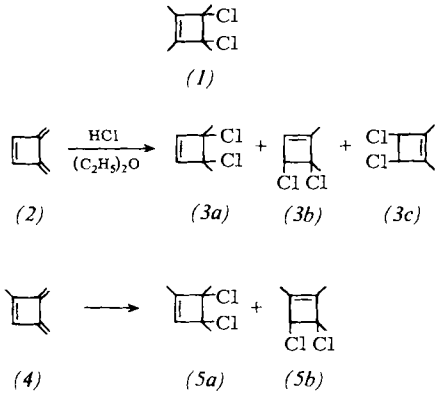
The present article deals with acid-catalyzed rearrangements and thermal valence isomerizations in cyclobutenes. The characteristic features of small rings, i.e. their practically planar structure and the ring strain, are in fact the causes of the rearrangements discussed.

1. Acid-Catalyzed Rearrangements

The great stability of cyclobutenyl cations, which has now been known for some time, was first brought to our attention by the unusually high rate of solvolysis of dichlorotetramethylcyclobutene *(1)* [1]. Aqueous acetone converts this compound into the corresponding diols within a few minutes at room temperature. *Katz* [2] later proved the existence of stable cyclobutenylium salts by UV and NMR measurements. Possible reasons for this stability include the planar structure, the symmetry, the electron-donating effect of the methyl groups, and possibly a nonclassical 1,3-interaction, all of which should favor the fundamental ion on energy grounds.

The great stability of the ion leads to rapid dissociation of the chlorine atoms in *(1)*, particularly in the presence of complexing agents such as zinc chloride or tin tetrachloride. Recombination with the chloride ions in the two possible positions in the mesomeric ion leads to equilibration of the methyl groups, which *Katz* [3] detected by the appearance of a lone singlet in the NMR spectrum.

We found the same phenomenon during the addition of HCl to the trienes *(2)* and *(4)*, which can be obtained as described by *Huntsman* [4]. In the reaction of *(2)*, *Eberius* [5] obtained a mixture of the isomeric dichlorides *(3a)–(3c)*, which could be separated by gas chromatography, while *(4)* gave a mixture of *(5a)* and *(5b)*, which could not be separated in this way.



Rapid equilibration takes place in both cases with zinc chloride in ether. However, the equilibrium is completely displaced toward *(3c)* and *(5b)*, *i.e.* the compounds having both the maximum number of secondary chlorine atoms and the maximum number of methyl groups attached to doubly-bonded carbon atoms.

However, cyclobutenylium cations are formed by the protonation of methylenecyclobutenes as well as by the dissociation of chloride ions. This is illustrated by the ready addition of hydrogen chloride to *(2)* and *(4)*, as mentioned above. Other nucleophiles also add rapidly to the semicyclic methylene group in the presence of protonic catalysts. Thus an HCl concentration of only 10^{-3} mole/l is sufficient to cause the addition of methanol to the diene *(6a)* to form the ether *(7a)*, the half-reaction time being about 1 hour at 24 °C. The reaction of *(6b)* is twice as fast. How-

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75 Karlsruhe, Englerstr. 11 (Germany)

[**] Based on a plenary lecture to the Symposium on the Chemistry of Small Rings (Louvain, Belgium, September 12–15, 1967).

[1] *R. Criegee* and *G. Louis*, Chem. Ber. *90*, 417 (1957).

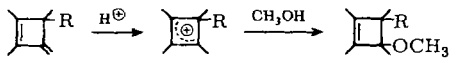
[2] *Th. J. Katz, J. R. Hall*, and *W. C. Neikam*, J. Amer. chem. Soc. *84*, 3199 (1962).

[3] *Th. J. Katz* and *E. H. Gold*, J. Amer. chem. Soc. *86*, 1600 (1964).

[4] *W. D. Huntsman* and *H. J. Risters*, J. Amer. chem. Soc. *85*, 3308 (1963); *89*, 342 (1967); *W. D. Huntsman, J. A. DeBoer*, and *M. H. Woosley*, *ibid.* *88*, 5846 (1966).

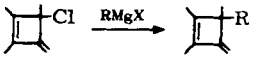
[5] *R. Criegee, W. Eberius*, and *H. A. Brune*, Chem. Ber. *101*, 94 (1968).

ever, it seems questionable whether the high reactivity of the methylenecyclobutenes is connected with the 1,3-interaction mentioned, since the reaction of 1-methyl-3-methylenecyclopentene, in which an interaction of this type is not to be expected, is only slightly slower [6].



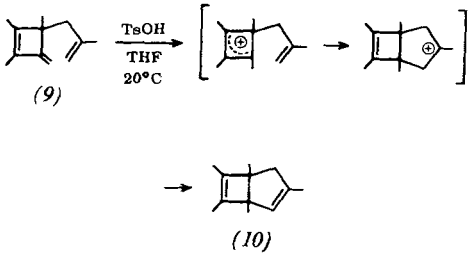
(6a), R = H *(7a)*, R = H
(6b), R = CH_3 *(7b)*, R = CH_3

The cyclobutenylium cation can react, not only with "foreign" nucleophiles, but also with nucleophilic groups in the same molecule. In this case the addition may be regarded as an intramolecular rearrangement. We shall consider only those reactions in which the nucleophilic group is an ethylene grouping in a side chain. Compounds of this type can be readily obtained from the dichloride *(1)* by treatment with quinoline to obtain the monochloride *(8)*, followed by reaction with unsaturated Grignard compounds.



(8)

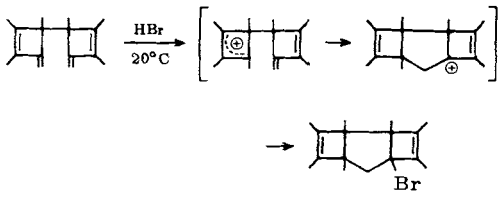
A simple example is the rearrangement of the methallyl compound *(9)* with *p*-toluenesulfonic acid (TsOH) in tetrahydrofuran (THF) at 20 °C. The bicyclo[3.2.0]-heptadiene derivative *(10)* is formed in 78 % yield. A cyclobutenyl cation and the bicyclic tertiary carbonium ion formed from it probably occur as intermediates [7]. Many ring closures of this nature are known, but the surprising point in this case is the mildness of the conditions.



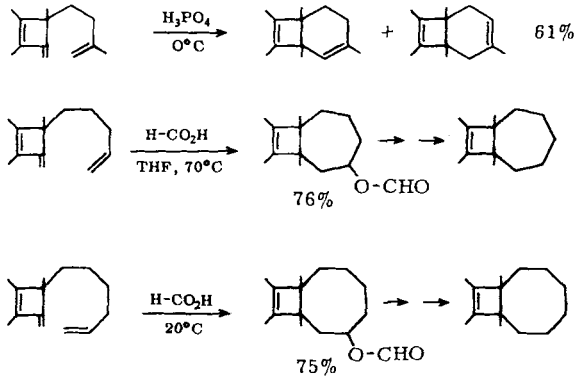
(9) *(10)*

The intermediate carbonium ions can also achieve stability by the addition of an anion, as was shown for a complicated case by *Dekker* in 1963 [8]. 1-Bromo-3,4,5,6,7,8,9-heptamethyltricyclo[5.2.0.$0^{3,6}$]nona-4,8-diene is formed in 88 % yield. In this case, stabilization of the intermediate by the loss of a proton would have led to an increase in strain.

Six-, seven-, and eight-membered rings can be fused on to the cyclobutene ring in the same way. The good yields obtained in ring closures of this type again



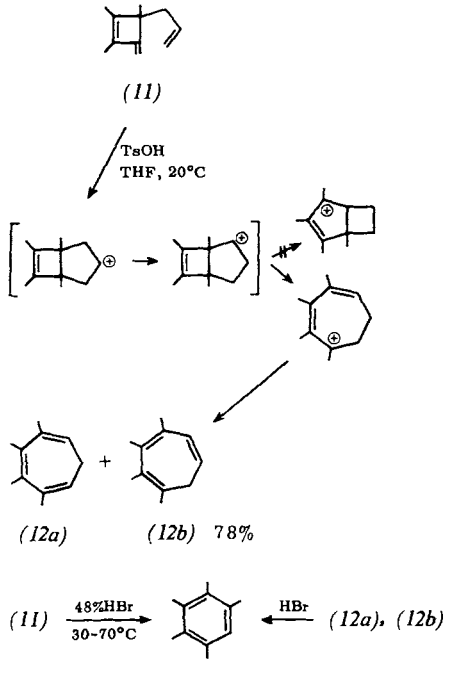
confirm the high stability of the intermediate cyclobutenyl cations [9] (see Scheme 1).



Scheme 1

In the last two cases shown, the formates obtained can be converted into the fundamental bicyclic hydrocarbons by conventional methods.

With cyclobutenes having allyl side chains and structures such that a secondary instead of the tertiary bicyclic carbonium ion is formed [as in *(11)*], complications occur as a result of further rearrangements and cycloheptatrienes and even benzene derivatives can be formed. The first step is thought to be the rearrangement of one carbonium ion into another by a hydride shift or by successive deprotonation and protonation. In any case, the result is an ion having the charge on



(11) *(12a)* *(12b)* 78%

[6] *J. Lukas*, Dissertation, Technische Hochschule Karlsruhe 1965.

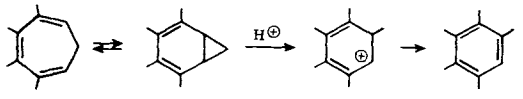
[7] *R. Criegee, H. Hofmeister*, and *G. Bolz*, Chem. Ber. *98*, 2327 (1965).

[8] *R. Criegee, J. Dekker*, and *H. A. Brune*, Chem. Ber. *96*, 2368 (1963).

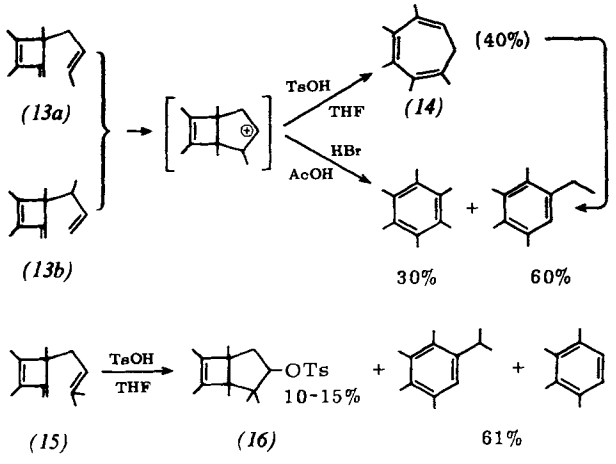
[9] *G. Bolz*, Dissertation, Technische Hochschule Karlsruhe 1967.

the C atom next to the bridgehead. This ion can change by a classical carbonium ion rearrangement either into another bicyclic ion or (with cleavage of the bicyclic bond) into a cycloheptadienyl cation. The strain in the system decreases only in the latter case. The reaction products obtained from *(11)* depend on the conditions. Methylated cycloheptatrienes *(12a)* and *(12b)* are formed with *p*-toluenesulfonic acid in THF, whereas 48 % hydrobromic acid gives an 80 % yield of pentamethylbenzene. This last rearrangement involves the cycloheptatrienes *(12a)* and *(12b)* as intermediates, since these are converted into pentamethylbenzene under the same conditions.

The rearrangement into the benzene derivative depends on the cycloheptatriene-norcaradiene valence isomerization. The norcaradiene derivative finally undergoes acid-catalyzed opening of the three-membered ring.



Similar rearrangements take place in compounds having 2-butenyl side chains, such as *(13a)*. Thus the reaction of the mixture of hydrocarbons *(13a)* and *(13b)* obtained in the Grignard synthesis proceeds *via* the common carbonium ion to give either pentamethylcycloheptatriene *(14)* or (with hydrobromic acid) a mixture of 30 % of hexamethylbenzene with 60 % of ethyltetramethylbenzene. The hydrocarbon *(15)* gives tetramethylisopropylbenzene and tetramethylbenzene as well as the secondary *p*-toluenesulfonate *(16)*.

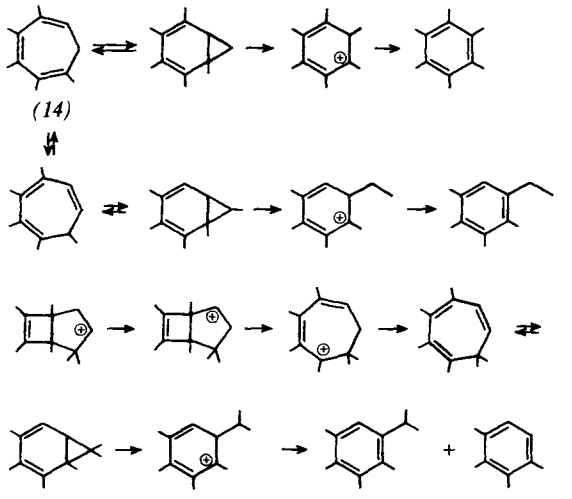


Some views on the course of the reaction are illustrated in Scheme 2.

Perhaps it should be mentioned that in all these examples the opening of the four-membered ring has nothing to do with thermal isomerization. This pyrolysis, which also leads to cycloheptatrienes, and which will be discussed later, takes place only above 350 °C.

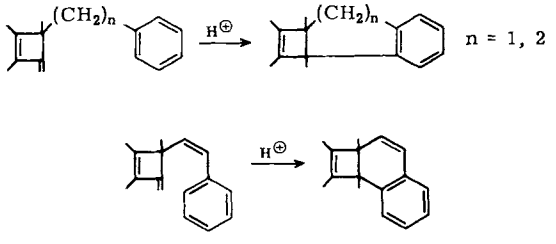
The cyclobutenyl cation can also make an electrophilic attack on an aromatic nucleus situated in the side chain[10]. The

[10] *E. J. Stark*, Dissertation, Universität Karlsruhe 1968; *C. Schweickhardt*, unpublished.



Scheme 2

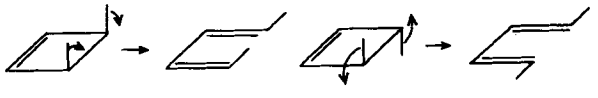
isomerization with acids leads in these cases to tricyclic compounds containing a benzene ring (see Scheme 3).



Scheme 3

2. Thermal Valence Isomerizations

The formation of a butadiene by pyrolysis of a cyclobutene is one of the simplest of valence isomerizations. The reaction is normally thermally irreversible since a cyclobutene cannot exist in detectable quantities in the equilibrium, owing to the difference in the energy levels of about 11.5 kcal[10a]. Exceptions occur among fluorinated derivatives and cyclic butadienes having a *trans* double bond[*], as well as in a few other cases[11]. Since a stereospecific reaction course was first observed by *Vogel* (1954)[12], the pyrolysis of cyclobutenes has been intensively studied by several research groups. The conrotation of the 3,4-substituents during the rearrangement was brilliantly explained by *Woodward* and *Hoffman*[13] in 1965.



[10a] *K. B. Wiberg* and *G. Szeimies*, Tetrahedron Letters *1968*, 1235.

[*] *E.g. cis,trans*-cycloocta-1,3-diene and *cis,trans*-cyclonona-1,3-diene, *K. M. Schumate, G. F. Fonken*, and *P. N. Neuman*, J. Amer. chem. Soc. *87*, 3996 (1965).

[11] See, *e.g., R. N. Haszeldine* and *J. E. Osborne*, J. chem. Soc. (London) *1955*, 3880; *R. Breslow et al.*; J. Amer. chem. Soc. *87*, 5132 (1965); *E. GilAv* and *J. Herling*, Tetrahedron Letters *1967*, 1.

[12] *E. Vogel*, Angew. Chem. *66*, 640 (1954).

[13] *R. B. Woodward* and *R. Hoffmann*, J. Amer. chem. Soc. *87*, 395 (1965).

However, this theory provides no information about the dependence of the activation energy, and hence of the reaction rate, on the number, nature, and arrangement of the substituents on the cyclobutene ring, nor can it predict accurately when conrotation will give way to disrotation, which is in itself energetically less favorable. At present such information can only be gained from empirical observations based on extensive series of experiments. A few observations of this type will be reported in connection with known data. The kinetics of the rearrangements can be measured by UV or NMR spectroscopy or by gas chromatography, depending on the case in question. Since sufficiently accurate rate measurements have not been carried out in every case at various temperatures, and frequently cannot be carried out at all, the temperatures at which the rate constant has a value of exactly 10^{-4} are used together with the activation energies as reference values. The half lives at this "characteristic reaction temperature" $T_{k=10^{-4}}$ are approximately 2 hours.

We shall now consider some results obtained by *Walters* [14] and by *Frey* [15], who investigated the valence isomerization of cyclobutene and some of its methyl derivatives in the gas phase (Table 1, upper part).

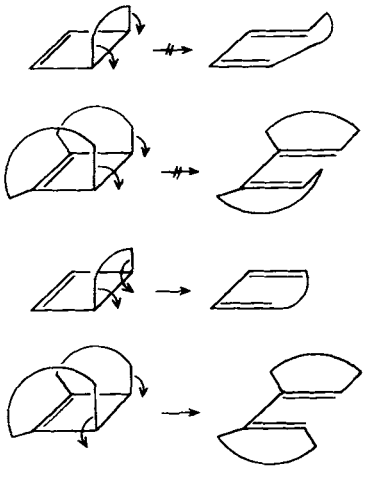
Table 1. Activation energy E_A and characteristic reaction temperature $T_k = 10^{-4}$ of the valence isomerization of cyclobutene and methylcyclobutenes.

Cyclobutene, Methyl on C—	E_A (kcal/mol)	$T_k = 10^{-4}$ (°C)	Ref.
—	32.5	145	[14]
1	35.1	155	[15]
3	31.5	121	[15]
1,2	36.0	168	[15]
1,3	33.0	135	[15]
1,4	33.4	143	[15]
1,2,3,4, *trans*	32.0	130	[15a]
1,2,3,4, *cis*	35.8	176	[15a]
1,2,3,3,4	34.0	163	[15a]
1,2,3,3,4,4	40	185	[15a]

It can be seen from the data available that methyl groups in the various positions affect the reaction rate, but that the order of magnitude is always approximately the same. This is confirmed by a number of measurements obtained in our own institute [15a]. These measurements were carried out in homogeneous solution. Since the rate showed no dependence on the solvent, the results should be comparable with those of reactions in the gas phase.

Interesting points arising from our results (Table 1, lower part) are that increasing substitution in positions 3 and 4 makes the reaction more difficult, and that there is a considerable difference in rate between *cis* and *trans* isomers, the *trans* compounds isomerizing much more readily than the *cis* isomers. This difference is found qualitatively even in the dichlorocyclobutenes, of which only the more stable *cis* isomer survives the pyrolysis from the starting material [16], and may be assumed to be due to the greater steric hindrance in the transition state of the *cis* compound, in which the incipient rotation brings a methyl group or a chlorine atom close to a hydrogen atom. In the tetrasubstituted compounds, it is even necessary for two methyl groups to approach each other.

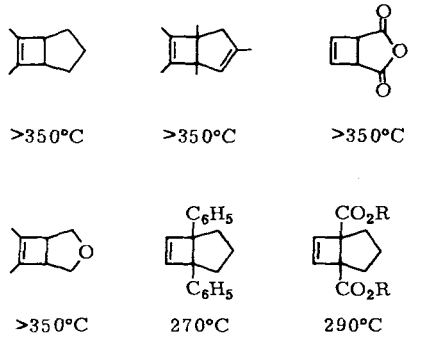
The situation is entirely different when a conrotation would lead to diolefins with at least one of the double bonds as a *trans* double bond in a relatively small ring. This would be the case in cyclobutenes in which one or more rings are fused to the *cis*-3,4 bonds of the cyclobutene (Scheme 4).



Scheme 4

In these cases, unstrained reaction products, and hence a less strained transition state, can normally result only from disrotation. However, since the double bond provides no electronic assistance in disrotation, the activation energy for the cleavage of the C–C bond must be much higher.

A particularly extensive literature exists on the bicyclo[3.2.0]heptenes and related compounds [17]. These compounds are characterized by a high thermal stability, and pyrolyze only above 350 °C. Isomerization to form cycloheptadiene or cycloheptatriene derivatives



Scheme 5

[14] *W. Cooper* and *W. D. Walters*, J. Amer. chem. Soc. *80*, 4220 (1958).

[15] *H. M. Frey*, Trans. Faraday Soc. *58*, 957 (1962); *59*, 1619 (1963); *60*, 83 (1964); *61*, 861 (1965).

[15a] *R. Criegee, D. Seebach, R. E. Winter, B. Börretzen*, and *H. A. Brune*, Chem. Ber. *98*, 2339 (1965).

[16] *R. Criegee, W. Hörauf*, and *W. D. Schellenberg*, Chem. Ber. *86*, 126 (1953); *M. Avram, I. Dinulescu, M. Elial, M. Farcasiu, E. Marcia, G. Mateescu*, and *C. D. Nenitzescu*, Chem. Ber. *97*, 372 (1964).

[17] For examples see *R. Criegee* and *H. Furrer*, Chem. Ber. *97*, 2949 (1964); *W. Adam, ibid. 97*, 1811 (1964); *R. Criegee, U. Zirngibl, H. Furrer, D. Seebach*, and *G. Freund, ibid. 97*, 2942 (1964).

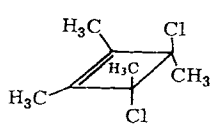
is generally complicated by secondary or side reactions. It is unimportant in these cases whether the fused five-membered ring is carbocyclic or heterocyclic, and whether it is saturated or unsaturated. Some examples are shown in Scheme 5. The characteristic reaction temperatures ($T_k = 10^{-4}$) for the pyrolysis are shown under the formulas.

The first four compounds in Scheme 5, which have only hydrogen or methyl groups at the bridgeheads, isomerize only above 350 °C. The reaction proceeds much more readily when the bridgehead substituents are phenyl or alkoxycarbonyl groups [18]. This can be explained by the assumption that the disrotation proceeds *via* short-lived diradicals, which are stabilized by these groups.

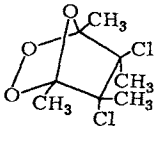
With larger fused rings, the valence isomerization must also yield larger rings. Consequently, the strain due to a *trans* double bond is smaller. It may therefore be expected that the conrotation mechanism will become possible again above a certain ring size. This should result in an increase in the reaction rate in such a system.

The acid-catalyzed ring closure reaction discussed in Section 1 permits the preparation of cyclobutenes with rings fused in position 3 and 4, which are suitable starting compounds for pyrolysis. However, the steric linkage of the two rings is important, whereas a *trans* linkage would lead to considerable strain in bicyclo-[3.2.0]heptenes and bicyclo[4.2.0]octenes, *trans* linkage of larger rings is quite feasible.

We have checked this question in the case of tetramethyl-bicyclo[6.2.0]decenes by a method developed by *Korber* [19] for the dichloride *(1)*. The problem was to determine whether the chlorine atoms in this compound were *cis* or *trans* to each other. In both cases the methyl groups can be classified into equivalent pairs, so that only one singlet is to be expected for each of the two types of methyl groups. The ozonide of *(1)* can occur in three forms *i.e.* one *trans* and two *cis* forms. Whereas the methyl groups in the *cis* forms are again grouped into equivalent pairs, this is no longer so in the *trans* form *(17)*. In this case the dihedral angles between the chlorine valences and the methyl valences are different, so that the methyl groups in positions 1 and 2 and those in positions 3 and 4 have different environments. The *trans* arrangement of the chlorine atoms in the ozonide, and hence also in the dichloride *(1)*, is confirmed by the observed splitting of the methyl singlet in the NMR spectrum [20].



(1)



(17)

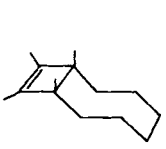
A similar situation is found in the hydrocarbon *(18)*. Whereas the methyl groups at the bridgeheads in *(18)* are equivalent both in the *cis* and in the *trans* form, this is true of the ozonide of *(18)* only in the *cis* form.

[18] *J. Rigaudy* and *P. Courtot*, Tetrahedron Letters *1961*, 95; *P. Courtot*, Ann. Chimie (13) *8*, 197 (1963); *R. Askani*, Chem. Ber. *98*, 2322 (1965).

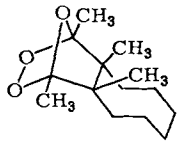
[19] *H. Korber*, Dissertation, Universität Karlsruhe 1968.

[20] This observation is contrary to an earlier belief. Cf. *R. Criegee* and *K. Noll*, Liebigs Ann. Chem. *627*, 1 (1959).

However, the NMR signal for the bridgehead methyl groups in the hydrocarbon *(18)* and in the ozonide *(19)* is a sharp singlet, so that the ring must be *cis*-fused.

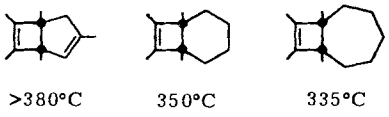


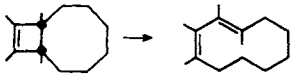
(18)



(19)

Scheme 6 shows the characteristic reaction temperature ($T_k = 10^{-4}$) for the pyrolysis of four hydrocarbons of the 4.5, 4.6, 4.7, and 4.8 series [9].





(20)

Scheme 6

Whereas the values for the first three compounds are similar, a large jump occurs between the third compound and the fourth, which contains an eight-membered ring. Thus the thermal isomerization proceeds much more readily in this case. The characteristic reaction temperature is almost the same as that of a tetrasubstituted monocyclic cyclobutene. As in the latter, conrotation evidently occurs. The reaction product must therefore be a *cis,trans*-cyclodecadiene *(20)*, which can be built from models without appreciable strain. In agreement with the behavior of unsubstituted *cis,trans*-1,3-cyclodecadiene, the compound gives no UV maximum [21]. The configuration of the diene cannot unfortunately be decided from the remaining spectral data. Investigations with systems containing larger rings, preferably with both types of fusion, are therefore desirable [*].

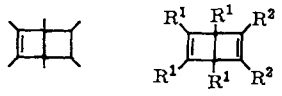
For quite different reasons, the valence isomerization proceeds more readily if the fused second ring is a four-membered or three-membered ring. The energetically favored conrotation is again no longer possible, but the disrotation is facilitated by the additional strain of the second ring. The values in Table 2 are selected from a large volume of data [15a].

The reaction temperatures are approximately the same as or lower than those found for hexamethyl-cyclobutene. Though the introduction of a double bond also produces a stable aromatic system in the second four-membered ring, and though the enthalpy of reaction should be increased by about 36 kcal, the

[21] *A. T. Blomquist* and *A. Goldstein*, J. Amer. chem. Soc. *77*, 998 (1955).

[*] *P. Radlick* and *W. Fennical* recently (Tetrahedron Letters, *1967*, 4901) isomerized the unsubstituted bicyclo[6.2.0]dec-9-ene at 200 °C and obtained *cis,trans*-cyclodeca-1,3-diene in 95% yield.

Table 2. Activation energy E_A, characteristic reaction temperature $T_k = 10^{-4}$ and reaction enthalpy ΔH in the pyrolysis of compounds *(21a)–(21d)* [15a].



(21a) *(21b)-(21d)*

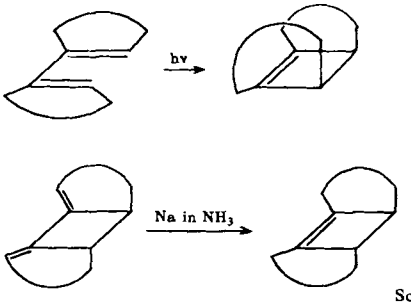
	R^1	R^2	E_A (kcal/mole)	$T_k = 10^{-4}$ (°C)	ΔH (kcal/mole)
(21a)			42	195	
(21b)	CH_3	CH_3	37 [21a]	150	−59.5 [21a]
(21c)	CH_3	CO_2CH_3	28	97	−67
(21d)	H	H		55	

reaction rate shows no sudden increase. The effect of the substituents is greater than that of the second double bond. The fact that this double bond has any effect at all can be explained by the higher strain of a cyclobutene ring as compared with a cyclobutane ring.

Only one example of a cyclobutene with a fused three-membered ring is known. Disrotatory ring opening again takes place readily, leading in this case to cyclopentadiene [22].

A final series of investigations was concerned with cyclobutenes having a ring fused in each of the 1,4 and 2,3 positions. There are two possible stereoisomers of compounds of this type, in which the side rings are fused to C atoms 3 and 4 of the cyclobutene in the *cis* or *trans* position. The *cis* compounds are *meso* forms and the *trans* isomers are racemic forms. The compounds with six-, seven-, and eight-membered side rings were investigated.

As was shown by *Crowly* [23] and later by *Dauben* [24] in the case of the 6.4.6 ring compound, one series is formed by exposure of biscycloalkenyls to light. *Reinhardt* [25] obtained the other two *meso* forms in the same way. This author also obtained the three isomeric racemates by Birch reduction of the tricyclic dienes, which were obtained from the monocyclic allenes with six, seven, and eight ring atoms [26] (Scheme 7).



Scheme 7

[21a] *J. F. M. Oth*, personal communication.

[22] *J. I. Brauman, L. E. Ellis*, and *E. E. van Tamelen*, J. Amer. chem. Soc. *88*, 846 (1966); *J. I. Brauman* and *D. M. Golden*, *ibid. 90*, 1920 (1968); the activation energy is 26.9 kcal, $T_k = 10^{-4}$ is 48 °C.

[23] *K. J. Crowley*, Tetrahedron *21*, 1001 (1965).

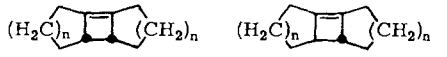
[24] *W. G. Dauben, R. L. Cargill, R. M. Coates*, and *J. Saltiel*, J. Amer. chem. Soc. *88*, 2742 (1966).

[25] *R. Criegee* and *G. Reinhardt*, Chem. Ber. *101*, 102 (1968).

[26] *J. W. Ball* and *S. R. Landor*, J. chem. Soc. (London) *1962*, 2298; *G. Wittig* and *P. Fritze*, Angew. Chem. *78*, 905 (1966); Angew. Chem. internat. Edit. *5*, 846 (1966); Liebigs Ann. Chem. *711*, 82 (1968).

Valence isomerization can lead with conrotation to bicyclic compounds having *cis* double bonds in both rings only in the case of the racemic forms. All the racemic compounds should therefore isomerize at lower temperatures than the *meso* compounds. This is confirmed by the results of measurements.

Scheme 8 shows the characteristic reaction temperatures ($T_k = 10^{-4}$) of the hydrocarbons *(22a)* to *(22f)*.



(22a), n = 2 261°C *(22d)*, n = 2 87°C
(22b), n = 3 273°C *(22e)*, n = 3 109°C
(22c), n = 4 261°C *(22f)*, n = 4 119°C

Scheme 8

The *cis*-cyclobutene derivatives require a temperature 140–180 °C higher than that of the *trans* derivatives for isomerization. The activation energies in the first group (indicated in measurements which have been carried out) are 12 to 18 kcal higher than in the second group.

There are two interesting features here. The particularly ready isomerization of the 6.4.6 racemate is a reflection of the high strain in this system, which is evident even with Dreiding models. Even more remarkable is the fact that the three *meso* tricyclic compounds pyrolyze much less readily than the racemic isomers, but more readily than the bicyclic compounds with fused rings in the 3,4 position, though disrotation occurs in both cases and the decrease in strain on isomerization should be similar. If it is assumed, as mentioned above, that unstable diradicals occur as intermediates in disrotation, the bicyclic compounds (all of which have methyl groups at the condensation points) should react more rapidly, since the diradicals in these cases would be ditertiary. Four reasons can be suggested for the greater activity of the tricyclic compounds:

1. In the case of the tricyclic compounds, only two H atoms come close to each other in the transition state during the disrotation, whereas two methyl groups are involved in the case of the bicyclic compounds.

2. The isomerization of the tricyclic compounds leads to an increase in the entropy of the system, since the products are biscycloalkenyls having free rotation about the central C–C bond.

3. The formation of *cis* double bonds requires an outward disrotation of the large groups in the tricyclic compounds, but an inward disrotation in the bicyclic compounds. An inward disrotation is possible only if the four carbon atoms of the cyclobutene ring are simultaneously twisted out of the planar position. This presumably means that the transition state would have a very high energy.

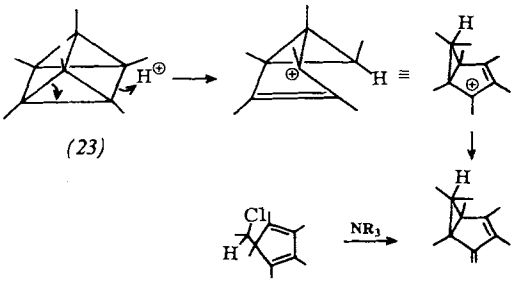
4. Ring opening in the tricyclic compounds yields dienes with true conjugation, whereas the absence of conjugation in the dienes formed from the bicyclic compounds is shown by the absence of a UV maximum.

Moreover, a strong transannular interaction is to be expected in the reaction products in this case.

It is not possible to tell from the existing experimental data which of these factors is actually involved.

3. Acid-Catalyzed Isomerization of Hexamethylprismane

So far we have considered only isomerizations of cyclobutenes. However, at least one example should now be given of an isomerization of a cyclobutane that is extremely readily rearranged by acids. When the saturated hydrocarbon hexamethylprismane *(23)*, which consists of three four-membered rings and two three-membered rings, is treated with catalytic quantities of trifluoroacetic acid at room temperature in CCl_4 solution it isomerizes within a few hours. In contrast to the thermal or metal-catalyzed rearrangement, however, neither of the valence isomers hexamethyl-Dewar-benzene or hexamethylbenzene is formed; the reaction proceeds instead by a hydrogen shift to give an almost quantitative yield of pentamethylmethylene-bicyclo[3.1.0]hexene *(25)*. The reaction is stereospecific, since of the two possible stereoisomers, the only one formed is that containing an *exo*-methyl group on C-6. This substance has already been obtained by *Schäfer* [27], together with small quantities of the *endo* isomer, by treatment of hexamethyl-Dewar-benzene *via* the cyclopentadiene derivative *(24)* [27a] with bases. The reaction course shown in Scheme 9 may be regarded as probable.



(23) *(24)* *(25)*

Scheme 9

Hexamethyl-Dewar-benzene cannot occur as an intermediate in this reaction, since it remains unchanged under the same conditions. The proton opens a bond between two four-membered rings. The driving force of the reaction is the decrease in the high ring strain of the prismane system.

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German version: Angew. Chem. *80*, 585 (1968)
Translated by Express Translation Service, London

[27] *W. Schäfer* and *H. Hellmann*, Angew. Chem. *79*, 566 (1967); Angew. Chem. internat. Edit. *6*, 518 (1967); *H. Hellmann*, Chimia *22*, 50 (1968).

[27a] This compound was originally formulated by the authors as 5-chloro-1,2,3,4,5,6-hexamethyl-1,3-cyclohexadiene.

Small Antiaromatic Rings [**]

BY R. BRESLOW [*]

According to quantum mechanical calculations, systems with $4n\,\pi$ electrons ought to have anti-aromatic character, i.e. be destabilized by resonance. This prediction is examined for the case of cyclopropenyl anion, the simplest system having $4n\,\pi$ electrons ($n = 1$). Isolation of compounds containing the cyclopropenyl anion has not, as yet, been achieved; however, kinetic measurements indicate the existence of the ion and confirm the unusual properties predicted.

1. Introduction

Extensive efforts have been devoted to the study of cyclic conjugated systems with $4n + 2\,\pi$ electrons; from such studies the quantum-mechanical prediction of aromaticity has in general been well confirmed. By contrast, the predictions of molecular quantum mechanics for $4n\,\pi$ electron systems have not been so extensively explored. It is, of course, quite clear by now that such molecules as cyclobutadiene [1] are not aromatic (strongly stabilized by resonance) but it is not clear whether this compound is simply nonaromatic (not appreciably stabilized by resonance, and highly reactive because of strain, *etc.*) or whether it is actually anti-aromatic (destabilized by resonance).

We have discussed the definition of "anti-aromaticity" previously [2, 3], and have pointed out that there are

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[**] From a Plenary lecture given at the International Symposium on the Chemistry of Small Rings (Louvain, Belgium, 12–15 September 1967).

[1] *M. P. Cava* and *M. J. Mitchell*: Cyclobutadiene and Related Compounds. Academic Press, New York 1967.

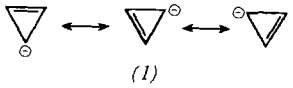
[2] *R. Breslow*, Chem. Engng. News *43*, No. 26, p. 90 (1965).

[3] *R. Breslow*, *J. Brown*, and *J. Gajewski*, J. Amer. chem. Soc. *89*, 4383 (1967).

various ways of defining "the opposite of aromaticity", depending on whether magnetic, spectroscopic, kinetic, or thermodynamic criteria are used. Although the various manifestations of aromatic character are, in fact, closely related, we prefer to emphasize the thermodynamic definition in which aromaticity describes a particularly large negative contribution by electron-delocalization to the energy of a cyclic conjugated system. Thus an *anti-aromatic* system is one in which electron delocalization considerably raises the energy.

2. Quantum Mechanical Predictions

Before discussing the evidence for antiaromaticity let us see whether quantum mechanics contains a prediction of such an unusual situation. It turns out that the most striking predictions – as well as the best evidence – are for cyclopropenyl anion *(1)*, a 4 π electron system.



(1)

$H_2C{=}CH{-}CH_2^{\ominus}$

(2)

By a simple Hückel calculation the delocalization energy of *(1)* is 0.00 β. Thus comparing it with the components of the conjugated system – a double bond and a carbanion – we would call it non-aromatic. However, it is common to refer aromatic compounds to open-chain analogs, comparing benzene with linear hexatriene for instance. If we compare cyclopropenyl anion *(1)* with allyl anion *(2)*, considering the latter an example of normal conjugation, then *(1)* is antiaromatic since *(2)* has 0.82 β of resonance energy. From a comparison of cyclic and open-chain systems [4] it can be seen that both cyclopropenyl cation (2 electrons) and cyclopentadienyl anion (6 electrons) are predicted to be strongly stabilized relative to their linear analogs, as is known experimentally, but that both the cyclopropenyl anion and the cyclopentadienyl cation are predicted to be destabilized relative to the linear analogs.

A similar prediction arises from more sophisticated calculations. In Table 1 are presented the results of a π-electron calculation on cyclopropenyl and allyl anions using the standard Pariser-Parr parameters [5] and including a complete configuration interaction treatment [6]. The table also lists the results of such calculations for cyclopentadienyl and linear pentadienyl cations, in which only some of the excited configurations were considered. In all cases simple regular geometries were assumed, although the actual molecules might well undergo distortions.

[4] For a graphical method see *R. Breslow* and *E. Mohacsi*, J. Amer. chem. Soc. *85*, 234 (1965).

[5] *R. G. Parr*: The Quantum Theory of Molecular Electronic Structure. Benjamin, New York 1963.

[6] We wish to thank Prof. *M. Karplus* and Dr. *D. Lazdins* for making their computer program available.

Table 1. Results of PPP–SCF–CI calculations.

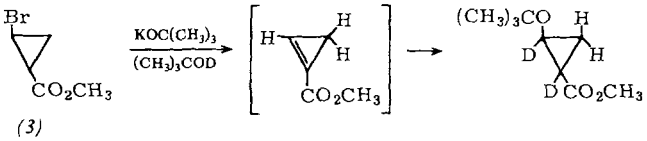
Molecule	Singlet energy (eV)	Triplet energy (eV)
Cyclopropenyl anion *(1)*	– 61.448	– 62.290
Allyl anion *(2)*	– 61.903	– 59.164
Cyclopentadienyl cation	–123.147	–123.465
Pentadienyl cation	–105.014	–

In comparing these systems a "core correction" for the change in carbon-carbon interaction has to be applied (1.60 eV in the three-carbon case and 19.06 eV in the five-carbon case). The result is a prediction that the singlet state of *(1)* is antiaromatic by 2.0 eV, and that of cyclopentadienyl cation by 0.9 eV. These calculations confirm the prediction of the simple Hückel method that both cyclic 4 π electron systems are destabilized relative to open-chain analogs, but that the effect is greater in the cyclopropenyl anion than in the larger cyclopentadienyl cation. This is a general result: the small cyclopropenyl anion is the best place to look for evidence of antiaromaticity.

A second fact derivable from Table 1 is that both the cyclopropenyl anion and the cyclopentadienyl cation are predicted (assuming symmetrical polygonal geometry) to have triplet ground states. However, again the prediction is stronger for the smaller ring: the singlet-triplet gap is 0.842 eV for cyclopropenyl anion and only 0.318 eV for cyclopentadienyl cation. An additional point of interest is that the singlet states are lowered more in energy when excited configurations are included in the calculation than are the triplet states, so this configuration-interaction calculation decreases the predicted energy advantage of the triplets by 0.3 eV for the C_3 system and 0.15 eV for the C_5 system.

3. Attempts to Synthesize the Cyclopropenyl Anion

With such striking quantum-mechanical predictions it became clear that the cyclopropenyl anion was a system of major interest, perhaps surpassing that of the cation [7]. It was already known that this anion was not strongly stabilized. For instance, *Wiberg* had shown [8] that treatment of β-bromocyclopropanecarboxylic ester with base caused elimination to a cyclopropene which exchanged its vinylic [9], but not its allylic, hydrogen. Further evidence corroborating the proposition that electrons added to cyclopropenyl



(3)

[7] See *R. Breslow, J. Groves*, and *G. Ryan*, J. Amer. chem. Soc. *89*, 5048 (1967), and earlier work.

[8] *K. B. Wiberg, R. K. Barnes*, and *J. Albin*, J. Amer. chem. Soc. *79*, 4994 (1957).

[9] The acidity of the vinyl protons has also been studied in later work: *R. Breslow* and *L. J. Altnan*, J. Amer. chem. Soc. *88*, 504 (1966), and further literature cited there.

cations go into high-energy orbitals was obtained from our electrochemical studies[10] on cyclopropenyl cations by oscillopolarography (Table 2). As the Table shows, reduction of the cyclopropenyl cations to radicals takes approximately 1 eV more energy than does reduction of triphenylmethyl cation, and this corresponds well to the predictions of M.O. theory, since β for electrochemical reductions is of the order of 2 eV.

Table 2. Electrochemical reduction potentials [a].

$R^+ \xrightarrow{e} R^\bullet$

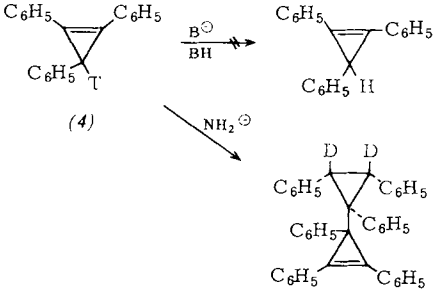
$E_{1/2}$ = Half-wave potential, *D.E.* = delocalization energy.

R^+	$E_{1/2}$ (eV)	$\Delta D.E._{red}$ (β)
Triphenylcyclopropenyl	−1.13	−0.504
Diphenylcyclopropenyl	−1.02	−0.504
Anisyldiphenylcyclopropenyl	−1.24	−0.504
Dainisylphenylcyclopropenyl	−1.37	−0.565
Trianisylcyclopropenyl	−1.49	−0.700
Triphenylmethyl	−0.09	0

[a] Solutions 0.2 mM in cation perchlorates in dry acetonitrile with 0.1 M tetraethylammonium perchlorate were examined by oscillopolarography against $Ag/AgClO_4$ electrode taken as +0.380 V *vs.* saturated calomel electrode.

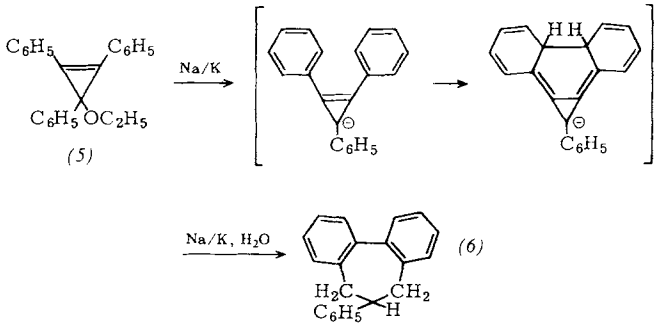
In this work it proved impossible to attain potentials which would add a second electron to afford the anion, since reduction of solvent occurred first. Although this helps to confirm the predictions of M.O. theory on which the proposition of antiaromaticity in the anion is based, it is not, of course, direct evidence about the anion.

Several other unsuccessful attempts have been made to isolate derivatives of cyclopropenyl anion, and such work is actively continuing. For instance, with *P. Dowd* we investigated[11] the treatment of [3-T]-triphenylcyclopropene *(4)* with various bases, and found that no exchange of the tritium could be detected with base under conditions much more vigorous than those required to exchange [1-T]-triphenylmethane. With some strong bases triphenylcyclopropene affords a dimer, but mechanistic studies show that the anion is not involved; the mechanism of this process has been discussed[11].



(4)

Reduction of triphenylcyclopropenyl ethyl ether *(5)* with sodium-potassium alloy might be expected to furnish the triphenylcyclopropenyl anion, but the product is in fact[12] a dibenzocycloheptene derivative *(6)*. Quenching part way through the reaction affords starting ether *(5)* and the final product *(6)* with no triphenylcyclopropene; if the triphenylcyclopropenyl anion is involved it rearranges rapidly. Interestingly, if the final mixture is quenched in D_2O, the product *(6)* is about one third trideuterated and one half dideuterated.



(5) *(6)*

Recently, *T. Higgs*[13] confirmed that tribenzoylcyclopropenyl anion is present in equilibrium in strongly basic solution.

4. Kinetic Investigations

In the absence at the present time of isolable derivatives of cyclopropenyl anion we must turn to kinetic evidence on stability. The correlation between kinetic and thermodynamic acidity has been examined by many investigators, and is summarized in *Cram*'s monograph[14]. Within closely related series kinetic and thermodynamic acidities usually run parallel (the Brønsted Law), and when solvents are much more acidic than the substrates reprotonation of enolate ions, *etc.*, is almost diffusion controlled; rates and equilibria must therefore run parallel for related structures. A correlation between the rate of ionization and the stability of the product ion would, of course, be expected; for almost all exchange processes the ionization step is rate determining.

However, several cases of exchange have been found[15], in studies utilizing all three hydrogen isotopes, in which k_H/k_D is less than 1.0. Such an inverse isotope effect shows that the C–H bond is not breaking in the rate determining step; in such special cases, therefore, the exchange rate is apparently determined by diffusion of solvent into and out of a solvated carbanion complex.

Recently the isotope effect for hydrogen exchange in cyclopropanecarbonitrile has been measured, and k_H/k_D has been found[16] to be 1.9. Although the authors suggest this is so low that ionization is probably not rate determining, we feel that with a positive isotope effect of this magnitude there is no

[10] *R. Breslow, W. Bahary,* and *W. Reinmuth,* J. Amer. chem. Soc. *83,* 1763 (1961).

[11] *R. Breslow* and *P. Dowd,* J. Amer. chem. Soc. *85,* 2729 (1963).

[12] *P. Dowd,* Ph.D. Thesis, Columbia University, New York 1962.

[13] *T. Higgs,* unpublished work.

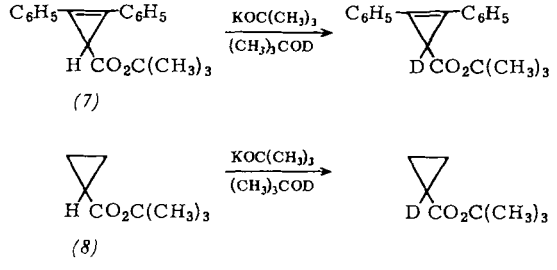
[14] *D. J. Cram:* Fundamentals of Carbanion Chemistry. Academic Press, New York 1965.

[15] Ref. [14], pp. 28 and 29.

[16] *W. Th. van Wijnen, M. van Wijnen, H. Steinberg,* and *Th. J. de Boer,* Tetrahedron *23,* 3763 (1967).

need to involve any unusual hypotheses. Accordingly, in what follows we will discuss rates of exchange in terms of the stability of the product ion, as is usual, while keeping in mind possible special steric effects in the transition states.

The earliest evidence for a remarkable destabilization of cyclopropenyl anion was the finding [17], with *Battiste*, that deuterium exchange in a cyclopropene ester *(7)* proceeds at least 300 times slower than that in a cyclopropane ester *(8)* [8]. (This exchange rate and that mentioned in the following example refer to

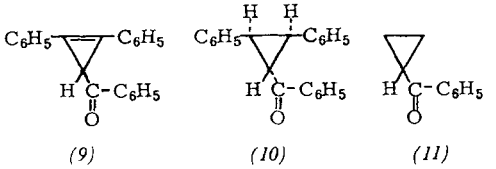


(7)

(8)

similar conditions and at ≈ 25 °C.) This was a remarkable observation, since the anion derived from *(7)* should have extra stabilization from conjugation with the double bond and through it with the two phenyl groups. The enolate ion of *(7)* [cf. *(12)*] deuterates very rapidly at C-1. Isomerization of the double bond at the position between C-1 and C-2 (conjugation with the ester group) with subsequent addition of solvent across the double bond [18] takes place much more slowly.

Striking as this observation was, later work showed that these preliminary kinetic data actually underestimate the destabilization in a cyclopropenyl anion. Kinetic studies on 3-benzoyl-1,2-diphenylcyclopropene *(9)* show that its base-catalyzed exchange is 6000 times slower than that of the corresponding cyclopropane derivative *(10)*, and that this difference is reflected in the activation energies, not entropies [3].



(9) *(10)* *(11)*

	(9)	*(10)*	*(11)*
Rate of exchange	1	6000	2000
E_a	26 (kcal/mole)	20.3 (kcal/mole)	—
log *A*	11.2	10.6	—

As expected, phenyl substituents on the cyclopropane increase the rate slightly by an inductive effect.

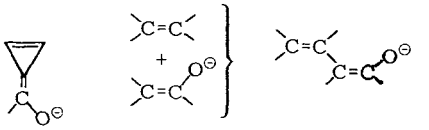
[17] *R. Breslow* and *M. Battiste*, Chem. and Ind. *1958*, 1143.

[18] *M. Battiste*, Ph. D. Thesis, Columbia University, New York 1958.

5. Experiments on the Significance of the Kinetic Behavior

The factors which might be involved in a 6000-fold decrease in exchange rate in the case of *(9)*, compared with *(10)*, have been discussed in detail [3] and can be summarized briefly.

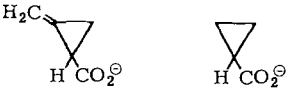
1. Antiaromaticity of the cyclopropenyl anion. The interaction between the double bond and the developing negative charge may actually be destabilizing. Ordinary Hückel calculations do not suggest this, but Pariser-Parr-Pople SCF calculations show a loss of stability (about 0.34 eV or about 2.0 eV, respectively) in the enolate ion *(12)* compared with the open-chain analogs *(13)* and *(14)*.



(12) *(13)* *(14)*

2. Steric effects. In this category one can imagine three principal effects. One is a possible difference in I Strain on ionization of the cyclopropene, because of its smaller bond angle. We have presented arguments [3] that this is unlikely to be a major factor. A second possible effect is relief of eclipsing in the cyclopropane ionization; again this does not seem to play an important role in cyclopropane chemistry. The third possible effect is eclipsing in the cyclopropenyl anion between the activating group and the other groups (phenyls) in the cyclopropene plane. This last effect is excluded by our finding that replacement of the phenyls by smaller methyl groups actually leads to a decrease, not increase, in the rate of exchange in the cyclopropene. It is also excluded by data mentioned below for a cyclopropene carbonitrile.

It should be mentioned that the introduction of a trigonal carbon in a cyclopropane need not decrease the rate of base-catalyzed exchange. *Bottini* has found [19] that deuterium exchange in methylenecyclopropanecarboxylate ion *(15)* is 10^5 times faster than in the simple cyclopropanecarboxylate *(16)*.



(15) *(16)*

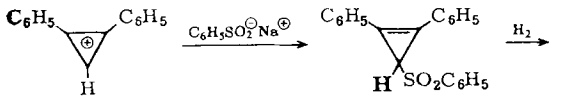
100000 1

Although in this comparison steric factors similar to those discussed above could also play a role, with about half the magnitude of that in the case of cyclopropene, the normal conjugative and inductive effects of a double bond strongly accelerate the exchange. The comparison between the effect of a double bond exocyclic or endocyclic [in *(15)* and *(9)*] to the cyclo-

[19] *A. T. Bottini* and *A. J. Davidson*, J. org. Chemistry *30*, 3302 (1965).

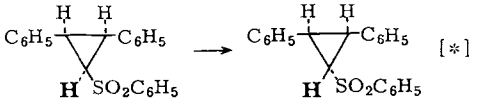
propane anion is particularly striking, and reflects the comparison between normal open-chain and cyclic antiaromatic conjugation.

A comparison has also been made between cyclopropane and cyclopropene exchange rates with other activating groups, for example sulfonyl groups [3]. Some suggestions have been made [20] that carbanions next to sulfonyl groups may have grossly different



(17)

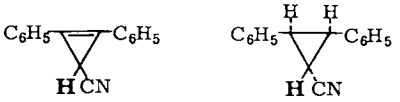
1



(18)

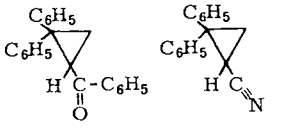
1000

hybridization from, for instance, those next to carbonyl. Our data show that the antiaromatic effect, whatever its origin, is observed for such an anion as *(17)* also. Perhaps more striking is the observation on the compound *(19)* with a cyano group as activating substituent [21]. Since the cyano group is smaller than a benzoyl group, many of the steric effects we have mentioned should be smaller in this case, but PPP-SCF calculations suggest that the electronic antiaromatic effect should be larger. (Essentially because the cyano group removes charge less effectively so that the hybrid anion has more cyclopropenyl anion character.) Experimentally, the apparent antiaromaticity is the largest so far observed, which is consistent with the electronic explanation.



(19) 1 *(20)* 10700

All of the possible steric explanations for the apparent antiaromaticity of cyclopropenyl anions involve postulated difficulties with rehybridization of the cyclopropene carbon to flat trigonal geometry. *Walborsky* has observed [22] that deuterium exchange in some optically active cyclopropane derivatives occurs with partial retention of configuration, and one of the explanations offered for this is non-planarity of the intermediate anion. If steric effects were responsible for the apparent antiaromaticity then optically active cyclopropenes should show an even greater tendency to exchange without racemization. If on the other hand antiaromatic electronic interactions are involved in the cyclopropenyl anions, then one would expect a decreased k_e/k_r (e = exchange, r = racemization) since repulsion by the double bond should force more negative charge into the activating group thus flattening the carbon. Such increased flattening as more charge disperses into the activating group presumably explains the difference in *Walborsky*'s data [22,23] for the ketone *(21)* and the nitrile *(22)*.



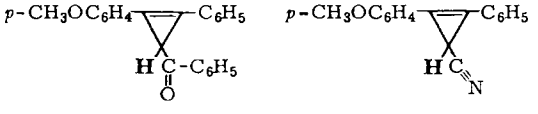
(21) *(22)*

Table 3. Some k exchange/k racemization values.

Compound	Solvent	k_e/k_r	Ref.
(21)	CH_3OH	1.64	[22,23]
(22)	CH_3OH	8080	[22,23]
(22)	$(CH_3)_3COH$	77	[22,23]
(23)	C_2H_5OH	1.0 ± 0.1	[21]
(24)	$(CH_3)_3COH$	4.0 ± 0.2	[21]

We have prepared [21] an optically active cyclopropenyl ketone and carbonitrile by resolution of the corresponding cyclopropenecarboxylic acid, and standard conversion of the carboxyl group into the other functions. The observation is that k_e/k_r for the cyclopropenyl ketone *(23)* is much less than that for the cyclopropyl ketone *(21)*; in the case of the carbonitriles, the value for *(24)* is smaller than that for *(22)*. This is again consistent with the idea that electronic antiaromaticity is involved (see Table 3).

One must consider the possibility that *Walborsky*'s retention data reflect "asymmetric solvation" of the anion although he specifically rejects this alternative [22]. Even if this were the explanation, the increased racemization would result from an increased tendency in the cyclopropenecarbonitrile anion for



(23) *(24)*

protonation on nitrogen rather than on carbon, again because of electronic antiaromatic interaction. It need hardly be added that the increased tendency for racemization in the cyclopropenes cannot be due to a *stabilizing* interaction of the flattened anion with the double bond, since the exchange rate is decreased in the cyclopropenes.

There is an additional quantum-mechanical prediction about some antiaromatic systems which is of interest. Systems with $4n$ π electrons and C_3 or greater symmetry may have triplet ground-states. Predictions from PPP–SCF–CI calculations on cyclopentadienyl cation and cyclopropenyl anion have already been

[20] For a summary cf. ref. [14], pp. 110ff.

[*] Rates of exchange were measured for the hydrogen atoms printed in bold type.

[21] *R. Breslow* and *M. Douek*, unpublished.

[22] *H. M. Walborsky, A. A. Youssef*, and *J. M. Motes*, J. Amer. chem. Soc. *84*, 2465 (1962).

[23] *H. M. Walborsky*, private communication.

described in Section 2: assuming symmetric geometry, the triplet states were much lower in energy than the singlets.

Experimentally, symmetric derivatives of cyclopropenyl anion are not yet available (cf. Section 3[13]); however, triplet states have been detected for several cyclopentadienyl cations. Since this work has been described in detail recently[24], only the principal conclusions will be cited.

Pentachlorocyclopentadienyl cation is a ground state triplet. Pentaphenylcyclopentadienyl cation is a ground state singlet, but its triplet state is only 0.35–1.15 kcal/mole higher. Apparently this molecule can distort away from perfect five-fold symmetry; the results also confirm the general conclusion that the energetic advantage of triplet state is decreased in larger molecules.

In molecules with less symmetry, such as β-naphthyltetraphenylcyclopentadienyl cation, a triplet state is even higher in energy. However, NMR spectra show that the triplet state and the ground singlet state are in rapid thermal equilibrium. The existence of such a rapid equilibrium vitiates the chemical criteria often applied to such molecules as cyclobutadiene to determine whether they are singlets or triplets.

The aromaticity of various new systems which fit *Hückel*'s $4n + 2$ rule, including cyclopropenyl cation, is by now well established. The even more interesting properties of some $4n$ π electron systems – antiaromaticity and in some cases triplet ground states – must be explored further. However, it seems that several of the most unusual predictions of molecule quantum mechanics about such systems have in fact been confirmed.

Received: November 20, 1967 [A 645 IE]
German version: Angew Chem. *80*, 573 (1968)

[24] *R. Breslow, H. W. Chang, R. Hill,* and *E. Wasserman,* J. Amer. chem. Soc. *89*, 1112 (1967).

Syntheses of Cyclopropylcarbonyl Compounds[**]

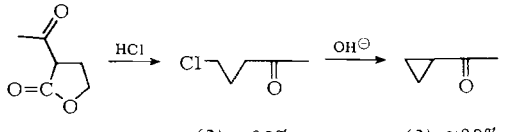
BY J. M. CONIA[*]

There are three important direct routes to cyclopropylcarbonyl compounds: 1. Cyclization of chains of three carbon atoms, the first or third of which is adjacent to a carbonyl or potential carbonyl carbon atom (this type includes syntheses by intramolecular alkylation of γ-halogeno ketones or related compounds in alkaline media); 2. insertion of a methylene group or substituted methylene group into the olefinic double bond of an α,β-unsaturated carbonyl compound; and 3. introduction of an acetonyl group into the double bond of an olefin. However, cyclopropylcarbonyl compounds can also be obtained from 1,2-epoxycyclobutane and 2-bromocyclobutanone derivatives by ring contraction. Another possibility is the dehalogenation of α,α-bis(bromomethyl)cycloalkanones. This review concludes with a discussion of these little known routes and of a particularly suitable method which involves the reaction of methylene iodide, a Zn–Cu couple, and α,β-unsaturated ketones.

1. Intramolecular Alkylation

1.1. Cyclization of γ-Substituted Ketones

The more recent publications in this connection deal mainly with improved syntheses of ketones intended for subsequent conversion into cyclopropyl ketones *(3)* by the action of bases. Thus methyl cyclopropyl ketones can be synthesized *e.g.* from α-acetyl-γ-lactone *(1)* by treatment with hydrochloric acid to obtain the γ-chloro ketone *(2)*, followed by cyclization with sodium hydroxide, potassium hydroxide, or sodamide[1,2].



(1) *(2)*, ≈90% *(3)*, ≈80%

α-Substituted α-acetyl-γ-lactones give methyl cyclopropyl ketones having a substituent in the α-position of the ring[3]. Corresponding β-substituted cyclopro-

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Caen (France)

[**] Based on a plenary lecture delivered at the Symposium on Small Rings (Louvain, Belgium, September 12–15, 1967).

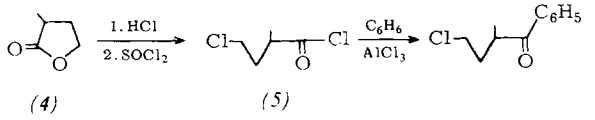
[1] *G. W. Cannon, R. E. Ellis,* and *J. R. Leal,* Org. Syntheses *31*, 74 (1951).

[2] *G. W. Cannon, A. A. Santilli,* and *P. Shenian,* J. Amer. chem. Soc. *81*, 1660 (1959).

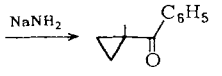
[3] *M. Julia, S. Julia,* and *Y. Noel,* Bull. Soc. chim. France *1960*, 1708.

pyl ketones are obtained from the β-substituted γ-chloro ketones [4].

Phenyl cyclopropyl ketones *(6)* can also be obtained from unacetylated lactones, *e.g. (4)*, which are hydrolyzed by hydrochloric acid and give γ-chlorinated acyl chlorides *(5)* on treatment with thionyl chloride. A Friedel-Crafts reaction of the acyl chloride *(5)* with benzene leads to the γ-chlorinated phenyl ketone, which then yields the desired phenyl cyclopropyl ketone *(6)* on treatment with sodamide [1,2].

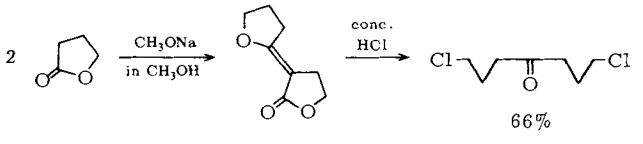


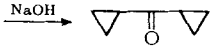
(4) *(5)*



(6), 58%

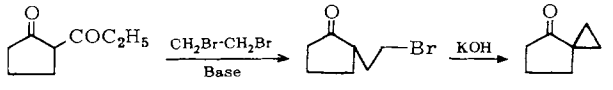
Dicyclopropyl ketone *(7)* can be obtained directly from γ-butyrolactone in an overall yield of 50–60% [5].





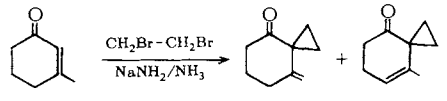
(7), 70%

The starting compound may also be a keto ester such as *(8)*, which is converted into the spiro ketone *(9)* by alkylation with 1,2-dibromoethane and ring closure with KOH [6].



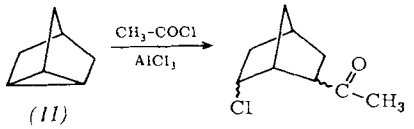
(8) *(9)*

A similar double alkylation should also be possible in α,β-unsaturated ketones *(10)* [7].

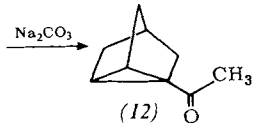


(10)

One method that may occasionally be of interest for the synthesis of cyclopropyl ketones is the simultaneous acetylation and chlorination of a cyclopropane. This process yields an open-chain γ-halogeno ketone, which is recyclized by treatment with a base. 1-Acetylnortricyclene *(12)* can be obtained in this way from nortricyclene *(11)* in an overall yield of 40–60% [8].

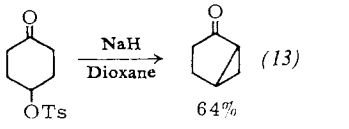


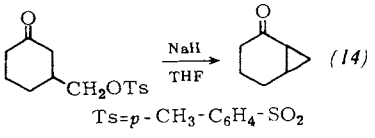
(11)



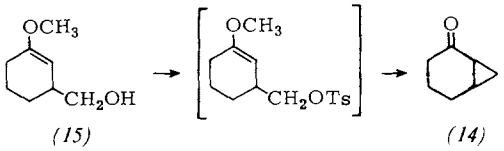
(12)

Cyclic ketones containing a *p*-toluenesulfonyl group on the γ-carbon atom inside or outside the ring yield interesting bicyclic ketones such as *(13)* and *(14)* on α,γ-elimination [9,10].





2-Norcaranone *(14)* can also be obtained from the enol ether *(15)* by cyclization of the *p*-toluenesulfonate in pyridine [11].



(15) *(14)*

1.2. Reaction of α,β-Unsaturated Ketones with Ylides

A very versatile variant of the intramolecular alkylation is the reaction of ylides, particularly dimethyloxosulfonium methylide *(16)*, with α,β-unsaturated ketones. It is well known that the reaction of dimethylsulfonium methylide $(CH_3)_2S{=}CH_2$ with ketones of this type leads, not to cyclopropyl ketones, but to epoxides. On the other hand, the reaction with dimethyloxosulfonium methylide leads, with loss of di-

[4] *M. Julia, S. Julia,* and *J. Amaudric du Chaffaut,* Bull. Soc. chim. France *1960*, 1735.

[5] *H. Hart* and *O. E. Curtis,* J. Amer. chem. Soc. *78*, 112 (1956).

[6] *R. Mayer* and *H. J. Schubert,* Chem. Ber. *91*, 768 (1958).

[7] *M. S. Newman, V. de Vries,* and *R. Darlak,* J. org. Chemistry *31*, 2171 (1966).

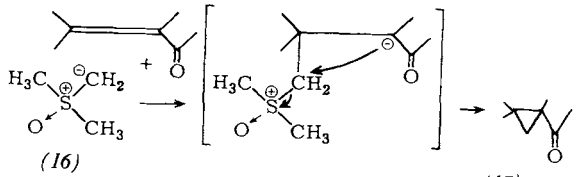
[8] *H. Hart* and *R. A. Martin,* J. org. Chemistry *24*, 1267 (1959).

[9] *N. H. Nelson* and *G. A. Mortimer,* J. org. Chemistry *22*, 1146 (1957).

[10] *G. Stork* and *J. Ficini,* J. Amer. chem. Soc. *83*, 4678 (1961).

[11] *O. L. Chapman* and *P. Fitton,* J. Amer. chem. Soc. *85*, 41 (1963).

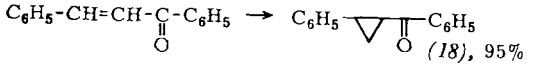
methyl sulfoxide, to the cyclopropyl ketones *(17)* [12, 13, 15]. The reagent is readily obtainable from trimethyloxosulfonium iodide and sodium hydride.



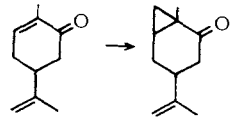
(16) *(17)*

$+ (CH_3)_2S{\rightarrow}O$

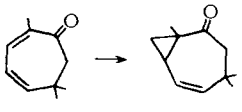
This reaction permits the synthesis of many cyclopropyl ketones [*e.g. (18)–(21)*] derived from enones and even dienones.



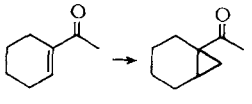
(18), 95%



(19), 81%

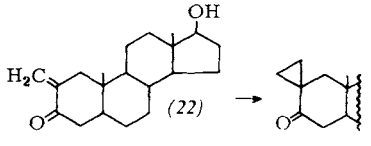


(20), 88%

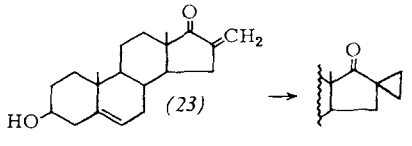


(21), 53%

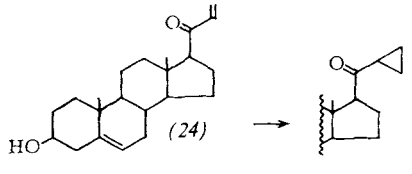
It can also be used successfully with keto steroids [14]. In this case the basic reagent (NaH) simultaneously liberates the unsaturated ketone [*e.g. (22)–(24)*] from the Mannich base and the ylide from the oxosulfonium salt.



(22)



(23)



(24)

[12] *E. J. Corey* and *M. Chaykovsky*, J. Amer. chem. Soc. *84*, 3782 (1962).

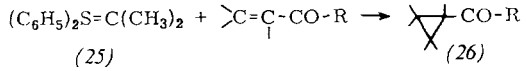
[13] *E. J. Corey* and *M. Chaykowsky*, J. Amer. chem. Soc. *87*, 1353 (1965).

[14] *H. G. Lehmann, H. Müller*, and *R. Wiechert*, Chem. Ber. *98*, 1470 (1965).

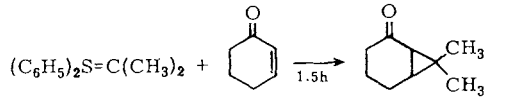
[15] *C. Agami*, Bull. Soc. chim. France *1967*, 1391; *C. Agami* and *C. Prevost*, *ibid. 1967*, 2299.

The synthesis of cyclopropyl ketones from α,β-unsaturated ketones and dimethyloxosulfonium methylide loses its importance when the ketones are unstable in alkaline solution. Though mesityl oxide still gives good yields (approximately 40 %), methyl vinyl ketone and phenyl vinyl ketone simply resinify [15], and the starting material can be isolated unchanged from the mixture with 3-penten-2-one. The corresponding cyclopropyl ketones can be more successfully prepared with the aid of Simmons reagent (see Section 2.1).

Diphenylsulfonium isopropylide *(25)* reacts with the olefinic double bond of α,β-unsaturated carbonyl compounds, and is thus excellently suited for the synthesis of geminal dimethylcyclopropyl ketones such as *(26)* and *(27)* [16].

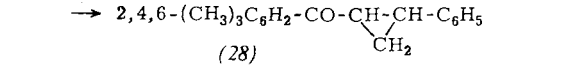


(25) *(26)*



(25) *(27)*, 74%

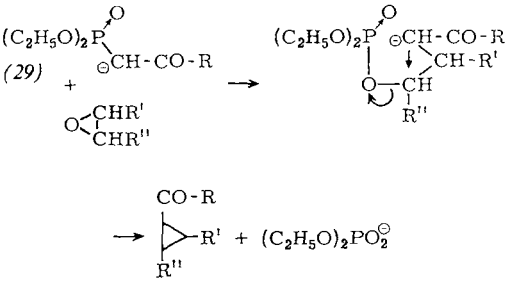
Little is known about the formation of cyclopropyl ketones from phosphonium ylides and α,β-unsaturated ketones. One example is the synthesis of the cyclopropyl ketone *(28)* from triphenylphosphonium methylide (methylenetriphenylphosphorane) and mesityl styryl ketone, the carbonyl group of which is strongly sterically hindered [17].



(28)

1.3. Reaction of Epoxides with Ylides

The reaction of stabilized phosphonium ylides with epoxides, which leads in the case of the ylide ester $(C_6H_5)_3P{=}CH{-}COOC_2H_5$ to the expected cyclopropyl esters, can be successfully extended to the synthesis of corresponding ketones. Ketone ylides (*e.g.* the carbanion of the diethyl β-oxophosphonate *(29)*) give numerous cyclopropyl ketones in an apparently general reaction with epoxides [18].



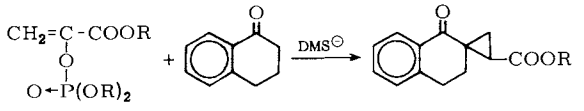
(29)

[16] *E. J. Corey* and *M. Jautelat*, J. Amer. chem. Soc. *89*, 3912 (1967).

[17] *J. P. Freeman*, Chem. and Ind. *1959*, 1254.

[18] *H. Normant* and *G. Sturtz*, C. R. hebd. Séances Acad. Sci. *256*, 1800 (1963); *G. Sturtz*, Bull. Soc. chim. France *1964*, 2343.

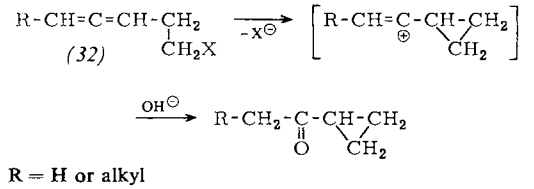
A synthesis that proceeds *via* an intermediate of the same type, despite the use of different starting compounds, is the reaction of triethylphosphoenol pyruvate *(30)* with a compound containing an active methylene group in the presence of a strong base. In this way, tetralone gives the spirocyclopropyl ketone *(31)* with an ester group attached to the three-membered ring [19].



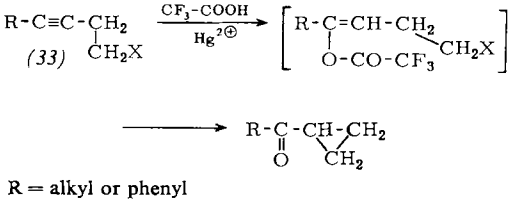
(30) *(31)*, 80%

1.4. Other Syntheses of Cyclopropyl Ketones

Mention should also be made of new cyclization reactions such as the solvolysis of allene sulfonates *(32)*, which proceeds *via* a vinyl cation [20], and the reaction of acetylenesulfonates *(33)* with trifluoroacetic acid, which leads in the presence of Hg^{2+} to cyclopropyl ketones [21].



R = H or alkyl
X = sulfonate



R = alkyl or phenyl
X = sulfonate

2. Insertion Reactions

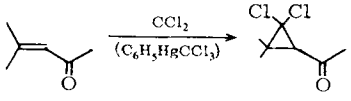
2.1. Insertion in α,β-Unsaturated Ketones

The cyclopropylcarbonyl system can also be synthesized by direct insertion of a substituted or unsubstituted methylene group into the olefinic double bond of an α,β-unsaturated carbonyl compound or by the insertion of an acetonyl group into the double bond of an olefin.

The direct insertion is apparently difficult to achieve. Thus the action of diazomethane or phenyldiazomethane on chalcone or other ketones leads *via* a pyrazoline to, at best, very small yields of cyclopropyl ketones [22].

In the reaction of halogeno- and dihalogenocarbenes the α,β-unsaturated ketones and aldehydes are probably unable to withstand the strongly basic conditions required for the formation of the carbenes. The synthesis of halogenated cyclopropyl ketones cannot be achieved even by blockage of the carbonyl group *e.g.* by acetalization, since the double bond then frequently migrates to the β,γ-position.

On the other hand, the reaction of dichlorocarbene (which is formed under mild conditions from $C_6H_5-HgCCl_3$) with mesityl oxide *(34)* leads to very good yields of dichlorodimethylcyclopropyl methyl ketone *(35)* [23].



(34) *(35)*, 83%

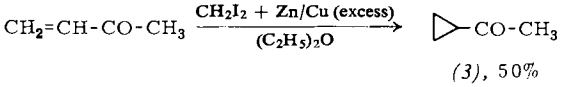
The Simmons reaction

$$CH_2I_2 + Zn/Cu + \text{olefin} \rightarrow \text{cyclopropane derivative}$$

can also be applied to unsaturated compounds containing functional groups such as –OH, –OAc, or –COOR and to many α,β-unsaturated ketones [35,36].

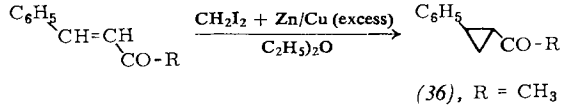
We found that no cyclopropylcarbonyl compounds are obtained when the reaction is carried out with aldehydes (acrolein, crotonaldehyde, cinnamaldehyde), but that the reaction mixture simply resinifies.

However, cyclopropyl ketones are readily formed from vinyl ketones and from untautomerizable, α,β-unsaturated ketones with no hydrogen in the γ-position. On heating in ether for 48 h methyl vinyl ketone gives a 50 % yield of methyl cyclopropyl ketone *(3)* together with unreacted starting ketone and resinous compounds. Nevertheless, this is the best method for the preparation of methyl cyclopropyl ketone.



(3), 50%

trans-Benzilideneacetone is also readily converted into the *trans* isomer of 1-phenyl-2-acetylcyclopropane *(36)* (40 % yield). The reaction with *trans*-chalcone leads to *(37)* in yields that vary considerably with the reactivity of the Simmons reagent.



(36), R = CH_3
(37), R = C_6H_5

[19] *U. Schmidt*, Angew. Chem. *77*, 216 (1965); Angew. Chem. internat. Edit. *4*, 238 (1965).

[20] *M. Hanack* and *J. Häffner*, Chem. Ber. *99*, 1077 (1966).

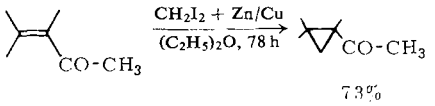
[21] *M. Hanack*, *I. Herterich*, and *V. Vötl*, unpublished; see *M. Hanack* and *H. J. Schneider*, Angew. Chem. *79*, 687 (1967); Angew. Chem. internat. Edit. *6*, 666 (1967).

[22] *L. I. Smith* and *W. B. Pings*, J. org. Chemistry *2*, 23 (1937); *R. J. Mohrbacker* and *N. H. Cromwell*, J. Amer. chem. Soc. *79*, 401 (1957).

[23] *D. Seyferth*, *J. M. Burlitch*, *R. J. Minasz*, *J. Yich-Pui Mui*, *H. D. Simmons jr.*, *A. J. H. Treiber*, and *S. R. Dowd*, J. Amer. chem. Soc. *87*, 4259 (1965).

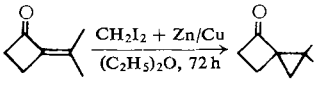
The behavior of tautomerizable α,β-unsaturated ketones is interesting. Whereas 3-methyl-2-cyclopenten-1-one and 3-methyl-2-cyclohexen-1-one (as well as isophorone) do not react, the corresponding unmethylated compounds add to the methylene group in good yields. This offers a very simple synthesis of 2-norcaranone *(14)* (90 % yield after 36 h).

Under the same conditions, mesityl oxide sometimes remains unchanged and sometimes resinifies, to a greater or lesser extent, whereas the α-methylated derivative (3,4-dimethyl-3-penten-2-one) yields the expected cyclopropyl ketone.



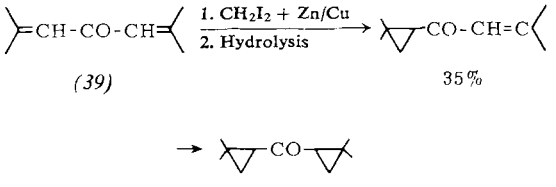
73%

Pulegone and 2-isopropylidenecyclopentan-1-one do not react, while 2-isopropylidenecyclobutan-1-one gives the expected spiro ketone *(38)* together with resin and unreacted starting ketone.



(38), 37%

Dienones appear to react well. Thus phorone *(39)*, unlike mesityl oxide, reacts first with one methylene group and then, after hydrolysis, with a second.



(39)

35%

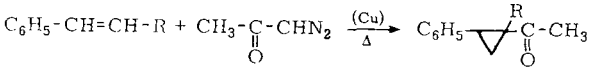
dl + meso
80%

The α,β-unsaturated ketones can therefore be divided into two classes according to their reaction with Simmons reagent (ICH_2ZnI). In addition to ketones that give the normal olefin reaction, *i.e.* the formation of cyclopropyl ketones (a prior 1,4 addition has never been observed), there are others in which the carbonyl group takes part in the reaction; these compounds probably give a stable complex from which the original ketone is regenerated on hydrolysis.

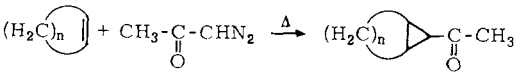
It is not easy to predict how an α,β-unsaturated ketone will behave, since small differences in structure can cause a complete change in behavior. The results are influenced by steric hindrance of the carbonyl group, the nature of the enone system, the polarity of the carbonyl group, *etc.* In our experience, all unsaturated ketones with which the Simmons reagent does not give insertion of a methylene group (*e.g.* many β-substituted ketones) can be readily alkylated *e.g.* with sodium *tert*-pentoxide (see, *e.g.*, ref. [37]); the opposite is the case with the other unsaturated ketones (*e.g.* many α-substituted ketones).

Ketocarbenes offer an interesting method for the preparation of cyclopropyl ketones from olefins, since these carbenes can be readily prepared from diazomethane derivatives by heating, by exposure to light, or by the action of catalysts.

Acetylcarbene, which is prepared from diazoacetone, adds readily to the double bond of olefins. Thus the reactions with styrene, stilbene, and cyclic olefins lead to the expected methyl cyclopropyl ketones *(36)*, *(40)*, and *(41)* [24].

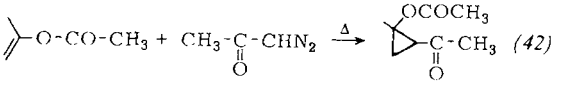


(36), R = H
(40), R = C_6H_5

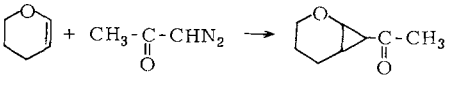


(41)

The reaction proceeds differently with benzene and thiophene, whereas with enol acetates and unsaturated heterocyclic compounds, such as dihydropyran and benzofuran, the normal products *(42)* and *(43)* are obtained.

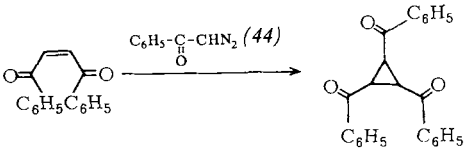


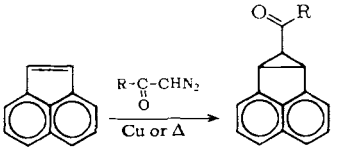
(42)



(43)

Similar results are obtained with diazoacetophenone *(44)* and similar compounds [25, 26].





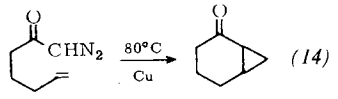
If the diazoketone itself contains a double bond, the thermally, photolytically, or catalytically (Cu) formed ketocarbene undergoes double ring closure. It is

[24] *J. Novack, J. Ratusky, V. Šneberg,* and *F. Šorm,* Chem. Listy *51*, 479 (1957); Collect. czechoslov. chem. Commun. *22*, 1835 (1957); Chem. Abstr. *51*, 10508e (1957).

[25] *R. J. Mohrbacker* and *N. H. Cromwell,* J. Amer. chem. Soc. *79*, 401 (1957).

[26] *H. Strzekcka* and *M. Simalty Siematycki,* C. R. hebd. Séances Acad. Sci. *252*, 3821 (1961).

possible in this way to prepare bicyclic or polycyclic ketones such as 2-norcaranone *(14)* [10] and tricyclo-[3.3.1.$0^{2,8}$]nona-3,6-dien-9-one *(45)* [27].



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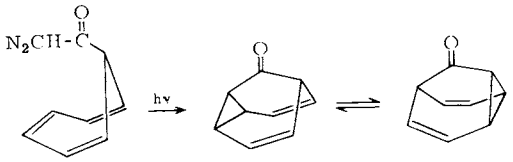


(45)

3. Cyclopropylcarbonyl Compounds by Ring Contraction

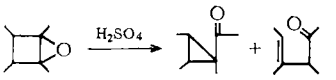
The three other methods for the synthesis of cyclopropylcarbonyl compounds, as well as the reaction with Simmons reagent, have been investigated particularly thoroughly in our laboratories.

Two of these methods use four-membered carbocyclic starting materials. These are the rearrangement of 1,2-epoxycyclobutane derivatives by acids or by heat to form cyclopropyl ketones or cyclopropyl aldehydes and the rearrangement of bromocyclobutanones by nucleophilic reagents or by water into cyclopropylcarbonyl compounds such as acids, esters, and amides, which can subsequently be converted into aldehydes and ketones. However, these two rearrangements are suitable only in exceptional cases for the preparative synthesis of cyclopropylcarbonyl compounds, since it is first necessary to prepare the cyclobutane derivatives. On the other hand, the dehalogenation of α,α-bis-(bromomethyl)cycloalkanones by zinc, which leads to spirocyclopropyl ketones (Section 4), and the reaction of Simmons reagent with α,β-unsaturated ketones (Section 2.1) are of preparative interest.

3.1. Ring Contraction of 1,2-Epoxycyclobutane Derivatives

Unlike the 1,2-epoxycyclohexanes, 1,2-epoxycyclopentanes exhibit no ring contraction reactions. However, 1,2-epoxycyclobutanes react differently: the action of sulfuric acid on 1,2,3,4-tetramethyl-1,2-epoxycyclobutane *(46)* leads to 1,2,3-trimethylcyclopropyl methyl ketone (ring contraction) and to the open-chain 3,4-dimethyl-4-hexen-2-one [28].

Substituted 1,2-epoxycyclobutanes, which are readily obtainable by the action of perbenzoic acid on the corresponding cyclobutenes, rearrange to give cyclo-

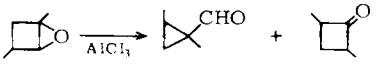


(46)

propylcarbonyl compounds. The ring contraction product predominates in the presence of protonic acids, whereas Lewis acids such as $AlCl_3$ lead to the formation of greater quantities of the unrearranged product, *i.e.* a substituted cyclobutanone [29].

In media containing sulfuric acid, 1,2-epoxycyclobutane, 1-methyl-1,2-epoxycyclobutane, and 1,2-dimethyl-1,2-epoxycyclobutane give only the ring-contraction products cyclopropanecarbaldehyde, 1-methylcyclopropanecarbaldehyde, and 1-methylcyclopropyl methyl ketone in yields of about 70 %, whereas in the presence of $AlCl_3$, the first epoxide gives 5 % of cyclobutanone and the second gives 30 % of 2-methylcyclobutanone.

In the case of more highly substituted epoxides, the nature of the acid has no influence, and mixtures of products of both types are obtained. Moreover, these epoxides rearrange even at room temperature and in neutral media. On the other hand, in the presence of $AlCl_3$, the epoxide *(47)* gives up to 70 % of 2,4-dimethylcyclobutanone (overall yield 70 %), which in our experience is one of the most difficult methylcyclobutanones to prepare.

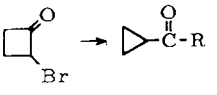


(47) 15% *cis* 15% *trans* 70% *cis* + *trans*

3.2. Ring Contraction of 2-Bromocyclobutanones

This very easy rearrangement, which can be initiated even by water, and which gives good yields of ring contraction products, has been the subject of a series of publications (cf. *e.g.* Parts 5, 6, 8, and 9 in the series "Investigation of Small Rings" [30]) (see Table 1). At least the rearrangements of this type that begin with a nucleophilic attack proceed by a mechanism similar to that of the semibenzilic acid rearrangement [30d, 31].

Table 1. Rearrangement of 2-bromocyclobutanone into cyclopropylcarbonyl compounds *(48)*.



(48)

R	Reagent	Yield (%)
OH	1. $NaOH/C_2H_5OH$; 2. H^+	85–90
OH	1. NH_4OH; 2. H^+	85–90
OH	1. Na_2CO_3/H_2O; 2. H^+	85–90
OH	H_2O (100 °C)	82
NH_2	liquid NH_3	70
OC_2H_5	$C_2H_5ONa/(C_2H_5)_2O$	67

[27] *W. von E. Doering* and *B. Ferrier*, see *W. von E. Doering* and *W. R. Roth*, Angew. Chem. *75*, 27 (1963); Angew. Chem. internat. Edit. *2*, 115 (1963).

[28] *R. Criegee* and *K. Noll*, Liebigs Ann. Chem. *627*, 1 (1959).

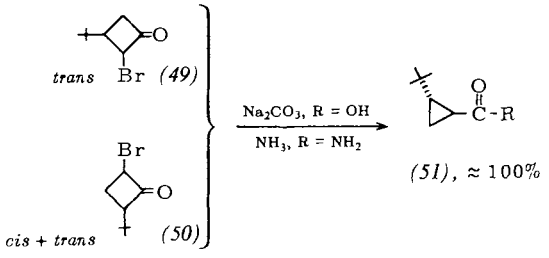
[29] *J. L. Ripoll* and *J. M. Conia*, Tetrahedron Letters *1965*, 979; Bull. Soc. chim. France *1965*, 2755.

[30] a) *J. M. Conia* and *J. L. Ripoll*, Bull. Soc. chim. France *1963*, 755; b) *ibid. 1963*, 763; c) *ibid. 1963*, 773; d) *J. M. Conia* and *J. Salaün*, *ibid. 1964*, 1957.

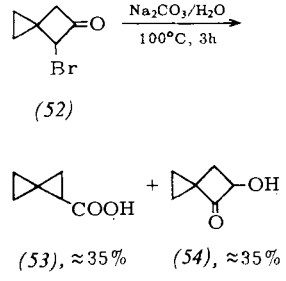
[31] *C. Rappe* and *L. Kunntsson*, Acta chem. scand. *21*, 163 (1967).

The exact function of the nucleophilic agent is unknown. Secondary amines, alkali metal phenoxides, and sodium acetate, which are all weak nucleophiles, give the substitution product [30a].

This rearrangement provides a route to particular cyclopropylcarbonyl compounds. For instance, we have been able to prepare some strongly sterically hindered cyclobutanones by this method. The 2-brominated 2-*tert*-butylcyclobutanones give no ring contraction, whereas other derivatives, such as *trans*-2-bromo-3-*tert*-butylcyclobutanone *(49)* and *cis*- and *trans*-2-bromo-4-*tert*-butylcyclobutanone *(50)* give the *trans* isomer of the ring contraction product *(51)* in almost quantitative yield from aqueous sodium carbonate solution or liquid ammonia [32].

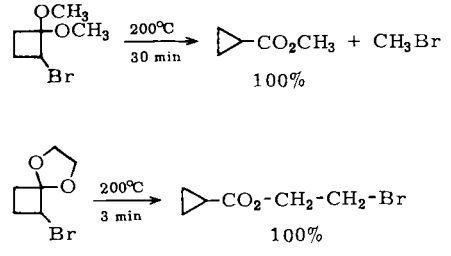


A similar ring contraction is also possible in some spirocyclobutanones. The brominated spirohexanone *(52)* can be converted into the acid *(53)* with a smaller ring and an isomerized substitution product *(54)* by the action of aqueous sodium carbonate [33].

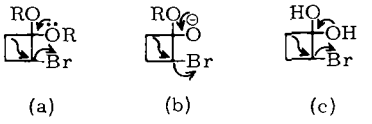


3.3. Ring Contraction of 2-Bromocyclobutanone Acetals [*]

A third method for the contraction of a four-membered ring has recently become known [32]: 2-Bromocyclobutanone acetals, which are readily prepared by the action of bromine on cyclobutanone in alcoholic solution, are converted quantitatively into cyclopropanecarboxylates on heating.

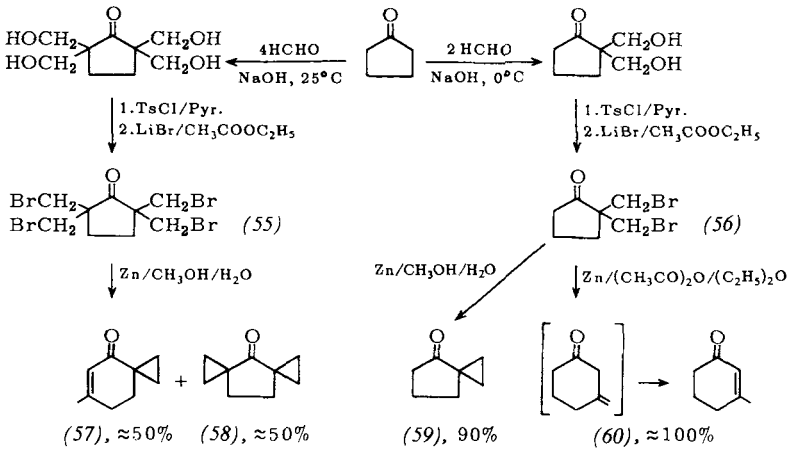


The mechanism (a) for this thermal rearrangement is probably similar to that which was shown [30d] to apply for ring contraction of 2-bromocyclobutanones in basic medium (b) (with RO^-) or in water alone (c).



4. Dehalogenation of α,α-Bis(bromomethyl)cycloalkanones

The dehalogenation of α,α-bis(bromomethyl)cycloalkanones (which are readily obtainable by the aldol condensation of cycloalkanones with formaldehyde) with the aid of zinc is another route to cyclopropyl ketones, or rather to spirocyclopropyl ketones. The solvent influences this reaction in a manner that cannot yet be explained. The normal ring closure to give the cyclopropane derivative and ring expansion, two reactions that are themselves interesting, also occur [34].



Thus 2,2-bis(bromomethyl)cyclopentanone *(56)* is quantitatively converted into the rearranged 3-methyl-2-cyclohexen-1-one *(60)* by zinc in acetic anhydride, whereas reduction in aqueous methanol leads almost exclusively by normal ring closure to the spiro ketone *(59)*. In aqueous methanol, 2,2,5,5-tetrakis(bromomethyl)cyclopentanone *(55)* gives the monospiro ketone *(57)* and the dispiro ketone *(58)*.

[32] *J. Salaün* and *J. M. Conia*, unpublished.

[33] *J. M. Conia* and *J. M. Denis*, unpublished.

[*] Section 3.3. was added in proof (June 24, 1968).

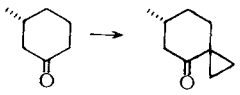
[34] *J. M. Conia*, *P. Lerivérend*, and *J. L. Bouket*, Tetrahedron Letters *1964*, 3189; *P. Lerivérend* and *J. M. Conia*, Bull. Soc. chim. France *1966*, 116, 121.

[35] *J. M. Conia* and *J. C. Limasset*, Tetrahedron Letters *1965*, 3151.

[36] *J. M. Conia* and *J. C. Limasset*, Bull. Soc. chim. France, in press.

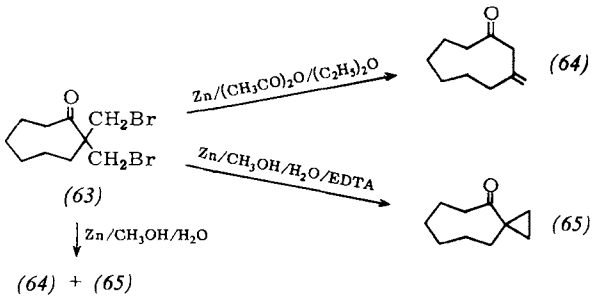
[37] *J. M. Conia*, Record chem. Progr. *24*, 43 (1963).

(−)-6-Methylspiro[2.5]octan-4-one *(62)* is obtained by a similar synthesis from (+)-3-methylcyclohexanone *(61)* [34]. Compound *(62)* is the first cyclopropyl ketone whose absolute configuration has been determined. Its Cotton effect does not correspond to the predictions of the octant rule.



(61) *(62)*

No ring expansion takes place on dehalogenation of 2,2-bis(bromomethyl)cyclohexanone with zinc; the spiro ketone is formed quantitatively in aqueous methanol after a normal ring closure. The higher cycloalkanone derivatives exhibit both reactions. 2,2-Bis(bromomethyl)cyclooctanone *(63)* is particularly interesting in this respect, since it can be reduced to



(63) *(64)* *(65)* *(64)* + *(65)*

the ring expansion product *(64)* in acetic anhydride/ether, to a mixture of *(64)* and the normal ring closure product *(65)* in aqueous methanol, or exclusively to the ketone *(65)* in aqueous methanol in the presence of ethylenediaminetetraacetic acid.

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Translated by Express Translation Service, London

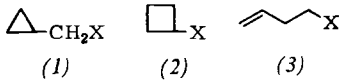
Recent Developments in the Stereochemistry of Cyclopropane Ring Opening [**]

BY S. SAREL, J. YOVELL, AND M. SAREL-IMBER [*]

This review article deals with the stereochemistry of the following ring opening reactions: 1. Homoallylic rearrangement of secondary and tertiary cyclopropyl alcohols in the presence of electrophilic reagents, 2. The addition of carboxylic acids to vinylcyclopropanes, 3. The thermal rearrangement of vinylcyclopropanes into cyclopentenes. An account is also given of the NMR spectroscopic determination of the conformations of substituted vinylcyclopropanes.

1. Introduction

The most striking feature of chloromethylcyclopropane is its enhanced reactivity in solvolytic S_N1 reactions that lead to the formation of cyclopropylmethyl *(1)*, cyclobutyl *(2)* (ring-expansion), and 3-butenyl *(3)* (ring-opening) compounds [1]. *Roberts* and his co-workers have formulated the carbonium ion intermediates which occur in the anionotropic interconversion of derivatives of *(1)*, *(2)*, and *(3)* as non-classical unsymmetrical "bicyclobutonium ion" intermediates [2]. More recently, *Schleyer* has presented evidence favoring the symmetrical "bi-sected" intermediates [3] put forward earlier by the other school [4–6].



(1) *(2)* *(3)*

The acid-catalyzed homoallylic rearrangement of cyclopropylmethanols, which was first investigated by *Bruylants* and co-workers in 1928 [7], and later ampli-

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[**] From a plenary lecture delivered at the Symposium on the Chemistry of Small Rings (Louvain, Belgium, September 12–15, 1967).

[1] Reviews: a) *R. Breslow* in *P. de Mayo*: Molecular Rearrangements. Interscience, New York 1963, Vol. 1, chapter 4; b) *N. C. Deno*, Progr. physic. org. Chem. *2*, 129 (1964); c) *M. Hanack* and *H. J. Schneider*, Angew. Chem. *79*, 687 (1967); Angew. Chem. internat. Edit. *6*, 666 (1967); Fortschr. chem. Forsch. *8*, 554 (1967).

[2] *R. H. Mazur, W. N. White, D. A. Semenov, C. C. Lee, M. S. Silver*, and *J. D. Roberts*, J. Amer. chem. Soc. *81*, 4390 (1959).

[3] *P. von R. Schleyer* and *G. W. Van Dine*, J. Amer. chem. Soc. *88*, 2321 (1966), and references therein cited.

[4] *C. U. Pittman jr.* and *G. A. Olah*, J. Amer. chem. Soc. *87*, 2998, 5123 (1965).

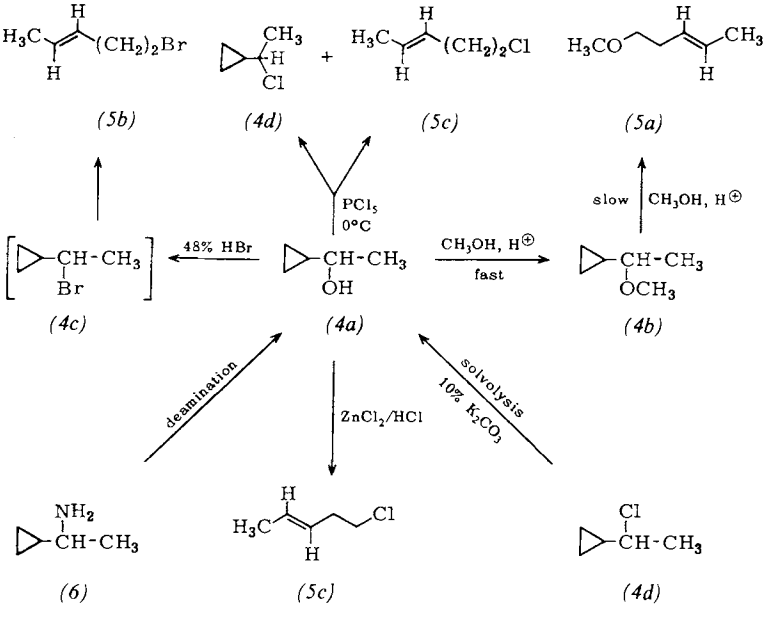
[5] *N. C. Deno, J. S. Liu, J. O. Turner, D. N. Lincoln*, and *R. E. Fruit jr.*, J. Amer. chem. Soc. *87*, 3000 (1965); *N. C. Deno, H. G. Richey jr., J. S. Liu, D. N. Lincoln*, and *J. O. Turner*, *ibid. 87*, 4533 (1965).

[6] *R. Hoffmann*, J. chem. Physics *40*, 2480 (1964); Tetrahedron Letters *1965*, 3819.

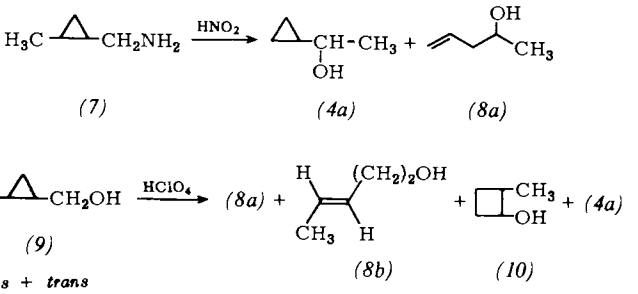
[7] *P. Bruylants* and *A. Dewael*, Bull. Cl. Sci., Acad. roy. Belgique *14*, 140 (1928).

fied by several groups[8], manifests significant differences with regard to rates and products relative to the above solvolytic and deamination reactions.

These are illustrated by the cases of 1-chloro-1-cyclopropylethane *(4d)*, (1-cyclopropylethyl)amine *(6)*, and 1-cyclopropylethanol *(4a)*. When the optically active enantiomer of *(6)* is deaminated[9] or *(4d)* is solvolyzed[10], the alcohol formed in both cases is the same racemic alcohol *(4a)* but not the homoallyl alcohol corresponding to *(5a)*. Furthermore, the acid catalyzed exchange of *(4a)* with $H_2{}^{18}O$ occurs without rearrangement[11]. In contrast, when *(4a)* is treated with methanolic HCl, the methyl ether *(4b)* is formed



trans-(2-methylcyclopropyl)methanol *(9)*. When this compound is treated with 1 N aqueous perchloric acid, the reaction products are mixtures composed of homo-



rapidly but the final product is the open-chain compound of the *trans* structure *(5a)*[12]. Likewise, the final product in treatment of *(4a)* with 48%-HBr is the *trans* compound *(5b)*[13], which could similarly be formed *via (4c)* (not observed). On the other hand, when *(4a)* is treated with PCl_5, a mixture of 88% *(4d)* and 12% *(5c)* is obtained[10].

The reaction product from the deamination of 1-aminomethyl-2-methylcyclopropane *(7)* is a mixture of alcohols, of the cyclopropylmethyl- *(4a)* and the homoallyl-structures *(8)*[14], but not of the cyclobutyl derivative *(10)*. A more complicated situation is found in the acid-promoted rearrangement of the *cis*- and allyl alcohols (predominant) *(8a)* and *(8b)*, 2-methylcyclobutanol *(10)*, and 1-cyclopropylethanol *(4a)*[15]. Although homoallyl alcohols are known to give rise to cyclobutyl derivatives on treatment with strong acids[16], this type of rearrangement has not previously been encountered in the acid-promoted rearrangement of secondary and tertiary cyclopropyl alcohols, or in the solvolysis of tertiary cyclopropylmethyl sulfonates[17].

2. Acid-Promoted Homoallylic Rearrangement of Secondary Cyclopropyl Alcohols

The homoallylic rearrangement of branched cyclopropyl alcohols of structures *(11)* and *(12)* can be effected by a large variety of protonic acids (48%-HBr, HCl, $HCl/ZnCl_2$, $HClO_4$, H_2SO_4, HCOOH, and CH_3COOH), acid chlorides (PX_3, PX_5, $SOCl_2$, and CH_3COCl), and acid anhydrides (acetic and trifluoro-

[8] a) *E. H. Farmer* and *F. L. Warren*, J. chem. Soc. (London) *1931*, 3231; b) *T. A. Faworskaja* and *S. A. Fridman*, Ž. obšč. Chim. *15*, 421 (1945); *18*, 2080 (1948); c) *L. I. Smith* and *McKenzie jr.*, J. org. Chemistry *15*, 74 (1950).

[9] *M. Vogel* and *J. D. Roberts*, J. Amer. chem. Soc. *88*, 2262 (1966).

[10] *M. Hanack* and *H. Eggensperger*, Liebigs Ann. Chem. *663*, 31 (1963).

[11] *H. G. Richey jr.* and *J. M. Richey*, J. Amer. chem. Soc. *88*, 4971 (1966).

[12] *R. G. Pearson* and *S. H. Langer*, J. Amer. chem. Soc. *75*, 1065 (1953).

[13] *M. Julia*, *S. Julia*, *T. S. Yu*, and *C. Neuville*, Bull. Soc. chim. France *1960*, 1381.

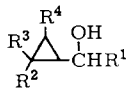
[14] a) *R. A. Sneen*, *K. M. Levandovski*, *I. A. I. Taha*, and *R. B. Smith*, J. Amer. chem. Soc. *83*, 4846 (1961); b) *C. Y. Wee* and *R. E. Robertson*, *ibid.* *88*, 2666 (1966).

[15] *M. Julia* and *Y. Noel*, Abst. of papers presented at the Journées de Chimie Organique, Soc. chim. France, Orsay, September 21–23, 1967.

[16] a) *K. L. Servis* and *J. D. Roberts*, J. Amer. chem. Soc. *73*, 2509 (1965); b) *M. Hanack*, *S. Kang*, *J. Haffner*, and *K. Gorler*, Liebigs Ann. Chem. *690*, 98 (1965).

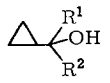
[17] a) *H. Hart* and *J. M. Sandri*, J. Amer. chem. Soc. *81*, 320 (1959); b) *H. Hart* and *P. A. Law*, *ibid.* *84*, 2462 (1962); *86*, 1957 (1964); c) *M. Hanack* and *H. Eggensperger*, Chem. Ber. *96*, 1259 (1963).

acetic anhydrides), at temperatures ranging from −20 to 120 °C and above, with reaction times varying from a few minutes to a few hours.



R^1 = Alkyl, Alkenyl, Aryl, Cyclopropyl; R^2 = Alkyl; R^3 = Alkyl, Hydroxymethyl, Carboxyl; R^3-R^2 or R^3-R^4 = -$(CH_2)_n$-

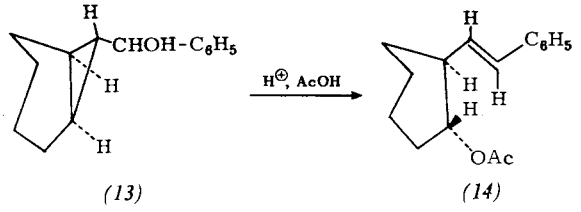
(11)



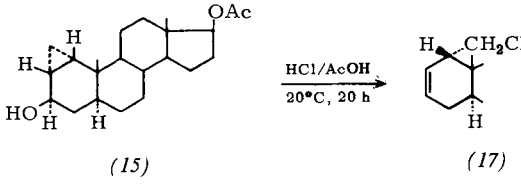
R^1 = CH_3; R^2 = Alkyl, Alkenyl, Alkinyl, Aryl, Cyclopropyl

(12)

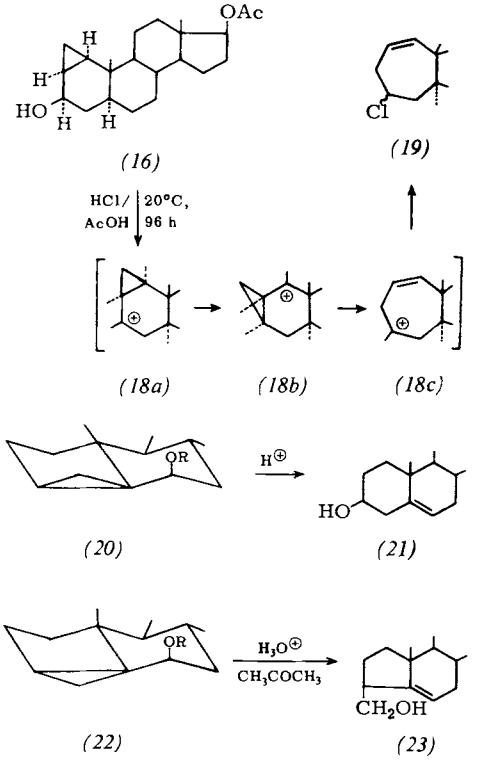
The stereochemistry at the double bond in the rearrangement products of *(11)* has not been thoroughly studied; however, there is sufficient evidence to conclude that small-ring opening and product formation occur in a stereoselective manner, giving rise to the formation of the *trans* isomer as main product. This is illustrated by the reactions *(13)*→*(14)*, *(15)*→*(17)*, *(16)*→*(19)*, *(20)*→*(21)*, and *(22)*→*(23)*.



(13) *(14)*



(15) *(17)*



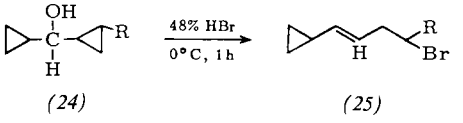
(16) *(19)* *(18a)* *(18b)* *(18c)* *(20)* *(21)* *(22)* *(23)*

An example of the type of stereochemical situation found in this series of rearrangements, is afforded by (bicyclo[4.1.0]hept-7-yl)benzyl alcohol *(13)*. Treatment of this compound with mineral acid in acetic acid leads to the formation of *trans*-2-(*trans*-styryl)cyclohexyl acetate *(14)* [18]. From product study it is apparent that the substituted C atom of the small ring retains its configuration in the process of ring fission and double-bond formation, whereas the bridgehead carbon atom undergoes inversion upon attack by the acetate ion.

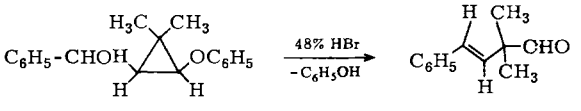
Of particular interest is the effect of the configuration of the bicyclo[4.1.0]heptyl system on the course of the rearrangement. If 1α,2α-methylene-3β-hydroxy-17β-acetoxy-5α-androstane *(15)*, in which the fused ring system of the bicyclo[4.1.0]heptyl grouping is more rigid, is treated with a saturated solution of HCl in glacial acetic acid, only compound *(17)* is formed. The rearrangement of the 1β,2β-methylene compound *(16)*, in which a *cis* relationship of the hydrogens on C-2 and C-3 results in a much less rigid conformation of the fused ring system, is slow and gives rise to formation of the seven-membered ring compound *(19)*.

The reaction is interpreted as proceeding *via* several classical homoallylic carbonium ions [*(18a)*→*(18b)*→*(18c)*→*(19)*] [19]. Similar positional effects have been observed in the steroidal fused-ring system of the bicyclo[3.1.0]hexane type. The 6α- or 6β-alkyloxy derivatives of 3α,5α-cyclocholestane *(20)* are known to yield cholesterol *(21)* [20]; under the same conditions 3β,5β-cyclo-6β-alkyloxycholestane *(22)* yields the A-nor β,γ-unsaturated primary alcohol *(23)* [21].

In the acid-catalyzed rearrangement of simple substituted dicyclopropylmethanols, the *trans* isomer again predominates in the product. Compound *(24)* (R = CH_3) gives *(25)* (R = CH_3) [17c]. In cyclopropylmethyl compounds of structure *(26)*, which carry a phenoxyl and a *gem*-dimethyl group on the cyclopropane ring, the bond opposite to the *gem*-dimethyl group is cleaved, and the *trans* isomer again predominates in the product *(27)* [22].



(24) *(25)*



(26) *(27)*

The stereochemistry of the rearrangement, however, is not determined by inductive effects alone; the acid strength and the reaction medium also play a major role in deciding the course of reaction. For example,

[18] *P. Besinet, R. Fraisse, R. Jacquier*, and *P. Viallefont*, Bull. Soc. chim. France *1960*, 1377.

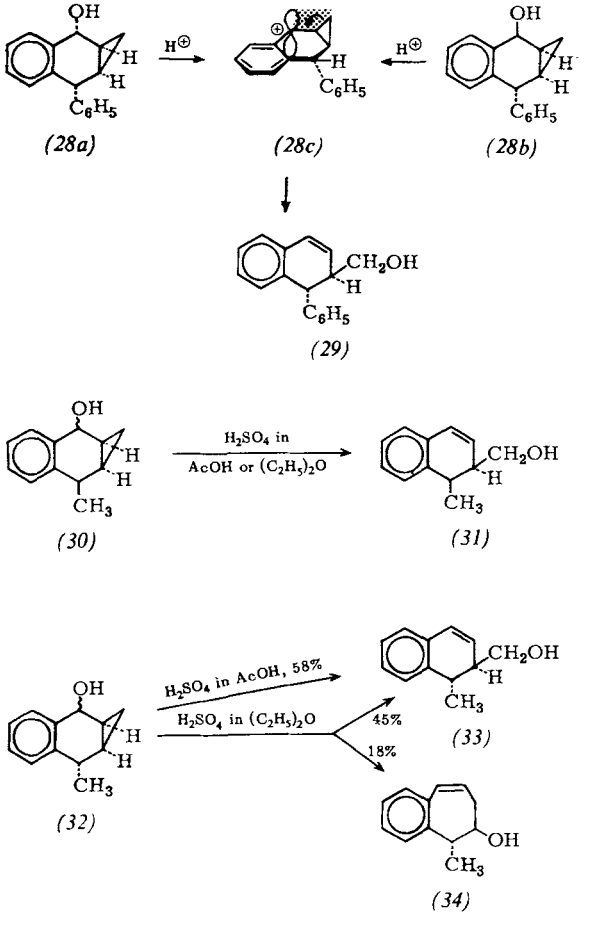
[19] *H. Laurent, H. Muller*, and *R. Wiechert*, Chem. Ber. *99*, 3836 (1966).

[20] *S. Winstein* and *E. M. Kosower*, J. Amer. chem. Soc. *81*, 4399 (1959).

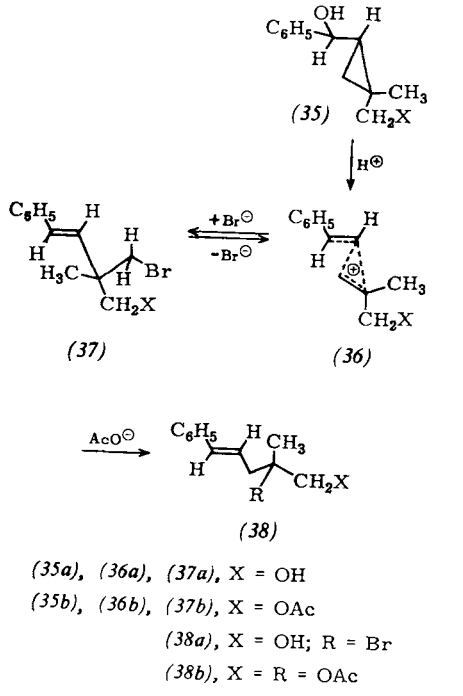
[21] *W. G. Dauben* and *J. A. Ross*, J. Amer. chem. Soc. *81*, 6522 (1959); see also, *N. L. Wendler* in *P. de Mayo*: Molecular Rearrangements. Interscience, New York 1963, Vol. II, p. 1075.

[22] *M. Julia* and *M. Baillarge*, Bull. Soc. chim. France *1966*, 734; *M. Julia et al., ibid. 1966*, 717, 732, 743.

the epimeric alcohols *(28a)* and *(28b)*, on treatment with acid, rearrange to the same alcohol *(29)*. Likewise, compound *(30)* gives preponderance to the analogous product *(31)* upon acid treatment in acetic acid or ether. However, the isomeric compound *(32)* on similar treatment in ether gives 1,2-dihydronaphthylmethanol *(33)* (45 %) and the 6,7-dihydro-5*H*-benzocycloheptyl derivative *(34)* (18 %) [13]. Apparently, the stereochemistry of the ring-opening in the conversion *(30)* → *(31)* is governed mainly by conjugative interactions of the type represented by formula *(28c)*, whereas in the conversion of *(32)* → *(33)* + *(34)* the solvent (ether) exerts influence on the mode of ring opening by diminishing the difference in energy between the respective modes [23].

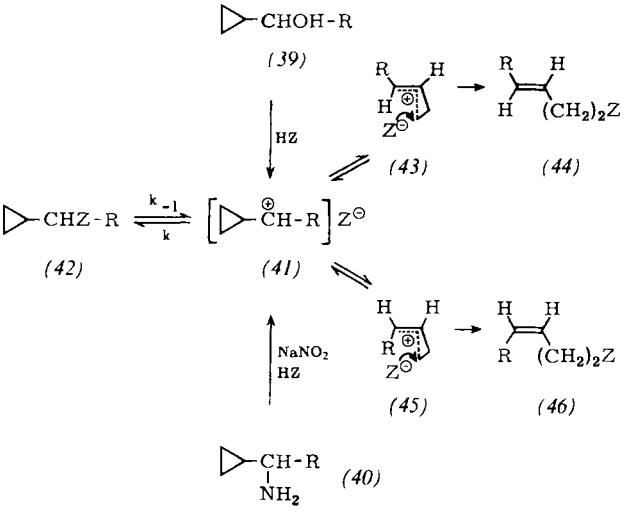


Of particular interest is the case of compound *(35a)*, which on treatment with 48 %-HBr, affords *(37a)* and not *(38a)* as implied from the inductive effect. However, in less stringent acidic conditions, such as 3.6 N H_2SO_4 in acetic acid, or even in sodium acetate/acetic acid, compounds *(37a)* and *(35b)* give rise to *(38b)* [24]. The ready rearrangement of *(37b)*, and the fact that cyclobutyl derivatives are not observed in the products, suggest that the rearrangement *(35)* → *(38)* may involve the non-classical carbonium ion *(36)*.



(35a), *(36a)*, *(37a)*, X = OH
(35b), *(36b)*, *(37b)*, X = OAc
(38a), X = OH; R = Br
(38b), X = R = OAc

The rearranged product from the acid and the phosphorus halide treatment of secondary cyclopropyl alcohol *(39)*, as well as the formation of compounds *(44)* and *(46)* from the deamination of dicyclopropylmethylamine *(40)*, R = cyclopropyl, can be explained in terms of initial formation of several isomeric carbonium-ion intermediates *(41)*, *(43)*, and *(45)*.



The rearrangement of *(39)* and *(40)* depends largely on the equilibrium *(42)* ⇄ *(41)*. If $k \gg k_{-1}$, cyclopropylmethyl compounds of structure *(42)* accumulate in the reacting system. If $k < k_{-1}$, the allyl compounds *(44)* and *(46)* are formed by way of the carbonium ions *(43)* and *(45)*. The preponderance of the *trans* isomer *(44)* in the rearrangement products can be best explained by the relative abundance of the low energy conformer *(43)*.

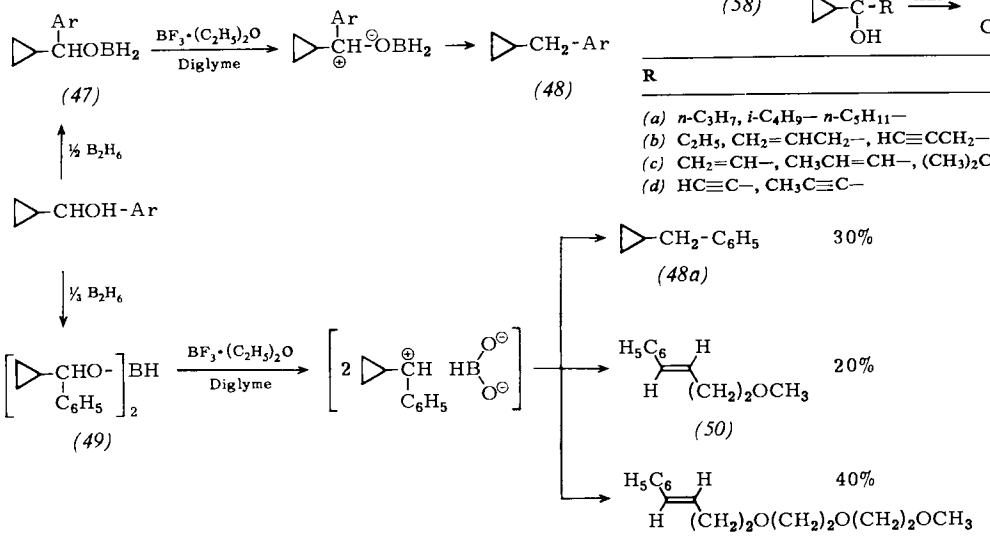
In this connection, the rearrangement of arylcyclopropylmethyloxyborane *(47)* and of bis(cyclopropylbenzoxy)borane *(49)* may be considered. When treated with BF_3-ether at 0 °C for a short time, compound *(47)* invariably gives *(48)* [25],

[23] *E. L. Eliel:* Stereochemistry of Carbon Compounds, McGraw-Hill, New York 1962, p. 375, 387; see also, *W. G. Dauben* and *E. J. Deviny*, J. org. Chemistry *31*, 3794 (1966); *W. G. Dauben* and *G. H. Berezin*, J. Amer. chem. Soc. *89*, 3449 (1967).

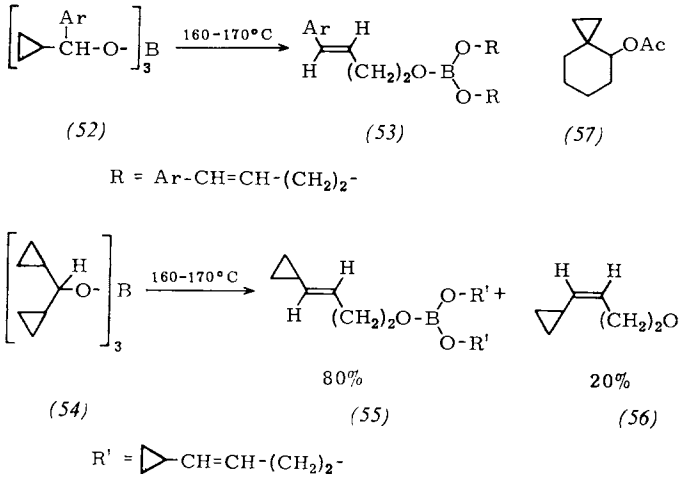
[24] *M. Julia, G. Mouzin*, and *C. Descoins*, C. R. hebd. Séances Acad. Sci. *264*, 330 (1967).

[25] *E. Breuer*, Tetrahedron Letters *1967*, 1849; see also, *H. M. Bell* and *H. C. Brown*, J. Amer. chem. Soc. *88*, 1473 (1966).

whereas *(49)* gives a mixture of *(48a)* and the open-chain compounds *(50)* and *(51)* [26]. In the presence of an excess of diborane the compounds of type *(41)* lead predominantly to a hydrogenolysis product [*(48)* or *(48a)* ≡ *(42)*, Z = H, R = Ar or C_6H_5]. In the presence of deficient amounts of diborane, the interconversion *(41)* ⇄ *(43)* is followed by an attack of the solvent (diglyme) to yield open-chain compounds [*(50)* and *(51)* ≡ *(44)*, R = C_6H_5, Z = OCH_3 or $OCH_2OCH_2OCH_3$].



At elevated temperatures, the organoborates *(52)* and *(54)* rearrange to the respective homoallyl derivatives *(53)* or *(55)* and *(56)* [27]. The thermal rearrangement shows solvent dependence. After one hour, the conversion in diglyme is 90%, in the less polar *o*-dichlorobenzene 50%, and negligible in the least polar solvent, decalin. In *o*-dichlorobenzene the conversion is complete after 4 hours [28].



That the observed ratio of *(55)*:*(56)* amounts to 4:1 is attributed to a change in the relative abundance of the preferred conformations *(43)* and *(45)* as a result of temperature increase (cf. [17c]). Recently, *Hanack* and co-workers suggested that the rearrangements during pyrolysis of *(57)* proceed *via* an ionic mechanism [29].

[26] *E. Breuer*, unpublished results. *W. Gerrard, M. F. Lappert*, and *H. B. Silver*, J. chem. Soc. (London) *1957*, 1647, report pertinent allylic rearrangements in alkoxyboron derivatives.

[27] *E. Breuer* and *S. Sarel*, Israel J. Chem. *4*, 16p (1966).

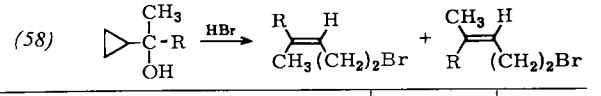
[28] *E. Breuer* and *S. Sarel*, Tetrahedron, in press.

[29] *M. Hanack, H. Schneider-Bernlöhr*, and *H. J. Schneider*, Tetrahedron *23*, 2195 (1967).

3. Homoallylic Rearrangements of Tertiary Cyclopropyl Alcohols

In contrast to the rearrangement of secondary cyclopropyl alcohols, in which only one stereoisomer is

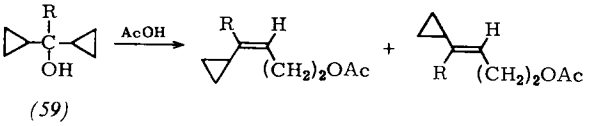
Table 1. Distribution of isomers in the HBr-catalyzed rearrangement of tertiary cyclopropyl alcohols *(58)* [30].



R	*trans* (%)	*cis* (%)
(a) *n*-C_3H_7, *i*-C_4H_9– *n*-C_5H_{11}–	preponderant	?
(b) C_2H_5, CH_2=$CHCH_2$–, HC≡CCH_2–	80	20
(c) CH_2=CH–, CH_3CH=CH–, $(CH_3)_2C$=CH–	60–65	40–35
(d) HC≡C–, CH_3C≡C–	6–5	94–95

formed, the rearrangement of tertiary cyclopropyl alcohols leads to the formation of several isomeric products (see Tables 1–3). In the rearrangement of compound *(58)* under the influence of hydrobromic acid (Table 1), the *cis*:*trans* distribution of products varies rather dramatically on passing from a sp-

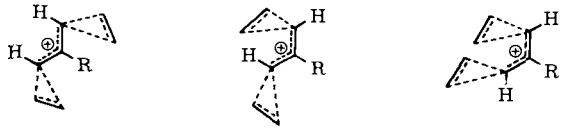
Table 2. Distribution of geometric isomers in acetic acid-promoted rearrangement of dicyclopropyl alcohols *(59)*, at 100 °C.



R	*cis* (%)	*trans* (%)	References
(a) C_6H_5C≡C–	85	15	[31]
(b) CH_3–	65	35	[32]
(c) *n*-C_3H_7	55	45	[32]
(d) *i*-C_3H_7	42	58	[31]
(e) *tert*-C_4H_9	0	100	[31]

hybridized C-atom attached to the carbinol carbon atom *(58d)*, to a trigonal C-atom *(58c)*. This variation is much less pronounced on passing to a tetrahedral C-atom[*(58b–58a)*] [30]. A similar tendency is observed in the dicyclopropyl alcohols (Table 2). The *trans* isomer predominates in the products from the rearrangement of *(58c)*, whereas in the products from *(59b)* the *cis* isomer predominates. The explanation conceivably rests in the conformational preference of the cyclopropane rings in the carbonium ion species *(60-I)*, *(60-II)*, and *(60-III)*.

[30] a) *M. Julia, Ch. Descoins*, and *Cl. Rissé*, Tetrahedron Suppl. 8, Part II, p. 443 (1966); b) *M. Julia, S. Julia, et al.*, Bull. Soc. chim. France *1964*, 2533.



(60-I) *(60-II)* *(60-III)*

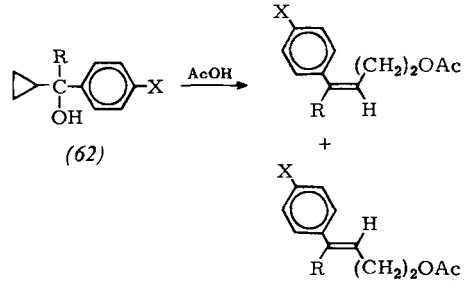
↓ ↓ ↓

cis *cis + trans* *trans*

The relative abundance of conformer *(60-III)* increases with increasing size of R, because of the nonbonded interactions between the cyclopropane and the methyl hydrogens of R.

The preferred formation of the *cis* isomer in the rearrangements of arylcyclopropylmethyl alcohols (Table 3), suggests that the *(61-I)* conformer dominates the

Table 3. Acetic-acid promoted rearrangement of arylcyclopropyl alcohols.



(62)

R	X	*trans* (%)	*cis* (%)	References
H	H	0	100	
(a) CH_3	H	0	100	[33]
(b) CH_3	CH_3	0	100	[33]
(c) CH_3	OCH_3	0	100	[33]
(d) CH_3	Cl	0	100	[33]
(e) *i*-Pr	H	75	25	[34]

ionic population in the assumed intermediate. Examination of models reveals that the aromatic nucleus in *(61-I)* can, indeed, comfortably assume coplanarity with the sp^2 C atom, the result being a gain in resonance energy; this is not the case so far as the *(61-II)*

(61-I) *(61-II)*

conformer is concerned. On replacement of the methyl group by an isopropyl group, however, the converse is true, presumably because the loss in energy due to the increased nonbonded interactions between the cyclopropane and the isopropyl hydrogens outweighs the loss in resonance energy.

[31] *M. Sarel-Imber*, unpublished results.

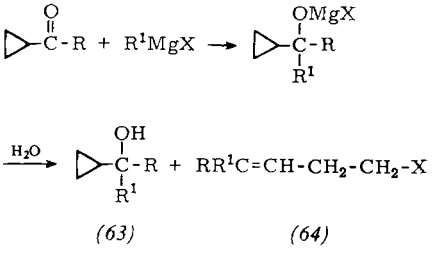
[32] *J. Yovell*, Doctoral Dissertation, The Hebrew University of Jerusalem, 1967.

[33] a) *S. Sarel, J. Yovell*, and *B. A. Weissman*, unpublished work; b) *B. A. Weissman*, M. Sc. Thesis, The Hebrew University of Jerusalem, 1968.

[34] *E. Breuer, E. Segall*, and *S. Sarel*, unpublished work.

4. Homoallylic Rearrangement of Cyclopropylmethoxymagnesium Halides

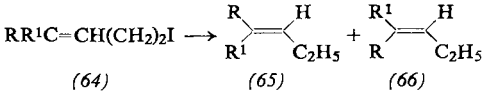
In our laboratory *Yovell*[32] observed that the addition of dicyclopropyl ketone to an excess of alkylmagnesium iodide in boiling ether gives rise to homoallylic products *(64)*, in addition to the desired alcohol *(63)*.



(63) *(64)*

The yield of *(64)* depends on the nature of the halogen and on the reaction conditions, and increases with increase in concentration of the organomagnesium halide, and with increase in temperature. The effect of the halogen on the yield of *(64)* increases in the order $Cl < Br \ll I$ [35].

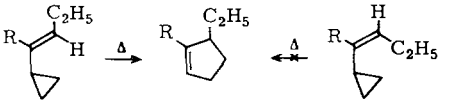
The homoallylic products *(64)* proved to be mixtures of stereoisomers. The respective parent compounds *(65)* and *(66)* were obtained by reduction with $LiAlH_4$ followed by preparative vapor-phase chromatography.



(64) *(65)* *(66)*

Structure determinations were based on spectroscopic, particularly NMR, findings; these will be discussed in Section 6.

The structure of the vinylcyclopropane derivatives *(67)* and *(68)* is derived from the difference observed in the ability of the isomeric pair to undergo thermal isomerization into cyclopentene: the *cis* structure was



(67) *(69)* *(68)*

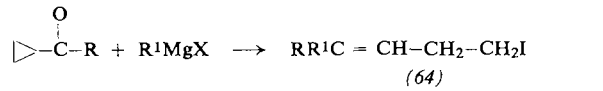
assigned to the isomer undergoing complete conversion into cyclopentene at 380–390 °C *(67)*→*(69)*, and the *trans* structure to the isomer that is stable in this temperature range.

The similar *cis-trans* distribution among the homoallylic compounds, whether derived from cyclopropyl alcohols and acetic acid (see Tables 2 and 3) or from cyclopropylmethoxymagnesium iodide (see Table 4), indicates that similar conformational factors determine the stereochemistry of the cyclopropane ring-opening in both reactions.

The homoallylic rearrangement of dicyclopropylmethoxymagnesium iodides could proceed by an ionic type mechanism in which ring-opening results from attack by iodide ion on the non-classical symmetrical homoallylic ion, represented by the three limiting conformations, *(60-I)*, *(60-II)*, and

[35] *S. Sarel, J. Yovell*, and *M. Sarel-Imber*, Israel J. Chem. *4*, 21p (1966).

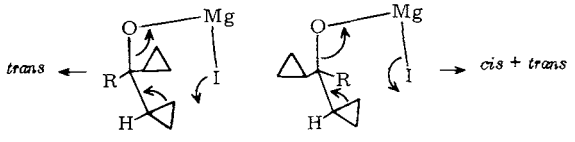
Table 4. Distribution of isomers in the homoallylic rearrangement of cyclopropylmethyloxymagnesium iodide.



(64)

R	R^1	*cis* (%)	*trans* (%)	References
Cyclopropyl	CH_3—	65	35	[32]
Cyclopropyl	*n*-C_3H_7	55	45	[32]
Cyclopropyl	*i*-C_3H_7	42	58	[31]
Cyclopropyl	*tert*-C_4H_9	—	100	[31]
C_6H_5—	CH_3	100	—	[32]
p-$CH_3OC_6H_4$—	CH_3	60	40	[32]
p-ClC_6H_4—	CH_3	100	—	[32]

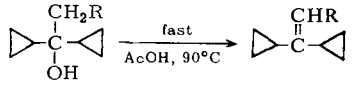
(60-III). Alternatively, the reaction could be envisioned as involving a cyclic "transition-state"[36], represented by two limiting antipode conformations *(70)* and *(71)*. Conformation *(70)* seems more crowded than *(71)*. To explain the effect of branching of R on *cis-trans* distribution in the products, the same stereochemical considerations should apply for either type of mechanism.



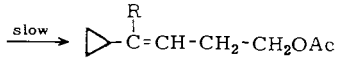
(70) *(71)*

5. Addition of Carboxylic Acid to Vinylcyclopropane

The acetic-acid promoted rearrangement of cyclopropyl alcohols of structures *(72)* and *(75)* is in fact a multireaction process[32,33,37,38] proceeding by way of elimination[37] followed by 1,5 addition[38] with simultaneous ring-opening.



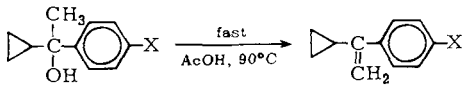
(72) *(73)*



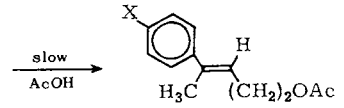
cis + trans (74)

By means of vapor-phase chromatography it can be shown that at the beginning there is a fast buildup of *(73)* or *(76)*, which is subsequently slowly converted into *(74)* (*cis* and *trans*) or *(77)* (*trans* only). The rate of dehydration and addition reactions decreases in the order *(75a)*→*(76a)* > *(72a)*→*(73a)* > *(72b)*→*(73b)* > *(75c)*→*(76c)* > *(75d)*→*(76d)*.

When the vinylcyclopropanes *(73)* and *(76)* are treated with acetic acid, the products are precisely the same as those obtained in the rearrangements of *(72)* (Table 2) and *(75)* (Table 3), respectively.



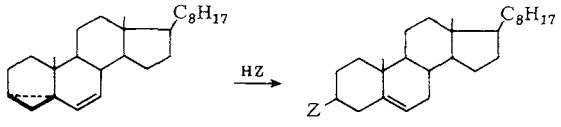
(75) *(76)*



(77)

(72a)–(74a), R = H; *(72b)–(74b)*, R = C_2H_5; *(75a)–(77a)*, X = OCH_3; *(75b)–(77b)*, X = CH_3; *(75c)–(77c)*, X = H; *(75d)–(77d)*, X = Cl.

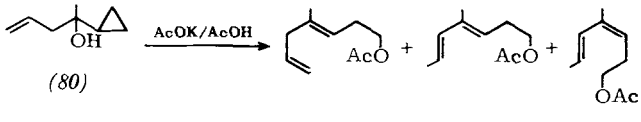
Riegel and co-workers have recently reported on this type of addition to the vinylcyclopropane system of 3,5-cyclocholest-6-ene *(78)* to *(79)*[39]. Conjugative additions of HCl to the vinylcyclopropane system in α- and β-cubebene also proceed according to the same scheme[40].



(78) *(79)*

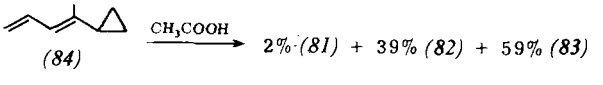
Z = OAc, CH_3O, OH, Cl, Br, I

That the homoallylic rearrangement of 1-cyclopropyl-1-methyl-3-buten-1-ol *(80)* can proceed by the above dehydration-addition path has been observed by *Julia et al.*[30]. If compound *(80)* is treated with potassium acetate in acetic acid, a mixture of open-chain acetates, consisting chiefly of *(82)* and *(83)*, is obtained. A similar mixture is formed when compound *(84)* is treated with acetic acid.



(80)

(81)	*(82)*	*(83)*
16%	30%	54%



(84)

The notable difference in the amount of *(81)* obtained by reaction of *(80)* relative to that obtained by reaction of *(84)* can be attributed to two possible modes of dehydrations in *(80)*: the one, leading to *(84)*, gives almost exclusively *(82)* and *(83)*, whereas the other, which yields 2-cyclopropyl-1,4-pentadiene, is likely to give *(81)*.

The ring-opening in the rearrangements of *(85)* into *(86)*[41], and of *(87)* into *(88)*[42], can be considered to involve the addition of HBr across the vinylcyclopropane moiety at some stage of the reaction.

[36] Compare, *M. S. Newman* and *G. Kangars*, J. org. Chemistry *31*, 1379 (1966).

[37] *S. Sarel, E. Breuer, et al.*, Israel J. Chem. *1*, 451 (1963).

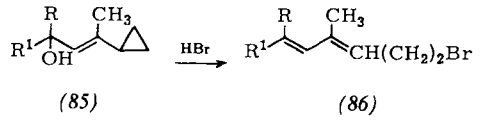
[38] *S. Sarel* and *R. Ben-Shoshan*, Tetrahedron Letters *1965*, 1053.

[39] *R. Riegel, G. B. Hager*, and *B. L. Zenitz*, J. Amer. chem. Soc. *68*, 2562 (1946).

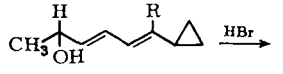
[40] *Y. Ohta, T. Saki*, and *Y. Hirose*, Tetrahedron Letters *1966*, 6365.

[41] *S. Julia, M. Julia*, and *P. Graffin*, Bull. Soc. chim. France *1964*, 3218.

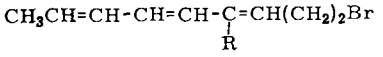
[42] *S. Julia, M. Julia, S.-Y. Tchen*, and *P. Graffin*, Bull. Soc. chim. France *1964*, 3207.



(85) *(86)*



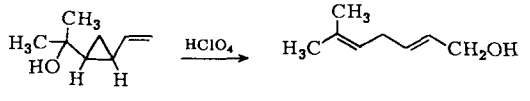
(87)



(88)

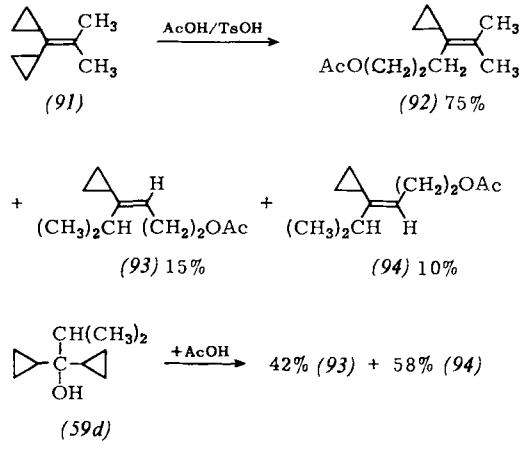
(85a), *(86a)*, R = R¹ = H; *(85b)*, *(86b)*, R = R¹ = CH_3; *(85c)*, *(86c)*, R = H, R¹ = CH_3; *(87a)*, *(88a)*, R = H; *(87b)*, *(88b)*, R = CH_3

Compound *(89)* is worthy of note as another example showing that substituents and reaction conditions play a major role in deciding the course of the reaction. When this compound is treated with $HClO_4$, the product is the open-chain primary alcohol *(90)* [43].



(89) *(90)*

The replacement of both olefinic protons in 1,1-dicyclopropylethylene, by methyl groups precludes the addition of acetic acid across the vinylcyclopropane system in *(91)*. However, in the presence of catalytic amounts of toluenesulfonic acid, a mixture of adducts



(91) *(92)* 75%

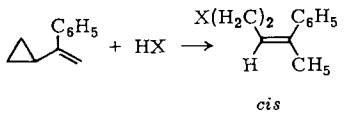
(93) 15% *(94)* 10%

(59d)

is obtained, which consists chiefly of *(92)*. The stereoisomers *(93)* and *(94)*, which are the only products from the rearrangement reaction of *(59d)*, are minor products in the catalyzed reaction. The proportion of *(92)*:*(93)*:*(94)* constitutes an equilibrium mixture [31]. Finally, it would be instructive to outline the stereochemical consequences of the mechanisms in addition reactions of the vinylcyclopropane systems.

[43] *A. Menet* and *G. Descotes*, Abst. papers presented at the Journées de Chimie Organique, Soc. chim. France, Orsay, September 21–23, 1967.

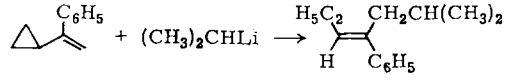
(a) carbonium-ion mechanism



[38]

cis

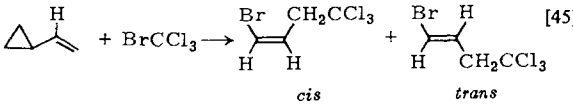
(b) carbanion mechanism



[44]

cis

(c) radical mechanism



[45]

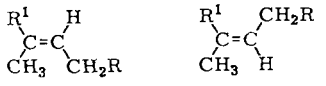
cis *trans*

Scheme 1

The addition reactions are stereoselective, whether they proceed *via* the carbonium ion, or *via* the carbanion. Neither of the two routes yields the cyclobutyl derivative.

6. Conformations of Substituted Vinylcyclopropanes

In the ^1H–NMR spectra of the stereoisomers *(67)* and *(68)*, the allylic methyl protons of the *cis* compound are shifted downfield relative to those of the *trans* isomer [32,46]. This is contrary to the prevailing view that the signals of the allylic methyl protons in the *cis* compound *(95)* appear at higher fields than those in the *trans* isomer *(96)* [30b,47].



(95) *(96)*

This apparent contradiction is explained in terms of variations in conformational preference of the cyclopropane ring in the two isomers.

Conflicting evidence has been presented as to whether the barrier to internal rotation in vinylcyclopropane is twofold or threefold in form [48–51]. Two limiting

[44] *J. A. Landgrebe* and *J. D. Shoemaker*, J. Amer. chem. Soc. *89*, 4465 (1967).

[45] *E. S. Huyser* and *L. R. Munson*, J. org. Chemistry *30*, 1436 (1965).

[46] *J. Yovell*, Israel J. Chem. *4*, 20p (1966).

[47] a) *S. A. Francis* and *E. D. Archer*, Analytic. Chem. *35*, 1363 (1963); b) *H. B. House*, *D. D. Traficante*, and *R. A. Evana*, J. org. Chemistry *28*, 348 (1963); c) *F. C. Stehling* and *K. W. Bartz*, Analyt. Chem. *38*, 1467 (1966).

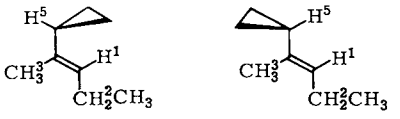
[48] a) *L. S. Bartell* and *J. P. Guillory*, J. chem. Physics *43*, 647 (1965); b) Tetrahedron Letters *1964*, 705; c) *G. J. Karabatsos* and *N. Hsi*, J. Amer. chem. Soc. *87*, 2864 (1965).

[49] *H. Günther* and *D. Wendisch*, Angew. Chem. *78*, 266 (1966); Angew. Chem. internat. Edit. *5*, 251 (1966).

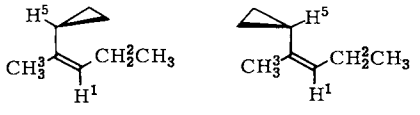
[50] a) *W. Lüttke* and *A. de Meijere*, Angew. Chem. *78*, 544 (1966); Angew. Chem. internat. Edit. *5*, 512 (1966); b) *O. Bastiansen* and *A. de Meijere*, Angew. Chem. *78*, 142 (1966); Angew. Chem. internat. Edit. *5*, 124 (1966).

[51] *G. R. DeMare* and *J. S. Martin*, J. Amer. chem. Soc. *88*, 5033 (1966).

conformations are envisioned for each of the isomers – a *cisoid* conformation *(97-I)* and *(98-I)*, and a *transoid* conformation *(97-II)* and *(98-II)* (the *S-trans* form [50]) in which the dihedral angle relating H^5 and the CH_3–C bond is 180 °.



(97-I) *(97-II)*



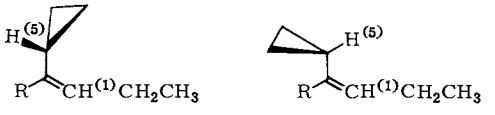
(98-I) *(98-II)*

In the case of the *cis* isomer, conformation *(97-I)*, rather than *(97-II)*, is preferred since there is less interaction between the methyl group and the cyclopropane ring. In the *trans* isomer, however, the greater interaction between the ethyl group and the cyclopropane ring renders the *transoid* conformation *(98-II)* more favorable than the *cisoid (98-I)*. On the basis of *Walsh*'s hypothesis [52], *(97-I)* and *(98-I)* should correspond to the low-energy conformation if the steric effects are negligible. The magnetic susceptibility of the cyclopropane ring [53] implies that the signals ascribable to the allylic methyl protons (H^3) in the *cisoid* conformation should be shifted downfield and that the corresponding protons in the *transoid* conformation, because of their proximity to the threefold axis of the cyclopropane ring, should be strongly shielded. These protons, conceivably, lie closer to the plane [4, 54]. As is to be expected the signal of the olefinic proton (H^1) in the *cisoid* conformation *(97-I)* and *(98-I)* appears upfield relative to the signal of the corresponding olefinic proton in the *transoid* conformation *(97-II)* and *(98-II)*. This suggests that the preferred conformer in the *cis* isomer is *(97-I)* and that in the *trans* isomer is *(98-II)*.

The ratio of the high-energy conformers (A) to low-energy conformers (B) in *cis*- and *trans*-2-cyclopropylpent-2-ene *(99)* [R = CH_3; X = H] was determined by the method of *DeMare* and *Martin* [51]. By plotting the values of δ_H1/δ_H3 against temperature changes, a slope of −0.210 is obtained. This permits the calculation of the dihedral angle between the cyclopropane-methine-hydrogen (H^5) and the CH_3–C=C bond, from the relative magnitudes of the H^3 and H^1 shielding shifts, $\Delta\delta_H3/\Delta\delta_H1$, by use of the point-dipole ring-current approximation method [54]. The upper-state dihedral angle in (A) is found to be 73 °, which is close to the value (79 ° in CCl_4) reported by *DeMare* and *Martin*, for the unsubstituted vinylcyclopropane [50, 55]. (These compare to electron-diffraction values of *ca.* 40 ° for bicyclopropyl [50b] and 0 ° (the *S-cis* form) for cyclopropylaldehyde [48a].) In view of this similarity, it is assumed that no significant variation in the dihedral angles of the high energy conformer (A) should occur as a result of branching of the saturated C atom in C–C=C, adjacent to the cyclopropane.

The A:B ratios in a series of substituted vinylcyclopropanes of the structure *(99)* have been estimated by two different approaches: (1) by the modified point-dipole approximation (MPDA) [54] and (2) by the ring-current model [53]. From the data assembled in Table 5, it can be seen that the values obtained by the MPDA method are in striking agreement with those derived from the ring-current model when the relevant molecular and electronic parameters are: A = 0.88 Å, N = 6 electrons, and/or A = 1.01 Å, N = 4.5 electrons.

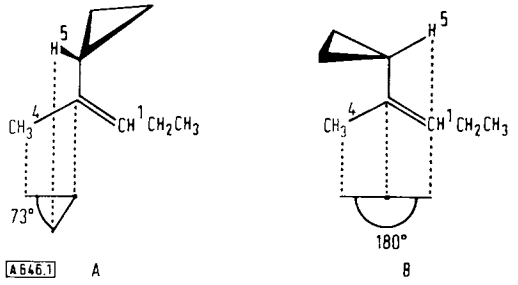
Table 5. Ratio of the conformations A:B in substituted vinylcyclopropanes *(99)* at room temperature (see also Fig. 1).



A B

Method	R = CH_3		R = n-C_3H_7		R = $(CH_3)_2CH$	
	cis	*trans*	*cis*	*trans*	*cis*	*trans*
Modified point-dipole approximation (*McConnell*)	76:24	53:47	97:3	87:13	100:0	100:0
Ring-current model						
(A = 0.88 Å, N = 6)	76:24	53:47	100:0	96:4	100:0	100:0
(A = 1.01 Å, N = 4.5)	75:25	52:48	100:0	95:5	100:0	100:0

The decrease of *S-trans* in the conformational population with increasing branching of R provides in essence a measure for the hindrance to free rotation of the cyclopropane exerted by the neighboring bulky substituents. This compares to a substitution effect in 2-substituted 1,3-butadienes, in which a bulky group R displaces the conformational equilibrium *S-cis* ⇄ *S-trans* in favor of the strainless *S-cis* conformation [56].



A646.1 A B

[52] *A. D. Walsh*, Trans. Faraday Soc. *45*, 179 (1949).

[53] *D. J. Patel, M. E. H. Howden*, and *J. D. Roberts*, J. Amer. chem. Soc. *85*, 3218 (1963).

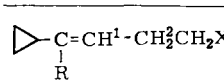
[54] a) *C. E. Johnson* and *F. A. Bovey*, J. chem. Physics *29*, 1012 (1958); b) *K. Tori* and *K. Kitahonoki*, J. Amer. chem. Soc. *87*, 386 (1965); c) *J. Tadanier* and *W. Cole*, J. org. Chemistry *27*, 4610 (1962).

[55] Compare also: a) *G. L. Closs* and *H. B. Klinger*, J. Amer. chem. Soc. *87*, 3265 (1965); b) *J. L. Pierre* and *P. Arnaud*, Bull. Soc. chim. France *1966*, 1690.

[56] *D. Craig, J. J. Shipman*, and *R. B. Fowler*, J. Amer. chem. Soc. *83*, 2885 (1961), reported that second order rate constant for the addition of maleic anhydride (at 25 °C in benzene) is 50 times as great for 2-neopentylbutadiene than for butadiene. See also: a) *J. Sauer*, Angew. Chem. *79*, 76 (1967); Angew. Chem. internat. Edit. *6*, 16 (1967); b) *E. L. Eliel, N. L. Allinger, S. J. Angyal*, and *G. A. Morrison*: Conformational Analysis. Interscience, New York 1966, p. 21.

It also provides a sensible explanation for the observed increase in $\delta_{trans}-\delta_{cis}$ values for the H^1 and H^2 protons in *(99)* with increasing branching of R (Table 6). Furthermore, this substantiates the view put forward earlier for the directive influence exerted by substituents in *(59)* on the steric course of cyclopropane ring-opening (Table 2).

Table 6. Effect of substituent on $\delta_{trans}-\delta_{cis}$ values of vinylic and allylic protons.

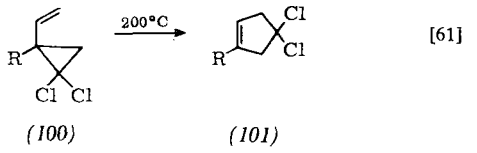
	R	X	$\delta_{trans}-\delta_{cis}$ (Hz) H^1	H^2
 *(99)*	CH_3	H	3.0	10.2
	CH_3	OAc	2.4	7.8
	n-C_3H_7	H	7.2	—
	n-C_3H_7	OAc	8.4	10.2
	i-C_3H_7	H	17.4	14.4
	i-C_3H_7	OAc	18.6	11.4

7. Thermal Rearrangement of Vinylcyclopropanes

Cyclopropanes are known to undergo three types of bond-reorganization processes: (i) geometric *cis-trans* isomerization [57], (ii) structural rearrangement to olefins [58], and (iii) vinylcyclopropane-cyclopentene rearrangement [59,60]. They are discernible thermodynamically by the quantity of their activation energy (ΔE). This is 60–65 kcal in the case of the isomerizations (i) and (ii) [57d], and about 50 kcal for reaction (iii). Processes of types (i) and (ii) are beyond the scope of this article, and will not be considered here.

Experience accumulated so far indicates that substitution in the vinylcyclopropane system, both on the ring and around the double-bond, exerts influence on rates of reaction and plays a determinative role in the course of thermal rearrangement into cyclopentene. The examples shown in Scheme 2 illustrate this effect.

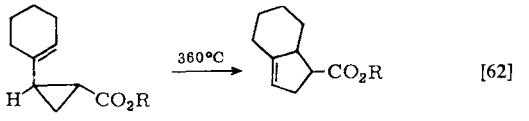
Ring Substitution:



[61]

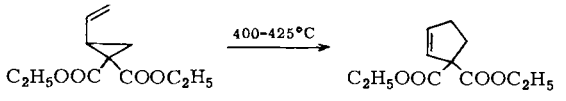
(100) *(101)*

R = CH_3, $k_1 \times 10^5$ = 6.5 sec^{-1}(200°C)
ΔE = 50.2 kcal (234°C)
R = H, CH_3



[62]

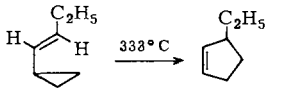
(102) *(103)*



[63]

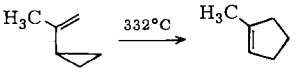
(104) *(105)*

Double-bond Substitution:



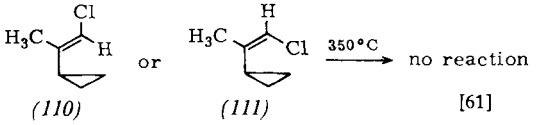
$k_1 \times 10^5$ = 5.91 sec^{-1}(332.7°C)
ΔE = 49.98 kcal

(106) *(107)* [59d]



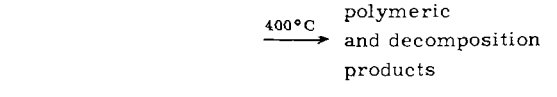
$k_1 \times 10^5$ = 3.32 sec^{-1}
ΔE = 50.9 kcal

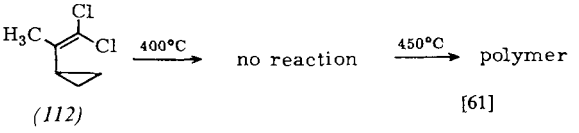
(108) *(109)* [64]



[61]

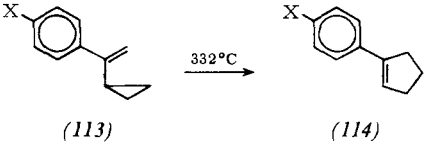
(110) *(111)*





[61]

(112)



$k_1 \times 10^5$ = 10.3 sec^{-1}(where X=H, CH_3, i-C_3H_7, OCH_3)
5.03 sec^{-1}(X=F) [65]

(113) *(114)*

[57] a) *B. S. Rabinovitch, E. W. Schlag,* and *K. B. Wiberg,* J. chem. Physics *28,* 504 (1958); b) *M. C. Flowers* and *H. M. Frey,* Proc. Roy. Soc. (London) *A 257,* 122 (1960); c) *H. M. Frey* and *D. C. Marshall,* J. chem. Soc. (London) *1963,* 5717; d) *D. W. Sester* and *B. S. Rabinovitch,* J. Amer. chem. Soc. *86,* (19465 64).

[58] a) *Pritchard, Sowden,* and *A. F. Trotman-Dickenson,* Proc. Roy. Soc. (London) *A 217,* 563 (1953); b) *M. C. Flowers* and *H. M. Frey,* J. chem. Soc. (London) *1962,* 1157; c) *J. P. Chesick,* J. Amer. chem. Soc. *82,* 3277 (1960); d) *H. M. Frey* and *D. C. Marshall,* J. chem. Soc. *1962,* 3052.

[59] a) *C. G. Overberger* and *A. E. Borchert,* J. Amer. chem. Soc. *82,* 1007 (1960); b) *M. C. Flowers* and *H. M. Frey,* J. chem. Soc. *1961,* 3547; c) *C. A. Wellington,* J. physic. Chem. *66,* 1671 (1962); d) *R. J. Ellis* and *H. M. Frey,* J. chem. Soc. *1964,* 4188; e) *C. J. Elliot* and *H. M. Frey, ibid. 1965,* 345; f) *C. J. Elliot* and *H. M. Frey, ibid. A 1966,* 553.

[60] a) *W. v. E. Doering* and *W. R. Roth,* Angew. Chem. *75,* 27 (1963); Angew. Chem. internat. Edit. *2,* 115 (1963); b) Tetrahedron, *19,* 715 (1963); c) *W. v. E. Doering* and *J. B. Lambert, ibid. 19,* 1989 (1963).

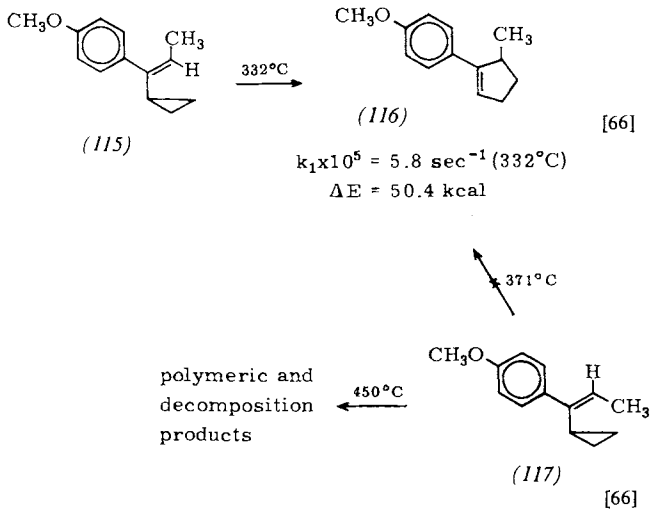
[61] *A. D. Ketley, A. J. Berlin, E. Gorman,* and *L. P. Fisher,* J. org. Chemistry *31,* 305 (1966).

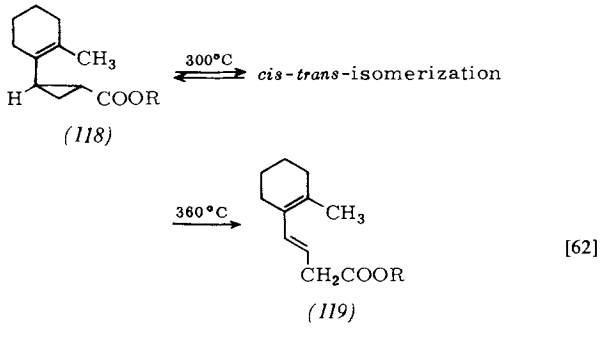
[62] *G. Stork,* Lecture at the 19th National Organic Chemistry Symposium, Amer. chem. Soc., Phoenix, Arizona, 1965.

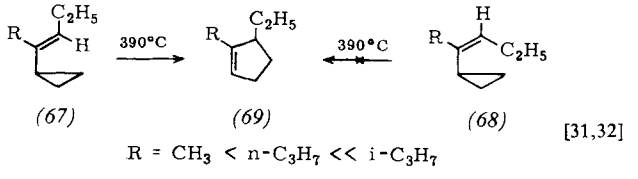
[63] *G. H. Schmid* and *A. W. Wolkoff,* J. org. Chemistry *32,* 254 (1967).

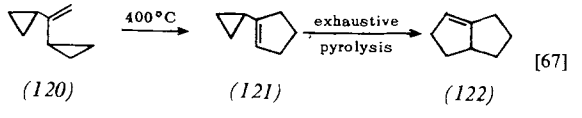
[64] *H. M. Frey* and *D. C. Marshall,* J. chem. Soc. (London) *1962,* 3981.

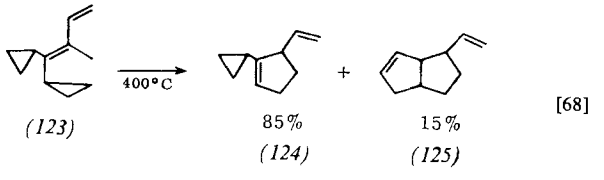
[65] *A. D. Ketley* and *J. L. McClanahan,* J. org. Chemistry *30,* 942 (1965).











Scheme 2

Comparative kinetic study has shown that substitution of chlorine on C-2 of vinylcyclopropane *(100)* enhances considerably its rate of rearrangement to the cyclopentene *(101)* relative to the conversion *(106)*→*(107)*. The exclusive formation of the cyclopentenes corresponding to the expected diradicals from *(100)* and *(105)* suggests that the rearrangement may not involve simultaneous bond rupture and bond formation [69].

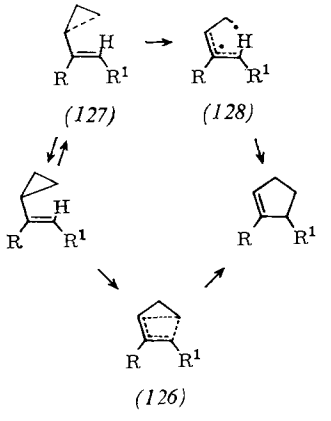
Introduction of chlorine on the terminal carbon of the double bond (compounds *(108)*, *(109)*, and *(110)*) apparently diminishes the interaction of the π-electrons in the opening of the small ring so that other types of thermal rupture of the ring must take place, demanding higher activation energy.

Of particular interest is the effect of alkyl substitution on the terminal carbon of the double bond. If a methyl or ethyl group is placed *cis* to the cyclopropyl, for example in compounds *(117)*, *(118)*, and *(68)*, (R = CH_3, *n*-C_3H_7, *i*-C_3H_7), the rate of thermal rearrangement is strikingly reduced and it also leads to formation of polymers and/or structural rearrangements to olefins. In contrast, when the alkyl group is situated *trans* to the cyclopropyl (examples: *(106)*, *(115)*, and *(67)* (R = CH_3, *n*-C_3H_7, *i*-C_3H_7)), it has no diminishing effect on rates of rearrangement.

In compound *(123)*, the terminal vinyl group does not seem to interact with the *cis* cyclopropyl group to give a seven-membered ring compound. Moreover, it probably actually inhibits rearrangement to the cyclopentene. The formation of *(124)* probably involves the rearrangement of the cyclopropyl group *trans* to the vinyl group.

The kinetic data for the conversion *(113)*→*(114)* show that the rates for all except the fluoro derivative are the same. This is an indication that the vinylcyclopropane rearrangement is relatively insensitive to polar effects, at least as transmitted through C-1.

The vinylcyclopropane rearrangement can be explained by a mechanism in which the rate-determining step is the opening of the cyclopropyl ring either to the diradical *(128)* or to the "expanded ring" *(127)* [57a,57d], followed by ring closure as a result of intramolecular coupling of the reactive ends of the diradical. On the other hand, it can also be interpreted in terms of concerted mechanism, proceeding directly through a Cope-type transition state such as *(126)* [64,69].



Recently, *Wilcott* and *Cargle* [70] were able to conclude, from NMR investigations, that in thermolysis of monodeuteriovinylcyclopropane the loss of stereospecificity at the deuterium-labeled site in the cyclopropyl ring is at least five times as fast as the conversion to cyclopentene, thus substantiating the diradical mechanism. Interpretation of data from pyrolysis of

[66] *A. J. Berlin, L. P. Fisher,* and *A. D. Ketley,* Chem. and Ind. *1965*, 509.

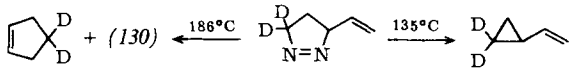
[67] *A. D. Ketley* and *J. L. McClanahan,* J. org. Chemistry *30*, 940 (1965); compare, *E. Vogel* and *R. Erb,* Angew. Chem. *74*, 76 (1962); Angew. Chem. internat. Edit. *1*, 53 (1962).

[68] *A. D. Ketley, J. L. McClanahan,* and *L. P. Fisher,* J. org. Chemistry *30*, 1659 (1965).

[69] a) *B. Grzybowska, J. H. Know,* and *A. F. Trotman-Dickenson,* J. chem. Soc. (London) *1961*, 4402; b) *H. M. Frey,* Trans. Faraday Soc. *58*, I, 516 (1962); c) *R. J. Ellis* and *H. M. Frey,* J. chem. Soc. (London) *1964*, 959; d) *K. W. Egger, D. M. Golden,* and *S. W. Benson,* J. Amer. chem. Soc. *86*, 5420 (1964).

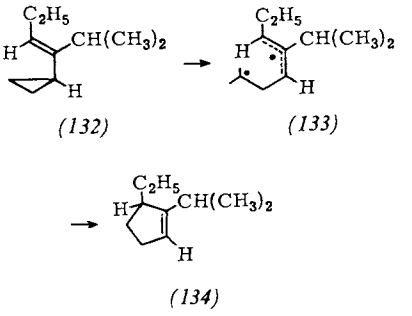
[70] *M. R. Wilcott* and *V. H. Cargle,* J. Amer. chem. Soc. *89*, 723 (1967).

(129) at various temperatures led *Crawford* and *Cameron* [71] to the conclusion that the ring closure of the assumed diradical intermediate to *(130)* should be considerably greater than to the cyclopentene *(131)*.



(131) *(129)* *(130)*

The enhanced tendency to thermal rearrangement of *(132)* relative to *(67)*, where R = CH_3, *n*-C_3H_7, can be attributed to conformational factors. The conversion *(132)*→*(134)*, evidently, requires only slight



(132) *(133)* *(134)*

conformational changes throughout, since the conformation of *(132)* in the ground state is almost the same as in the activated state *(133)*.

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German version: Angew. Chem. *80*, 592 (1968)

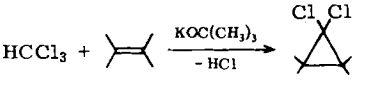
[71] *R. J. Crawford* and *D. M. Cameron*, Canad. J. Chem. *45*, 691 (1967).

Synthesis of Cyclopropyl Ethers and Cyclopropanols by Carbene Transfer – Acetolysis of Cyclopropyl *p*-Toluenesulfonates[**]

BY U. SCHÖLLKOPF[*]

The reaction of chloromethyl phenyl ether with butyllithium in olefins yields phenoxycyclopropanes. 1-Chloro-1-phenoxycyclopropanes can be prepared in a similar manner, though the yields are poor. Alkoxycyclopropanes are formed when dichloromethyl alkyl ethers are treated with methyllithium/lithium iodide in the presence of olefins. Cyclopropanols can be obtained in good yields by reaction of (β-chloroethoxy)cyclopropanes either with butyl- or ethyllithium or with bases. – As was shown by acetolysis experiments with cyclopropyl p-toluenesulfonates having a known steric configuration, the rearrangement of a cyclopropyl derivative into an allyl cation proceeds in accordance with the Woodward-Hoffmann-DePuy rule. The solvolysis of exo-bicyclo[n.1.0]alkyl p-toluenesulfonates is assumed to proceed via "semi-open" intermediates, which are somewhere between an allyl cation and a cyclopropyl cation.

1. Introduction



(1)

Following kinetic studies by *Hine* [1] on the mechanism of the alkaline hydrolysis of haloforms, *Doering* and *Hoffmann* [2] allowed chloroform to react with potassium *tert*-butoxide in olefins and obtained dichlorocyclopropanes *(1)*.

This was the first step in the rapid development of carbene chemistry. At the same time it provided an extremely flexible synthetic principle, *i.e.* "carbene transfer", which offered ready access to many heterosubstituted cyclopropanes [3] and cyclopropenes [3], and so gave great momentum to research on small rings [3].

The reason for the use of the loose term "carbene transfer" to describe the process is that it is not clear in most cases how the three-membered ring is formed. Though it is certain that α-metal-α-halogen compounds are formed as intermediates, there is some controversy as to whether the reaction of these with the

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[**] Based on a Plenary Lecture to the Symposium on the Chemistry of Small Rings (Louvain, Belgium, September 12–15, 1967).

[1] *J. Hine*, J. Amer. chem. Soc. *72*, 2438 (1950) and more recent work.

[2] *W. v. E. Doering* and *A. K. Hoffmann*, J. Amer. chem. Soc. *76*, 6162 (1954).

[3] For summaries, see *B. Jerosch-Herold* and *P. P. Gaspar*, Fortschr. chem. Forsch. *5*, 89 (1965); *E. Chinoporos*, Chem. Reviews *63*, 235 (1963); *W. Kirmse*, Angew. Chem. *71*, 537 (1959); *73*, 161 (1961); *H. Kloosterziel*, Chem. Weekbl. *59*, 77 (1963); *W. E. Parham* and *E. E. Schweizer*, Org. Reactions *13*, 55 (1963); *W. Kirmse*: Carbene Chemistry. Academic Press, London, New York 1964; particular attention to the synthesis of cyclopropenes has been paid by *A. W. Krebs*, Angew. Chem. *77*, 10 (1965); Angew. Chem. internat. Edit. *4*, 10 (1965); *G. L. Closs* in *H. Hart* and *G. J. Karabatsos*: Advances in Alicyclic Chemistry. Vol. 1, Academic Press, New York, London 1966, p. 53.

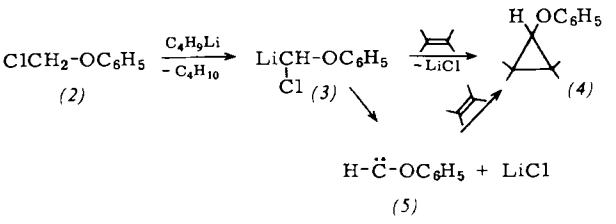
double bond is direct, *i.e.* carbenoid[4], or indirect, *via* a carbene (cf. *e.g.* Scheme 1).

Carbene transfer is excellently suited for the synthesis of alkoxy- and aryloxycyclopropanes[5]. This and a good synthesis of cyclopropanols are described in the first part of this article, while the second part is devoted to the acetolysis of cyclopropyl *p*-toluenesulfonates. The object of these investigations, which are at present being carried out jointly with *Schleyer* and his co-workers (Princeton University), is to carry out an experimental check on the *Woodward-Hoffmann-DePuy* rule for the stereochemistry of the conversion of a cyclopropyl derivative into an allyl cation.

2. The Syntheses

2.1. Phenoxycyclopropanes

Phenoxycyclopropanes *(4)* are formed (cf. Table 1, column 6) when chloromethyl phenyl ether *(2)*[6] is allowed to react with butyllithium at −15 to −20 °C in the presence of an olefin[7] (see Scheme 1).

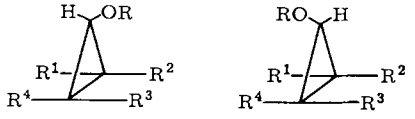


Scheme 1. Synthesis of phenoxycyclopropanes *(4)* (with alternative mechanisms).

It can be assumed (see above) that the reaction starts with a metalation, *i.e.* a hydrogen-metal exchange. The resulting phenoxychloromethyllithium *(3)* which is thermally extremely labile and has not yet been intercepted, then reacts with the olefinic double bond, either in a carbenoid reaction[4] or *via* phenoxycarbene *(5)* (cf. Scheme 1 and below).

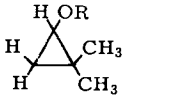
As far as can be seen from investigations so far, the synthesis can also be applied to ring-substituted chloromethyl aryl ethers. For example, the reaction of chloromethyl 2,4-dichlorophenyl ether with butyllithium in isobutene yields 50 % of 2-(2,4-dichlorophenoxy)-1,1-dimethylcyclopropane *(6)*[7]. Heterocyclic chloromethyl ethers should react similarly.

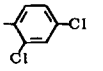
Table 1. Cyclopropyl ethers and cyclopropanols prepared.



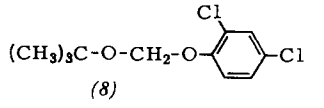
Olefin	R¹	R²	R³	R⁴	R=C₆H₅ [a] yield (%)	R=C₆H₅ [a] *endo*: *exo*	R=C₆H₅ [b] yield (%)	R=C₆H₅ [b] *endo*: *exo*	R=CH₃ [b] yield (%)	R=CH₃ [b] *endo*: *exo*	R=n-C₆H₁₃ [b] yield (%)	R=n-C₆H₁₃ [b] *endo*: *exo*	R=CH₂—CH₂Cl yield (%)	R=CH₂—CH₂Cl *endo*: *exo*	R=H yield (%)
Isobutene	H	H	CH_3	CH_3	65		24		55		79		78		87 [c] 73 [d]
trans-2-Butene	H	CH_3	H	CH_3	69		70		52				57		94 [c] 85 [c]
cis-2-Butene	H	CH_3	CH_3	H	59	≈3.7:1	67	≈3:1	49	≈7:1			74	≈3:1	
2-Methyl-2-butene	H	CH_3	CH_3	CH_3	53	≈3.1:1	78	≈2.1:1					23	≈1.4:1	59 [c]
2,3-Dimethyl-2-butene	CH_3	CH_3	CH_3	CH_3	70		68						63		91 [c]
Ketene diethyl acetal	H	H	OC_2H_5	OC_2H_5											
Ethyl vinyl ether	H	H	H	OC_2H_5					51						
Styrene	H	H	H	C_6H_5									70		81 [c]
Butadiene	H	H	H	$CH=CH_2$					65		76				
Cyclopentene	H	$-(CH_2)_3-$		H					16	≈1:2	20	≈1:2	57	≈1:2.3	74 [c]
Cyclopentadiene	H	$-CH=CH-CH_2-$		H					51	≈3.8:1	70	≈3.8:1	86		
Cyclohexene	H	$-(CH_2)_4-$		H	40	≈1:2.4	40	≈1:1	31	≈1:1.7	36	≈1:3.6	48	≈1:4	94 [c]
Cycloheptene	H	$-(CH_2)_5-$		H									36	≈1:1.5	64 [c]
Cyclooctene	H	$-(CH_2)_6-$		H					43	≈2:1			65	≈1:1.8	93 [c]
p-Dioxene	H	$-O-(CH_2)_2-O-$		H	21	≈1:2.4									

[a] From $ClCH_2-OC_6H_5$, C_4H_9Li, and olefin.
[b] From Cl_2CH-OR, $CH_3Li \cdot LiI$, and olefin.
[c] Conversion of $-OCH_2-CH_2Cl$ into $-OH$ with C_4H_9Li followed by hydrolysis.
[d] Conversion of $-OCH_2-CH_2Cl$ into $-OH$ with base followed by hydrolysis.



(6), R = 

(7), R = C_6H_5



(8)

In addition to the adducts *(4)*, small quantities of pentyl phenyl ether *(9)* are also formed. It is not yet known whether this is due to a Wurtz reaction (Scheme 2, a) or to a carbenoid

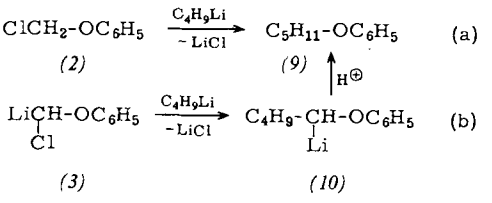
[4] For definition, see *G. L. Closs* and *R. A. Moss*, J. Amer. chem. Soc. *86*, 4042 (1964); Cf. also *W. Kirmse*, Angew. Chem. *77*, 1 (1965); Angew. Chem. internat. Edit. *4*, 1 (1965); *G. Köbrich*, Angew. Chem. *79*, 15 (1967); Angew. Chem. internat. Edit. *6*, 41 (1967).

[5] Cf. *H. Gross* and *E. Höft*, Angew. Chem. *79*, 358 (1967); Angew. Chem. internat. Edit. *6*, 335 (1967).

[6] *H. J. Barber*, *R. F. Fuller*, *M. B. Greene*, and *H. T. Zwartoun*, J. appl. Chem. *3*, 266 (1953); *C. S. Davis* and *G. S. Lougheed*, Org. Synthesis *47*, 23 (1967).

[7] *U. Schöllkopf*, *A. Lerch*, and *J. Paust*, Chem. Ber. *96*, 2266 (1963).

reaction of phenoxychloromethyllithium *(3)* with butyllithium to form phenoxypentyllithium *(10)*, followed by protonation (Scheme 2, b). If potassium *tert*-butoxide is used instead of butyllithium, substitution becomes the principal reaction. An example of this is the reaction of this base with chloromethyl 2,4-dichlorophenyl ether (in cyclohexene), which gives (2,4-dichlorophenoxy)-*tert*-butoxymethane *(8)* in 77 % yield[7].



Scheme 2. Possible modes of formation of pentyl phenyl ether, (a) by Wurtz reaction, (b) by carbenoid coupling.

The structure of the phenoxycyclopropanes *(4)* is clearly shown by their NMR spectra[7]. Conclusive evidence is provided by the high resonance field strengths of the cyclopropyl protons[8] and the magnitudes of the geminal[9] and vicinal[10] coupling constants. This is illustrated by the spectrum of 1,1-dimethyl-2-phenoxycyclopropane *(7)*, which is of the readily analyzable ABX type[11] (Fig. 1). Satisfactory agreement is found between the calculated and experimental spectra taking $|J_{AB}$ 5.9 Hz, $|J_{BX}|$ 3.1 Hz, J_{AX} 6.6 Hz, and $\delta_X = 6.7\,\tau$, $\delta_A = 9.36\,\tau$, and $\delta_B = 9.67\,\tau$. The chemical shifts are appreciably higher than those of corresponding hydrogen atoms in open-chain phenyl alkyl ethers. The relatively low value of the geminal coupling constant J_{AB} indicates an H–C–H angle of 114–118 °[10], as is also assumed in cyclopropanes[12].

With olefins having no center of symmetry and no axis of symmetry along the double bond, two stereoisomers (*exo* and *endo* isomers) are formed. The main product with *cis*-2-butene or 2-methyl-2-butene is the *endo* isomer, while cyclohexene and *p*-dioxene give mainly the *exo* isomers (cf. Table 1).

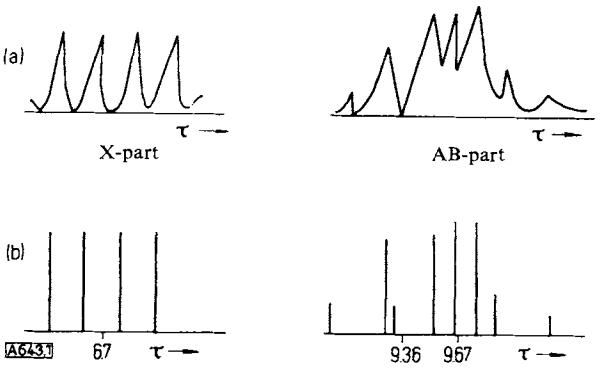


Fig. 1. (a) Observed and (b) calculated NMR spectrum of the cyclopropyl protons of 1,1-dimethyl-2-phenoxycyclopropane *(7)*.

This suggests a delicate and rather complex interplay of steric and electronic factors in the transition state of the cycloaddition[13].

Since empirical[9b] and theoretical considerations[9b] indicate that the spin-spin coupling of *cis* protons in the three-membered ring is more effective than that of *trans* protons, the configuration of the isomers can be deduced from their NMR spectra. Figure 2 shows (schematically) the α-proton signals; the ratio of the areas of the signals corresponds to the ratio of the isomers. In the adducts of open-chain olefins, the stronger of the two signals shows the greater splitting, and this signal must therefore be assigned to the *endo* epimer. The reverse is found for the adducts of cyclohexene and *p*-dioxene.

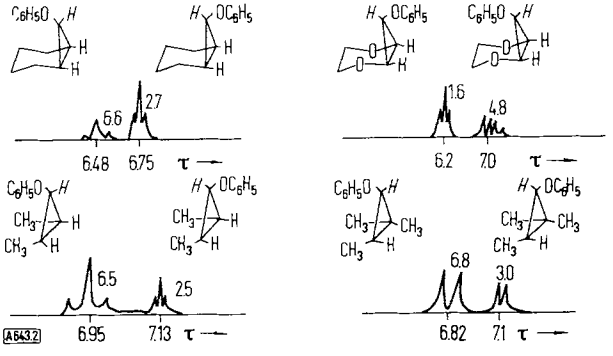


Fig. 2. NMR signals of the α protons of stereoisomeric phenoxycyclopropanes (the figures above the signals are the coupling constants in Hz). ($J_{cis} > J_{trans}$ in the three-membered ring.)

Apart from the hydrogen atom of the *p*-dioxene adduct, the (*endo*!) hydrogen atom of the *exo* isomer absorbs at higher field strengths (see Fig. 2). As we concluded[14], and as was recently demonstrated quantitatively by *Longone*[15], a cyclopropyl proton *cis* or *trans* to a C–C bond is situated in the anisotropy region of this bond in such a way that it experiences shielding or deshielding, respectively (Fig. 3). This effect, which we also observed with alkoxycyclopropanes (see Fig. 5) as well as with phenylthio-[16] and phenylselenocyclopropanes[17], can be used for the determination of configurations if the coupling constants cannot be deduced from the spectra.

[8] The reason for the increased screening of cyclopropyl protons is not yet clear. It may be due to a ring current produced by the relatively mobile bonding electrons in the magnetic field; cf. *D. J. Patel, M. E. Howden,* and *J. D. Roberts.* J. Amer. chem. Soc. *85*, 3218 (1963); *K. B. Wiberg* and *B. J. Nist, ibid. 83*, 1226 (1961).

[9] (a) For the angular dependence of geminal coupling constants, see *H. S. Gutowsky, M. Karplus,* and *D. M. Grant,* J. chem. Physics *31*, 1278 (1959). Though objections have been made to this relationship, the values found for cyclopropanes agree (in magnitude) with the expected values (4.5–7 Hz). Cf. (b) *J. D. Graham* and *M. T. Rogers,* J. Amer. chem. Soc. *84*, 2249 (1962); *K. B. Wiberg* and *B. J. Nist, ibid. 85*, 2788 (1963); *D. J. Patel, M. E. Howden,* and *J. D. Roberts, ibid. 85*, 3218 (1963); *H. M. Hutton* and *T. Schaefer,* Canad. J. Chem. *41*, 684, 1623, 2429 (1963); *U. Schöllkopf, G. J. Lehman, J. Paust,* and *H.-D. Härtl,* Chem. Ber. *97*, 1527 (1964).

[10] For the angular dependence of vicinal coupling constants, see *M. Karplus,* J. chem. Physics *30*, 11 (1959); for the vicinal coupling constants of *trans* and *cis* protons in the three-membered ring, see [9b].

[11] Regarding the definition, cf. *J. A. Pople, W. G. Schneider,* and *H. J. Bernstein*: High Resolution Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry. McGraw-Hill, New York 1959, p. 98.

[12] Cf. *E. Goldish,* J. chem. Educat. *36*, 408 (1959).

[13] Cf. *U. Schöllkopf* and *H. Görth,* Liebigs Ann. Chem. *709*, 97 (1967).

[14] (a) *U. Schöllkopf* and *W. Pitteroff,* Chem. Ber. *97*, 636 (1964); (b) *U. Schöllkopf* and *J. Paust, ibid. 98*, 2221 (1965).

[15] *D. T. Longone* and *A. H. Miller,* Chem. Commun. *1967*, 447.

[16] *U. Schöllkopf, G. J. Lehmann, J. Paust,* and *H.-D. Härtl,* Chem. Ber. *97*, 1527 (1964).

[17] *U. Schöllkopf* and *H. Küppers,* Tetrahedron Letters *1963*, 105.

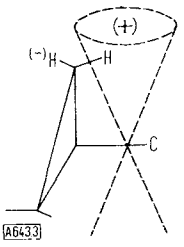


Fig. 3. Cyclopropyl protons in the anisotropy field of an adjacent C—C bond (schematic).

As was shown by experiments with *cis*- and *trans*-2-butene, the formation of the cyclopropane ring is *cis*-stereospecific. Therefore, the product-forming species can be regarded as electrophilic. In agreement with this conclusion, ketene diethyl acetal, with its electron rich double bond, is attacked 16 times as rapidly as isobutene (Table 2)[13]. However, 2-methyl-2-butene, which is also more nucleophilic, reacts only slightly faster, while 2,3-dimethyl-2-butene actually reacts more slowly than isobutene. The accelerating electronic affects are evidently balanced or outweighed in these cases by inhibiting steric effects. Similar, though less pronounced, behavior has been observed in addition reactions of other (electrophilic) carbenes[18].

Table 2. Competition constants (k_{rel}) of *(3)* or *(5)* for olefins (see Scheme 1).

Olefin	Isobutene	Ketene diethyl acetal	2-Methyl-2-butene	2,3-Dimethyl-2-butene	Cyclohexene
k_{rel} (−15 °C)	1	16	1.03	0.43	0.2

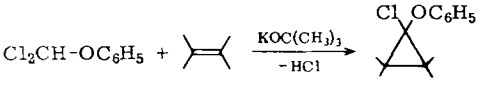
Two mechanisms (cf. Scheme 1) must be considered for the formation of the three-membered ring (this is also true of the syntheses described in Sections 2.2 and 2.3); these are the carbenoid[4] addition of phenoxychloromethyllithium *(3)* to the olefinic double bond and the course involving the phenoxycarbene *(5)*. Since both intermediates must be assumed to behave as electrophilic[4], the detection of the electrophilicity is of no help in deciding between the two possibilities. The results of another set of experiments (Table 3), in which fluoromethyl, chloromethyl, and bromomethyl phenyl ethers were allowed to react with butyllithium in cyclohexene under comparable conditions, also failed to provide the required evidence. On metalation with butyllithium containing LiBr, the *endo/exo* ratio of the phenoxynorcarane formed, and hence the selectivity of the intermediate, is almost independent of the nature of the leaving group (Table 3, column 2). This appears at first glance to support the carbene mechanism, since one could argue that in this case the lithium halide is eliminated before the product-forming step, and so has no specific influence in the transition state. However, the true situation is rather more complicated. The invariance of the isomer ratio appears to be accidental, since when butyllithium is used in the absence of salts, the ratio of the epimers shows a distinct increase in the order bromide, chloride, fluoride (Table 3, column 3). This observation could be interpreted as favoring the carbenoid mechanism [*(3)* → *(4)*][13], but it is unlikely that a change in medium would lead to a change in mechanism.

Table 3. *endo/exo* Ratios of the 7-phenoxynorcaranes formed from halogenomethyl phenyl ethers, butyllithium, and cyclohexene.

Halogen	with LiC_4H_9 (containing LiBr)	with LiC_4H_9 (salt free)
F	1:2.15	1:6.2
Cl	1:2.45	1:4.8
Br	1:2.1	1:4.3

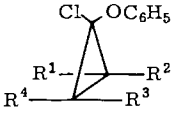
2.2. 1-Chloro-1-phenoxycyclopropanes

1-Chloro-1-phenoxycyclopropanes *(12)* are of interest as possible precursors for phenoxy-substituted, *i.e.* resonance-stabilized cyclopropyl cations. They are obtained (Table 4) (though only in poor yields, and not with all alkenes) on dehydrochlorination of dichloromethyl phenyl ether *(11)*[19] in olefins with potassium *tert*-butoxide[20].

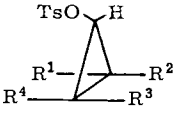


(11) *(12)*

Table 4. 1-Chloro-1-phenoxycyclopropanes *(12)* prepared. Comparison of the relative rate constants for the methanolysis of *(12a)*—*(12e)*[20] and the acetolysis of the *p*-toluenesulfonates *(13a)*—*(13e)*.



(12)



(13)

	Olefin	R^1	R^2	R^3	R^4	*(12)* yield (%)	m.p. (°C)	*(12)* + CH_3OH [b] k_{rel} (80 °C)	*(13)* + CH_3COOH k_{rel} (100 °C)
(a)	Isobutene	CH_3	CH_3	H	H	28–43	3–4	66.9	82.5
(b)	*trans*-2-Butene	H	CH_3	H	CH_3	5	—	61.7	65
(c)	*cis*-2-Butene	CH_3	H	H	CH_3	4 [a]	35–36	1	1
(d)	2-Methyl-2-butene	CH_3	CH_3	H	CH_3	42 [a]	*ca.*—20	34.4	20
(e)	2,3-Dimethyl-2-butene	CH_3	CH_3	CH_3	CH_3	11	34–35	10130	1375

[a] Only one isomer isolated.
[b] In the presence of $NaOCH_3$.

Experiments with butyllithium, which was found to be very effective in the preparation of non-halogenated phenoxycyclopropanes *(4)*, did not have the desired results in this

[18] Cf. *M. Jones jr., A. Kulczycki jr.*, and *K. F. Hummel*, Tetrahedron Letters *1967*, 183, and further literature cited there.

[19] *H. Laato* and *P. Lehtonen*, Suomen Kemistilehti *1964*, 169 (1964).

[20] *E. Ruban*, Dissertation, Universität Göttingen, 1968.

case, but led, irrespective of whether the reaction was carried out with or without olefin, to a complex mixture from which the following compounds could be isolated[21]: *cis*- and *trans*-1,2-dichloro-1,2-diphenoxyethylene, *cis*- and *trans*-1-chloro-1,2-diphenoxy-1-hexene, 1-butylpentyl phenyl ether, and *trans*-4-nonene. The phenoxydichloromethyllithium [$LiC(Cl_2)-OC_6H_5$] assumed to occur as an intermediate evidently undergoes a carbenoid reaction either with itself or with other organolithium compounds present in the solution. The ratio of the products depends on the experimental conditions; with three equivalents of butyllithium, for example, *trans*-4-nonene is formed in 82 % yield[21]. Further experiments will have to be performed to decide whether this reaction, which can also be carried out with other alkyllithiums, can have any importance for the synthesis of olefins[22].

In the experiments with *cis*-2-butene and 2-methyl-2-butene, only one isomer, which was presumably the "*endo*-chloro" form *(12c)* or *(12d)*, was found in each case. This configuration is assigned on the basis of the methanolysis constants of the compounds, which differ from each other and from those of the other members of the series by factors similar to those found for the acetolysis constants of the corresponding cyclopropyl *p*-toluenesulfonates *(13)*, the configurations of which have been proved (cf. Table 4). The *exo* isomers, which, according to the Woodward-Hoffmann-De Puy rule (see below), should be thermally less stable than the *endo* epimers, are probably lost during isolation. The isomeric purity of both products is demonstrated by their sharp melting points (cf. Table 4) and the linearity of the plots of $\ln[(V_0 - V_\infty)/(V_t - V_\infty)]$ against time for the methanolyses (Fig. 4).

Because the relative rates of solvolysis in the two series run parallel to each other, and because a concerted mechanism has been established for the acetolysis of the *p*-toluenesulfonates *(13a)–(13c)* (see below), we would assume that ionization and ring opening during methanolysis of the chlorides *(12a)–(12c)*, which affords allylic compounds or dienes[20], are concerted. Apparently the mesomeric effect of a phenoxyl oxygen atom is insufficient to lower the energy level of a cyclopropyl cation below that of the corresponding allylic cation[20].

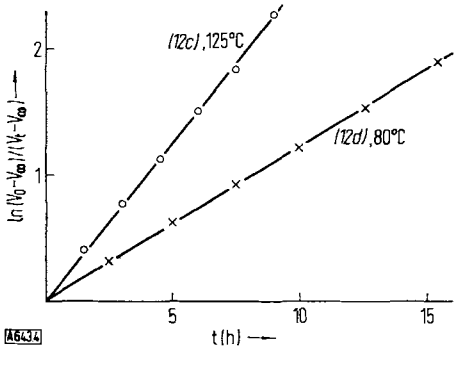


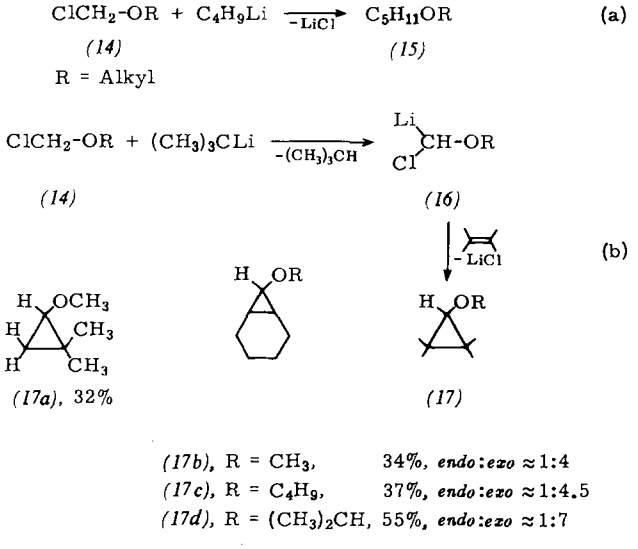
Fig. 4. Kinetics of the methanolysis of *(12c)* and *(12d)* [20] (in the presence of excess sodium methoxide). V = Volume of aqueous HCl (ml) on titration of aliquot samples.

[21] *E. Ruban*, Diplomarbeit, Universität Göttingen, 1966.

[22] Analogies are given by *K. D. Berlin* and *B. S. Rathore*, Tetrahedron Letters *1964*, 2547; *V. Franzen* and *L. Fikentscher*, Chem. Ber. *95*, 1958 (1962).

[23] According to *H. Böhme* and *A. Dörries*, Chem. Ber. *89*, 719 (1956), chloromethyl aryl ethers are solvolyzed more slowly than chloromethyl alkyl ethers. The differences in reactivity should, however, be smaller in the S_N2 reactions assumed here.

Unlike the chloromethyl aryl ethers, chloromethyl alkyl ethers *(14)* are not metalated but substituted by *n*-butyllithium[14a] (Scheme 3a). Replacement of the phenyl group by an alkyl group reduces the acidity of the methylene hydrogen atoms and simultaneously increases the ease of substitution of the halogen[23]. However, alkoxychloromethyllithiums *(16)* are formed in yields of at least about 50 % when the more bulky *tert*-butyllithium is used. On metalation in olefins, alkoxycyclopropanes *(17)* can be isolated in yields of up to about 60 %[14a] (cf. Scheme 3b).

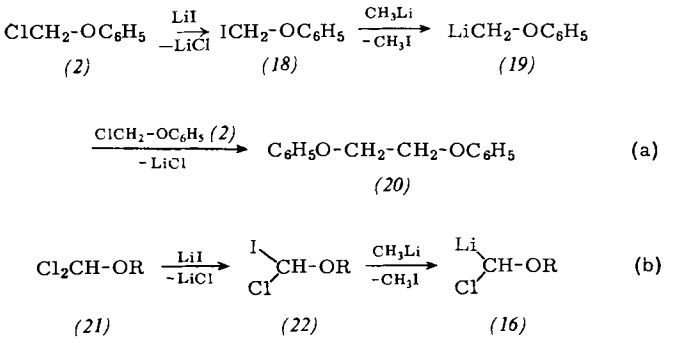


Scheme 3. Reaction of chloromethyl alkyl ethers (a) with *n*-butyllithium and (b) with *tert*-butyllithium in olefins.

However, this method is not recommended for the synthesis of *(17)*. *tert*-Butyllithium is an unsatisfactory reagent, which decomposes solvents and reacts with olefins to form undesirable by-products. It was therefore necessary to find a gentler method for the preparation of the metalated halogeno ethers *(16)*.

An indication of how this might be achieved was provided by the observation[24] that the reaction of chloromethyl phenyl ether *(2)* with methyllithium (instead of butyllithium) in isobutene led, not to 1,1-dimethyl-2-phenoxycyclopropane *(7)*, but surprisingly to 1,2-diphenoxyethane *(20)*. Since the methyllithium used had been prepared from methyl iodide, and so contained one mole of lithium iodide, the obvious interpretation (cf. Scheme 4, a) is that nucleophilic chlorine/iodine exchange first leads to the formation of iodomethyl phenyl ether *(18)*; this then undergoes a halogen-metal exchange with methyllithium to form phenoxymethyllithium *(19)*, which reacts with unreacted *(2)* to form *(20)*. If this interpretation were correct, the desired lithiochloromethyl alkyl ethers *(16)* would be obtained [*via* the intermediates *(22)*] on treatment of dichloromethyl alkyl ethers *(21)* with methyllithium (cf. Scheme 4, b).

[24] *J. Paust*, Diplomarbeit, Universität Heidelberg, 1963.



Scheme 4. Paths for the formation of (a) diphenoxyethane *(20)* and (b) lithiochloromethyl alkyl ethers *(16)* (cf. text).

This is in fact the case; if methyllithium is added dropwise to a solution of a dichloromethylalkyl ether *(21)* in an olefin until a positive Gilman test is obtained, alkoxycyclopropanes *(17)* are formed, sometimes in excellent yields (cf. Table 1, columns 10, 12 and 14).

The synthesis proceeds very rapidly even at ≈0 °C, and can therefore also be used with olefins that normally react with organolithium compounds, such as cyclopentadiene or butadiene. This and the ready availability of the dichloromethyl alkyl ethers *(21)*, which are obtained from formates and phosphorus pentachloride[5], ensure this method a wide field of application (cf. Table 1). It should be mentioned in passing that phenoxycyclopropanes *(4)* can also be obtained in this way from dichloromethyl phenyl ether *(11)*[20] (cf. Table 1, column 8).

As in the addition reactions of phenoxychloromethyllithium *(3)* or phenoxycarbene *(5)*, the isomer ratio of the adducts formed in the reactions with unsymmetrical olefins (cf. Table 1, columns 9, 11, 13, and 15) again point to a subtle interplay of steric and electronic factors in the transition complex. For example, "methoxycarbene" gives the *exo* form in the higher yield with cyclopentene, but the *endo* form with cyclopentadiene. Similarly, cyclooctene gives mainly *endo*-methoxybicyclo[6.1.0]nonane with "methoxycarbene", but mainly *exo*-(β-chloroethoxy)bicyclo[6.1.0]nonane with "(β-chloroethoxy)carbene". The *endo* additions are always favored in the case of open-chain olefins.

As with the phenoxycyclopropanes *(4)* (cf. Fig. 2), the configurations can again be definitely established from the NMR spectra (cf. Fig. 5). Mention should again be made of the relationship between the chemical shifts of the α-hydrogen atoms and their position in relation to the vicinal C–C bond.

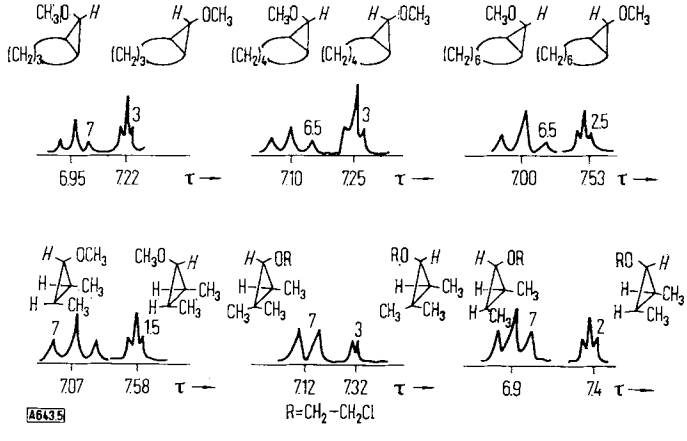
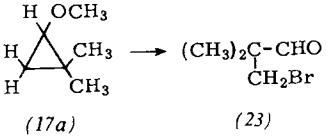


Fig. 5. NMR signals of the α protons of *exo*/*endo*-isomeric alkoxycyclopropanes *(17)* (the figures above the signals are the coupling constants in Hz).

Since cyclopropyl ethers should resemble the enol ethers in their reactivity, they should readily undergo electrophilic ring opening. So far as is known at present, this appears to be the case. For example, 2-methoxy-1,1-dimethylcyclopropane *(17a)* reacts with bromine in glacial acetic acid to give β-bromopivalic aldehyde *(23)* (yield 83 %)[25], a compound that can only be obtained in poor yields by conventional methods[25a].



(17a) *(23)*

2.4. Cyclopropanols

It seemed an obvious step to apply the above cyclopropyl ether synthesis to the preparation of (secondary) cyclopropanols *(33)*, for which no satisfactory synthesis was previously known. The problem was to find a group R that could be removed from the oxygen of cyclopropyl ethers *(17)* under such mild conditions that the three-membered ring would remain intact. The β-chloroethyl group was found to be particularly suitable.

The usual methods adopted for the synthesis of cyclopropanols are summarized briefly in Scheme 5. Unsubstituted cyclopropanol *(25)* is most readily obtained by *Cottle*'s method[26], in which magnesium bromide, ferric chloride, ethylmagnesium bromide, and acid are added in succession to epichlorohydrin *(24)*. A variant of this synthesis due to *DePuy*[27] is particularly suitable for the preparation of 1-arylcyclopropanols *(27)*. In this method, dichloroacetone is allowed to react with arylmagnesium chloride, and the magnesium salt *(26)* is subjected to treatment with $FeCl_3$/ethylmagnesium bromide/acid. 1-Alkylated cyclopropanols are obtained only in poor yields by this route. Another path to cyclopropanols proceeds *via* cyclopropyl acetates *(30)*, which can be cleaved with $LiAlH_4$ or (better) with methyllithium[27]. They are obtained either by *Emmons*'s method[28], which involves a Baeyer-Villiger rearrangement of the ketones *(28)*, or (very elegantly) by *Freeman*'s method[29], which involves thermolysis of pyrazol-1-in-3-yl acetates *(29)*. This method is also suitable for preparation

[25] *U. Schöllkopf* and *J. Paust*, unpublished. On standing, *(23)* yields a trimer of m.p. 86–87 °C.

[25a] *R. W. Sinclair*, University of Adelaide, personal communication.

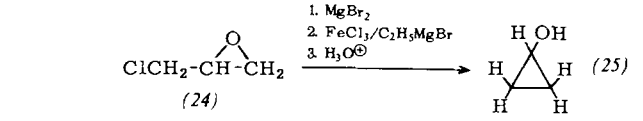
[26] *J. K. Magrene* and *D. C. Cottle*, J. Amer. chem. Soc. *64*, 484 (1942); *C. W. Stahl* and *D. C. Cottle*, *ibid. 65*, 1782 (1943).

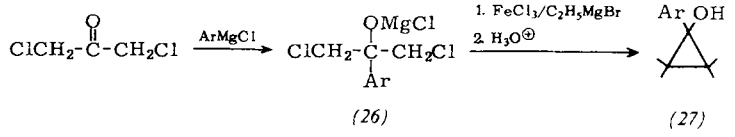
[27] *C. H. DePuy*, *G. M. Dappen*, *K. L. Eilers*, and *R. A. Klein*, J. org. Chemistry *29*, 2813 (1964). For a review, see *C. H. DePuy*, Accounts chem. Res. *1*, 33 (1968).

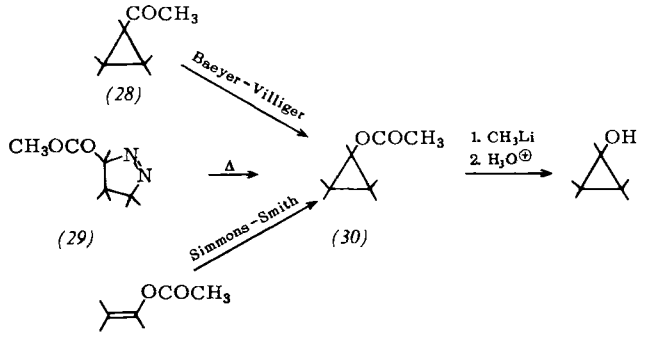
[28] *W. D. Emmons* and *G. B. Lucas*, J. Amer. chem. Soc. *77*, 2287 (1955).

[29] *J. P. Freeman*, J. org. Chemistry *29*, 1379 (1964).

of tertiary cyclopropanols [29a]. *Simmons-Smith* cyclopropanation of vinyl acetates [30] is possible in principle, but the yields are poor.

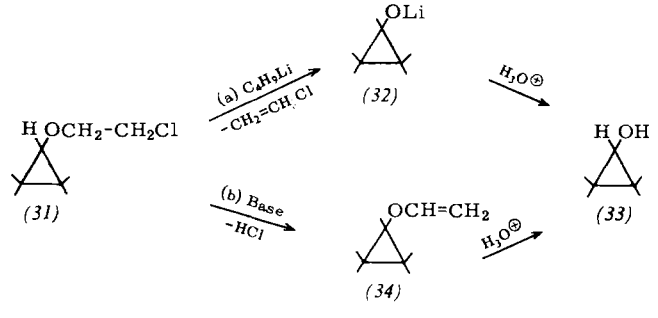






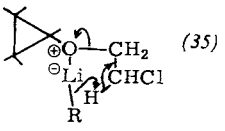
Scheme 5. Syntheses of cyclopropanols.

Two methods have proved particularly suitable for the conversion of β-chloroethyl cyclopropyl ethers *(31)* (cf. Table 1, column 14) into secondary cyclopropanols *(33)* (Table 1, column 16) [31]. One is the reaction of *(31)* with butyllithium (or ethyllithium), a single step leading in this case to the lithium cyclopropoxide *(32)*, together with vinyl chloride (cf. Scheme 6a). This method, which we discovered by accident and for which no analogy exists, gives good yields and is easy to use; it is therefore probably the best method in most cases (cf. Table 1, column 16 and footnote [c]).



Scheme 6. Conversion of β-chloroethyl cyclopropyl ethers *(31)* into cyclopropanols *(33)*.

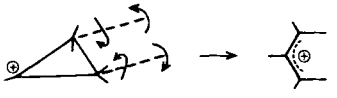
The mechanism of this remarkable reaction is not yet known. The organolithium reagent (R—Li) is presumably first complexed by the oxygen atom of *(31)* to form *(35)*, which decomposes as indicated by the arrows.



The other method (cf. Scheme 6, b) consists in the dehydrohalogenation of *(31)* with potassium hydroxide or potassium *tert*-butoxide, followed by hydrolysis of the resulting vinyl cyclopropyl ether *(34)* (cf. Table 1, column 16 and footnote [d]).

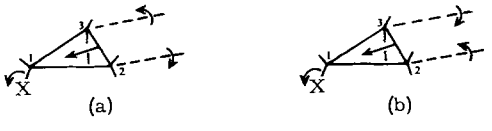
3. Acetolysis of Cyclopropyl *p*-Toluenesulfonates

According to the principle of conservation of orbital symmetry [32], the electrocyclic rearrangement of a cyclopropyl cation to an alkyl cation is disrotatory. Both possible directions of rotation (indicated by two pairs of arrows in Scheme 7) are electronically equally probable [33].



Scheme 7. Disrotatory rearrangement of a cyclopropyl cation into an allyl cation [32a].

If, however, ionization and ring opening occur synchronously, the rotation direction in which the ligand situated *cis* to the leaving group rotates inward and the *trans* ligand outward should be favored (cf. Scheme 9). This is shown by detailed Hückel calculations [32] carried out by *Hoffmann* and *Woodward* as a result of an observation reported by *DePuy* (cf. below).



Scheme 8. (a) Electronically favorable and (b) electronically unfavorable disrotation during the ionization of a cyclopropyl derivative with ring opening.
X = leaving group.

The reason for this can be best seen from the molecular models shown in Figure 6 [34]. The atomic orbitals on C-1, C-2, and C-3 are assumed for simplicity to be p orbitals. The orbital on C-1 (in the front of the photograph) is at an

[29a] Cf. also *Th. S. Cantrell* and *H. Schechter*, J. Amer. chem. Soc. *89*, 5868 (1967).

[30] *H. E. Simmons* and *R. D. Smith*, J. Amer. chem. Soc. *81*, 4256 (1959).

[31] *J. Paust* and *U. Schöllkopf*, Angew. Chem. *77*, 262 (1965); Angew. Chem. internat. Edit. *4*, 246 (1965); *U. Schöllkopf*, *J. Paust*, *A. Al-Azrak*, and *H. Schumacher*, Chem. Ber. *99*, 3391 (1966).

[32] a) *R. B. Woodward* and *R. Hoffmann*, J. Amer. chem. Soc. *87*, 395 (1965); *H. C. Longuet-Higgins* and *W. H. Abrahamson*, *ibid.* *87*, 2045 (1965); b) cf. also *W. Kutzelnigg*, Tetrahedron Letters *1967*, 4965.

[33] Cf. the results of the decomposition of stereoisomeric cyclopropyldiazonium ions: *W. Kirmse* and *H. Schütte*, J. Amer. chem. Soc. *89*, 1284 (1967); Chem. Ber. *101*, 1674 (1968).

[34] Designed by *W. Kutzelnigg*.

angle to the ring to demonstrate the fact that the configuration on this carbon atom at the beginning of the ionization is almost tetrahedral. The leaving group X is not shown; it should be imagined to be under (and partly bonded to) C-1. Better overlap of the orbitals is possible in the upper model [case (a), Scheme 8] than in the lower [case (b), Scheme 8].

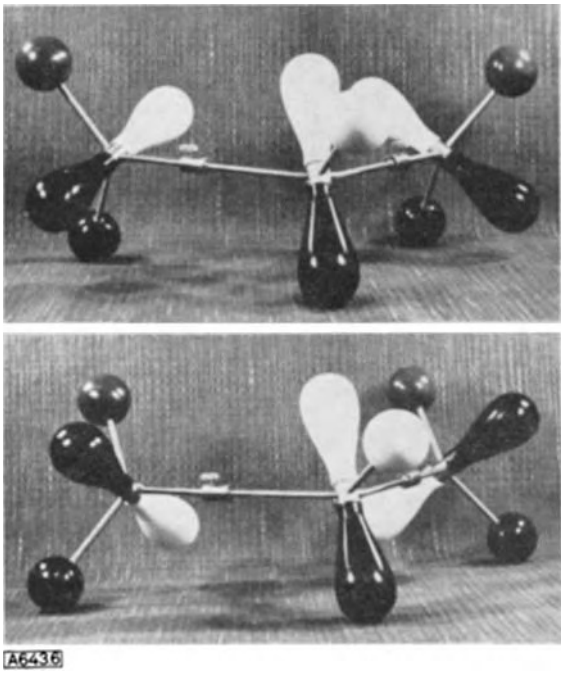


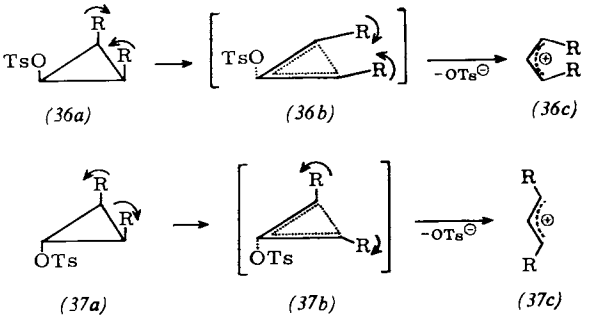
Fig. 6. Molecular models to illustrate the overlap of the orbitals (cf. text). The upper model corresponds to case (a) and the lower model to case (b) in Scheme 8.

To test this hypothesis, we converted the cyclopropanols obtained in the course of our synthetic investigations (cf. Section 2.4) into their *p*-toluenesulfonates [31] and studied the acetolysis of the latter [35, 36]. This reaction seemed well suited for such a study, since individual observations had already shown that this reaction proceeds by a concerted mechanism with formation of alkyl acetates.

Though the acetolysis of the unsubstituted cyclopropyl *p*-toluenesulfonate is slower than that of cyclohexyl *p*-toluenesulfonate by a factor of about 10^5 [37], it is still a few orders of magnitude faster than it should be, according to the Schleyer-Foote relation [38, 39], if it proceeded *via* a cyclopropyl cation. According to *DePuy* [40], *cis*- and *trans*-2-phenylcyclopropyl *p*-toluenesulfonates are acetolyzed 16 and 280 times as fast, respectively, as the unsubstituted compound at 100 °C. This is also incompatible with the intermediate formation of a cyclopropyl cation. In this case the phenyl group should retard the reaction because of its –I effect. *DePuy* [33] also suggested that the difference in the ease of solvolysis of the two epimers might be related to the direction of rotation of the phenyl group. As was mentioned earlier, this opinion led to theoretical investigations on the problem.

3.1. Acetolysis of Monocyclic 2,3-Dimethylcyclopropyl *p*-Toluenesulfonates [35]

If the Woodward-Hoffmann-DePuy rule is valid, the *endo p*-toluenesulfonates *(36a)* (R = CH_3) should be solvolyzed more slowly than the *exo* isomers *(37a)* (R = CH_3), since the "inward" disrotation should be associated with steric strain in the transition state *(36b)*, while "outward" disrotation, in which the transition state *(37b)* is less strained than the initial state, should lead to steric acceleration of the reaction (cf. Scheme 9). The direction of rotation should be recognizable from the configuration of the solvolysis products as well as from the (relative) rates of solvolysis, since *(36a)* should lead [*via (36c)*] to a *cis* product, and *(37a)* [*via (37c)*] to a *trans* product. However, this criterion must be used with caution in acetolysis, since subsequent isomerizations are possible.



Scheme 9. Ionization of 2,3-disubstituted cyclopropyl *p*-toluenesulfonates having *endo* and *exo* configurations (a): initial state, (b): transition state, (c): intermediate.

The acetolysis constants clearly show the dependence on structure and configuration expected from the Woodward-Hoffmann-DePuy rule [41] (cf. Table 5).

When two *cis*-methyl groups are introduced into cyclopropyl *p*-toluenesulfonate, their effect depends on whether they are *endo* or *exo* with respect to the leaving *p*-toluenesulfonate group. In the latter case their stabilizing effect on the transition state is clearly recognizable (factor 18000); if they are in the *endo* position, on the other hand, their electronic contribution is almost completely offset by steric hindrance (factor 4). Successive replacement of the hydrogen atoms in positions 2 and 3 of the *endo*-2,3-*cis*-dimethyl derivative by methyl groups leads to an increase in the rate of solvolysis (factors 20 and *ca.* 1400 respectively). This is understandable, since the added methyl groups stabilize the transition state electronically without increasing the steric hindrance. The considerable Pitzer strain in tetramethylcyclopropyl *p*-toluene-

[35] *P. v. R. Schleyer, G. W. van Dine, U. Schöllkopf,* and *J. Paust* J. Amer. chem. Soc. *88*, 2668 (1966).

[36] *U. Schöllkopf, K. Fellenberger, M. Patsch, P. v. R. Schleyer, G. W. van Dine,* and *T. Su,* Tetrahedron Letters *1967*, 3639.

[37] *J. D. Roberts* and *V. C. Chambers,* J. Amer. chem. Soc. *73*, 5034 (1951).

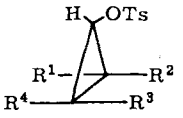
[38] *P. v. R. Schleyer* and *R. D. Nicholas,* J. Amer. chem. Soc. *83*, 182 (1961); *P. v. R. Schleyer, ibid. 86*, 1856 (1964).

[39] *C. S. Foote,* J. Amer. chem. Soc. *86*, 1853 (1967).

[40] *C. H. DePuy, L. G. Schnack,* and *J. W. Hauser,* J. Amer. chem. Soc. *88*, 3343 (1966), earlier literature cited there.

[41] A rough estimate of the k_{rel} values can be made with the aid of a formula that takes into account the expected electronic and steric contributions of the methyl groups to the energies of the ground state and the transition state. Satisfactory agreement is found between the calculated and the experimental values. Cf. [35].

Table 5. Relative acetolysis constants of methylated cyclopropyl *p*-toluenesulfonates.



R^1	R^2	R^3	R^4	k_{rel} (150 °C)
H	H	H	H	1 [a]
CH_3	H	H	CH_3	18000
H	CH_3	CH_3	H	4
CH_3	CH_3	CH_3	H	80
CH_3	CH_3	CH_3	CH_3	5500
CH_3	H	CH_3	H	260
CH_3	CH_3	H	H	330

[a] $k = 7.76 \times 10^{-6}$ sec^{-1} [37]

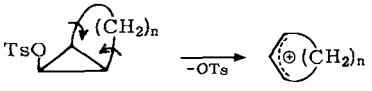
sulfonate probably accounts for the somewhat greater accelerating effect of the introduction of the fourth methyl group compared with that of the third. It is not surprising that 2,2-dimethylcyclopropyl and *trans*-2,3-dimethylcyclopropyl *p*-toluenesulfonates are solvolyzed at comparable rates, since the changes in strain associated with ring opening are roughly the same in both cases (one methyl group rotates inward and the other outward in each case), and the degree of stabilization of a transition state leading to an allyl cation by two methyl groups depends only to a limited extent on whether both groups are in the α- or γ-position, or whether one is in the α-position and the other is in the γ-position.

3.2. Acetolysis of *endo*- and *exo*-Bicyclo[*n*.1.0]alkyl *p*-Toluenesulfonates [36]

3.2.1. *endo* Series

Table 6 shows the acetolysis constants of the *endo*-bicyclo[*n*.1.0]alkyl *p*-toluenesulfonates *(38)* together with the products isolated.

Table 6. Relative acetolysis constants and acetolysis products of *endo*-bicyclo[*n*.1.0]alkyl *p*-toluenesulfonates *(38)*.



(38) *(39)*

(38), *n* =	k_{rel} (100 °C) [a]	products isolated
3	25000	*cis*-2-Cyclohexen-1-yl acetate [b]
4	62	*cis*-2-Cyclohepten-1-yl acetate
5	3.1	*cis*-2-Cycloocten-1-yl acetate [c]
6	3.5	*cis*-2-Cyclononen-1-yl acetate

[a] In relation to cyclopropyl *p*-toluenesulfonate; $k = 3.89 \times 10^{-8}$ sec^{-1} [37].

[b] At 75 °C.

[c] As well as 1,3-cyclooctadiene, which is evidently in equilibrium with the acetate.

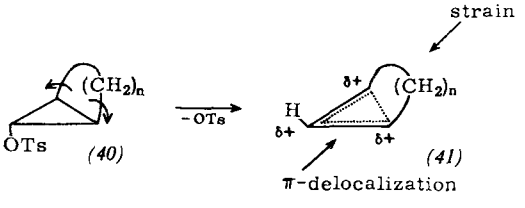
The values of k_{rel} are readily compatible with the reaction course *(38)* → *(39)*. They probably reflect the stability of the *cis*-cycloalkenyl cations. According to Dreiding models, the cyclohexenyl cation (n = 3 in *(39)*) is almost strain-free, while the cycloheptenyl and cyclooctenyl cations (n = 4 or 5, respectively, in *(39)*) exhibit both torsional and transannular strain. This explains the steep decrease in rate between the bicyclo[3.1.0] and the bicyclo[4.1.0] systems, although a reduction in Pitzer strain could also promote ionization in the former case. The cyclononenyl cation is found from the model to be more flexible than its seven- and eight-membered homologs. This could be the reason for the slightly higher reaction rate of bicyclo[6.1.0]nonyl *p*-toluenesulfonate. Further experiments should establish whether the ease of solvolysis generally increases again beyond n = 6.

The solvolysis products are also in agreement with the proposed course of the reaction (Table 6). Though thermodynamic control of the product is to be expected under the conditions used, *trans*-cycloalkenyl acetates can be ruled out as precursors since they do not always give the *cis* isomers with glacial acetic acid (cf. below).

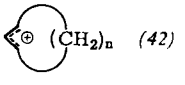
3.2.2. *exo* Series

The electronically favored "outward" disrotation for the ionization of the *exo*-bicyclo[*n*.1.0]alkyl *p*-toluenesulfonates [40] should be strongly hindered by strain factors, particularly when n is small. This presents the question of how the molecules behave on acetolysis. The results are shown in Table 7.

Table 7. Relative acetolysis rates and acetolysis products of *exo*-bicyclo[*n*.1.0]alkyl *p*-toluenesulfonates *(40)*.



(40) *(41)*



(42)

(40)	k_{rel} (100 °C) [a]	k_{rel} (150 °C) [b]	products isolated
n = 3	≪0.01 [c]		—
n = 4	1.7	0.9	*exo*-7-Norcaryl acetate, *cis*-cycloheptyl 1,3-diacetate (≈1:1)
n = 5	2500		*trans*- and *cis*-2-cycloocten-1-yl acetate, *cis*-cyclooctyl 1,3-diacetate [d]
n = 6	10000		*cis*-2-cyclononen-1-yl acetate [e]
1-Methyl-7-norcaryl *p*-toluenesulfonate		3.4	—
1,6-Dimethyl-7-norcaryl *p*-toluenesulfonate		10.4	—
1-Phenyl-7-norcaryl *p*-toluenesulfonate [f]		8.1	—

[a] In relation to cyclopropyl *p*-toluenesulfonate; $k = 3.89 \times 10^{-8}$ sec^{-1} [37].

[b] In relation to cyclopropyl *p*-toluenesulfonate; $k = 7.76 \times 10^{-6}$ sec^{-1} [37]

[c] Estimated value at 175 °C (darkening); no solvolysis at 150 °C.

[d] The first product is the precursor of the following two.

[e] As well as small quantities of an isomer, probably the *trans* compound.

[f] Prepared by *C. H. DePuy* [40].

The first sriking point is the extreme reluctance of the bicyclo[3.1.0]hexyl derivative to solvolysis. After being heated for three months at 150 °C in (acetate-buffered) acetic acid, more than 90 % of the compound could be recovered unchanged. This shows that the ionization of a cyclopropyl *p*-toluenesulfonate does in fact proceed by a concerted mechanism, as was assumed by *Schleyer*[38], *Foote*[39], and *DePuy*[40]. It also provides an impressive demonstration of the validity of the Woodward-Hoffmann-DePuy rule. The ionization is obviously strongly hindered if disrotation in the "correct" direction is prevented by strain. Solvolysis *via* a normal cyclopropyl cation or ionization with disrotation in the "wrong" direction (and this is particularly remarkable) evidently require a great deal of energy. It is probably permissible, therefore, to assume in the discussion of further results that the ionization begins with an "outward" disrotation. The increase in the ease of solvolysis with increasing *n* then shows that the resistance to ring opening decreases in this direction, *i.e.* that the stability of the intermediate cations increases. How should we picture these intermediates? Cations of the type *(42)* may be ruled out, since these give strain-free Dreiding models only beyond the 12- or 13-membered ring. We assume that the intermediates are somewhere between a cyclopropyl and an allyl cation, and can be formulated as "semi-open" [see *(41)*]. As illustrated in Figure 7, they lie in a potential minimum resulting from a balance between π-delocalization energy and strain energy.

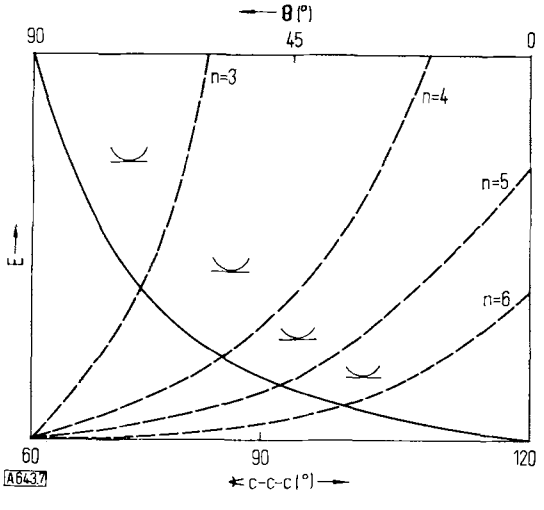
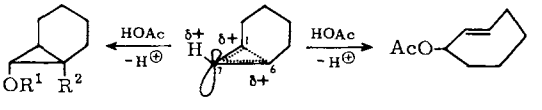


Fig. 7. Energy changes (schematic) during the outward disrotation of a bicyclo[*n*.1.0]alkyl cation of the type *(41)* (cf. text). ——: π-electron energy [42]; ----: strain energy; arcs: total energy; horizontal lines: energy levels of *(41)*; Θ: torsion angle formed by the plane through the geminal ligands and the cyclopropyl carbon atom and the cyclopropyl plane.

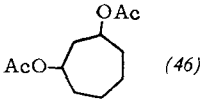
Owing to the gain in resonance energy associated with the disrotation[42], the *p*-toluenesulfonyl residue is released and a "nascent" cation is formed. The latter tends to twist further to form the stable allyl cation, thus leading to increased strain in the methylene bridge. The gain in resonance energy is initially greater than the increase in strain energy, so that the total energy decreases at first. At a certain point on the reaction coordinate, however, the situation is reversed, and further twisting then leads to an increase in the total energy of the ion. The shape, charge distribution, and energy content of the intermediate at the energy minimum are determined by *n*. The greater the value of *n*, the more strongly the intermediate resembles the stable allyl cation. Since a similar gradation must also be assumed for the energy levels of the transition states, we now have an explanation for the values of k_{rel}.

Corresponding to their midway position, intermediates of the type *(41)* should have three electrophilic centers, their cyclopropyl character increasing with decreasing *n* and their allyl character with increasing *n*. The solvolysis products of 7-norcaryl *p*-toluenesulfonate are interesting in this respect. The formation of both products [*exo*-7-norcaryl acetate *(43)* and *cis*-cycloheptyl 1,3-diacetate *(46)*] can be readily explained on the basis of the cation *(44)*, which adds acetic acid both at C-7 and at C-1 (C-6). The primary product in the latter case is *trans*-2-cyclohepten-1-yl acetate *(45)*, which is extremely highly strained[43] and adds acetic acid to form *(46)*.



(43), R^1 = Ac, R^2 = H
(47), R^1 = Ts, R^2 = D

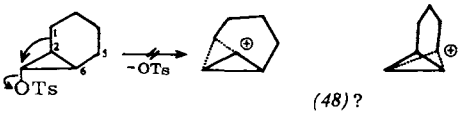
(44) *(45)*



(46)

The high stereoselectivity of the formation of *(43)* is remarkable. The *endo* isomer, which is stable under acetolysis conditions, cannot be detected either by gas chromatography or by NMR spectroscopy. This can hardly be explained by steric approach control in the attack of the nucleophile on C-7 of *(44)*, particularly since *(44)* should already be very flat. On the basis of a suggestion by *Kutzelnigg*[44], we assume that the orbital on C-7 (which has a pyramidal configuration) is not a pure p orbital, as was assumed in Figure 6, but possesses a certain s component, and is therefore more accessible on the *exo* side.

We originally thought that *(43)* was formed *via* the bridged ion *(48)*, which would result from neighboring-group participation of a bond between C-1 and C-2 (C-5 and C-6) during the ionization. However, *(48)*, in which the three cyclopropyl carbon atoms should be equivalent, can be ruled out since an acetolysis experiment with *(47)* showed that the labeled carbon atom retains its position.



(48)?

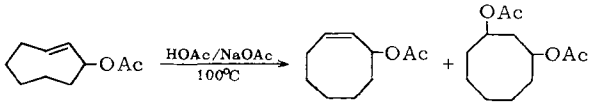
[42] According to detailed HMO calculations, a particularly large gain in delocalization energy occurs in the early stage of the change. Cf. *W. Kutzelnigg* [32b].

[43] *trans*-Cycloheptene and *trans*-cycloheptenone have recently been detected. Both exhibit a particularly strong tendency to undergo additions to the double bond. Cf. *E. J. Corey, F. A. Carey*, and *R. A. Winter*, J. Amer. chem. Soc. *87*, 935 (1965); *E. J. Corey, M. Tada, A. LeMahieu*, and *L. Libit, ibid. 87*, 2051 (1965); *P. E. Eaton* and *H. Lon, ibid. 87*, 2052 (1965).

[44] *W. Kutzelnigg*, personal communication. Cf. also [32b].

When $n > 4$, the allyl character evidently predominates in the intermediates. In any case, only monocyclic solvolysis products are then formed (cf. Table 7). The primary products are probably *trans*-2-cycloalken-1-yl acetates, but under acetolysis conditions these undergo *trans* → *cis* isomerization or [like *(45)*] add acetic acid at the double bond.

Whitham[45] has in fact shown that *trans*-3-cycloocten-1-yl acetate *(49)* is converted into the *cis*-isomer *(50)* and into



(49) *(50)*, ≈ 66% *(51)*, ≈ 33%

cis-cyclooctyl 1,3-diacetate *(51)* on heating in acetic acid/sodium acetate, *i.e.* under the conditions of *p*-toluenesulfonate solvolysis.

Why *(45)* and *(49)* should react with acetic anhydride to form *cis*-1,3-diacetates is an interesting problem that still awaits theoretical interpretation. On the other hand, the *cis-trans* isomerization *(49)* → *(50)* is readily interpreted as a concerted allylic shift, as has been demonstrated by *Goering*[46] in a number of other cases.

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[45] We are grateful to Prof. *Whitham* for this control experiment. Regarding the formation of *trans*-3-cycloocten-1-ol on hydrolysis of *exo*-bicyclo[5.1.0]octyl bromide, see *G. H. Whitham* and *M. Wright*, Chem. Commun. *1967*, 294.

[46] *H. L. Goering* and *W. J. Kimoto*, J. Amer. chem. Soc. *87*, 1748 (1965); *H. L. Goering* and *J. D. Doi*, *ibid. 82*, 5850 (1960); *H. L. Goering* and *E. F. Silversmith*, *ibid. 77*, 1129 (1955).

Recent Developments in the Adhesives Field

BY A. MATTING AND W. BROCKMANN[*]

The applications of adhesives have been greatly extended by the use of synthetic organic high polymers. It is possible nowadays to bond, not only wood, leather, and paper, but also glass, high-strength plastics, and metals with adhesives of this type. They give satisfactory adhesion, flexibility, and mechanical properties even at high temperatures. A particularly important advance was the introduction of chemically or mechanically blocked polymer systems, which can reduce the cost of curing equipment when used as adhesives.

1. Introduction

The use of adhesives has been known for thousands of years. In this process, a pasty or liquid substance that first wets the surfaces and then solidifies is applied between the parts to be joined. After solidifying, this substance transfers forces from one part to the other.

High molecular weight organic substances in colloidal form, which were obtained from plants, skins, muscle tissue, or bones, were used long ago as adhesives. These substances include collagen (molecular weight 20000 to 200000), which is still commonly used in aqueous solution as a glue for the bonding of wood, paper, and textiles. After the water has penetrated into the porous surfaces, the adhesive hardens.

The casein glues represent another group of natural adhesives. Casein (molecular weight about 300000) resembles the collagen glues in its technological behavior, but has the advantage that it can be made water-resistant[1,2]. Casein glues are still widely used, and give good results in the bonding of wood, though the strength and weather resistance of these glues cannot always satisfy rigorous requirements.

The use of casein adhesives for the bonding of wood is illustrated by the Schütte-Lanz rigid airship. The entire hull structure of these craft, which were built before and during the first world war, consisted of glued plywood girders. Despite the use of protective paints, however, these bonds could not withstand the effects of weather, particularly over the North Sea.

Natural adhesives made from blood and based on albumin and hemoglobin were used in pre-Roman times. Adhesives of this type can be modified with formaldehyde, ketones, phenols, and alcohols, and are still used in some countries for the manufacture

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[1] *E. Plath*: Taschenbuch der Kitte und Klebstoffe. 4th Edit., Wissenschaftl. Verlagsges., Stuttgart 1963.

[2] *R. S. R. Parker* and *P. Taylor*: Adhesion and Adhesives. Pergamon Press, London 1966.

of plywood. Starch and cellulose adhesives as well as rubber-based products, which can be modified in many ways, are cheap and widely used.

However, a demand has recently arisen for adhesives having such high cohesive strengths, adhesion values, and resistance to environmental factors that products of plant or animal origin are often no longer satisfactory.

Synthetic high polymers were first used successfully as adhesives some thirty years ago, initially in the wood industry. The technology of synthetic adhesives began with the bonding of wood by means of phenol-formaldehyde polycondensates. It soon became possible to form very strong bonds even to metals with organic bonding agents; the resulting bonds can transfer forces at temperatures as high as 450 °C.

2. Requirements for Adhesives

2.1. Wetting and Setting

Before setting, adhesives must be in a liquid or low-viscosity state to allow complete wetting of the adherends, the surfaces of which should adsorb as many molecules of adhesive as possible. Consequently, adhesives that are already in their final chemical state must be made into colloidal suspensions or solutions. If the surfaces are porous, they may absorb the solvent. With non-porous surfaces, however, the solvent must be able to evaporate before the parts are joined; contact pressure must also be applied. The strength of the bond depends on the molecular forces acting within the adhesive layers as the adherends are pressed together.

This is also true of fusible substances, such as tars or synthetic thermoplastic materials, which soften when heated and solidify again on cooling. Joints made with adhesives of this type have limited thermal stability.

A third possibility is to use substances that are applied and adsorbed in the low molecular weight state, and then converted on hardening into a high molecular weight product. The importance of adhesives of this type is that the chemical bonds formed during hardening give maximum strengths without excessive heating of the adhesive. These reactions generally proceed without critical volume changes, and any internal stresses produced are small. It is also possible by chemical crosslinking to convert the thermoplastic adhesive, which is originally in the form of prepolymerized filament molecules, into a three-dimensionally crosslinked network, and so to obtain a bond having good thermal and deformation behavior.

These adhesives are hardened after the parts to which they have been applied are brought together.

2.1.1. Initiation of Crosslinking

Some adhesives having prepolymerized molecules can be crosslinked by heating without the addition of catalysts; adhesives of this type need not consist of two or more miscible components. Typical examples are phenolic resins and their modifications. Pressure must be applied during hardening, in order to drive the water vapor formed during polycondensation out of the adhesive. These adhesives are used as solids (often in the form of films), as pastes containing solvents, or as aqueous dispersions. Expensive heating equipment and presses or autoclaves are usually required for curing, though the curing time is relatively short (about 30 to 90 min).

Other adhesives require the addition of a curing agent and possibly other components before application. These adhesives crosslink slowly at room temperature, and much more rapidly when heated. In the case of polyesters, for example, the curing agent consists of catalysts (mainly peroxides), whereas the crosslinking of epoxide resins involves the reaction of two substances, *e.g.* of the epoxide resin with primary or secondary amines, and proceeds with cleavage of the epoxide ring The curing time (during which the parts must be clamped together because the uncrosslinked adhesive cannot transfer forces) is about 6 to 24 hours. The time required can be shortened by heating, but more expensive equipment is then necessary.

Crosslinking can also be initiated by removal of a chemical or mechanical blockage in polymerizable mixtures (see Section 4).

2.2. Adhesion

In addition to ease of setting and a high cohesive strength, adhesive films must adhere firmly to the adherends. If the adherends are porous, as in the case of wood or paper, or if at least the surfaces can be swollen or dissolved by components of the adhesive, so that the latter can penetrate into the material, the adhesion is "mechanical", and depends only to a limited degree on the chemical structure of the materials. The adhesion may then be regarded as mechanical clamping.

If, on the other hand, the adherends are smooth and nonporous, so that there is no possibility of mechanical clamping, the adhesion is described as "specific". Even where the adherends are different, as in the case of plastics and metals, the strength of the joint after suitable surface treatment is often greater than the cohesive strength of the plastic. The adhesion is mainly due to the fact that intermolecular van der Waals forces, dipole-dipole (Keesom forces), and induced dipole interactions (Debye forces) contribute more to the bond energy than dispersion forces (London forces). To provide good adhesion in the bonding of polar or polarizable materials, therefore, the adhesive molecules must contain polar groups [3]. It is also possible to copolymerize monomers containing polar and reactive groups together with the main substance in order to obtain improved adhesion. Adhesives that contain no polar groups are suitable only for the bonding of non-polar and non-polarizable materials.

[3] *N. A. de Bruyne*, J. appl. Chem. *6*, 303 (1956).

The reactions that lead to adhesion at interfaces between similar and between dissimilar materials have not yet been satisfactorily explained. The ability of wetting adhesives to be adsorbed on the surfaces to be joined and to form primary bonds can be predicted from their chemical structure. However, our knowledge of the processes at the surfaces, *e.g.* of wood or metals, that determine the adhesive strength is still inadequate.

Nevertheless, it has been shown in isolated cases that even dissimilar materials can form chemical bonds, which are very much stronger than van der Waals forces. Thus the adsorption of aliphatic carboxylic acids on aluminum materials, the surfaces of which are nearly always covered with oxides and oxide hydrates, is followed by chemisorption [4]. When such surfaces are bonded by phenolic resin adhesives, aluminum phenoxides can be detected along the interfaces [5]. Moreover, the adhesive forces to plastics that are difficult to bond, such as polypropylene, have been greatly improved by grafting with reactive groups, *e.g.* dihydroxyboranyl or epoxy groups [6]. The properties necessary in an adhesive for the firm bonding of given substances after a specific pretreatment (*i.e.* after the surface of the solid has been "keyed") are known only empirically, and this knowledge is still inadequate.

2.3. Deformation Properties

Adhesive joints are composite articles in the technological sense; they often consist of parts that differ considerably in their nature. The behavior of a joint under load is not simply a function of the strength and adhesion of the components. In particular, it must not be regarded as homogeneous if the components have different deformation properties. Owing to the heterogeneous structure of the joint, the supportable load cannot simply be calculated as the mean stress from the total load and the loaded cross section, though the supportable load and the mean stress may be assumed to be equal under comparable conditions for a homogeneous article. Because of the difference in the deformation of the two components of a joint under the same load, the stress is non-uniform and exhibits pronounced peaks. The supportable load of the joint thus depends on the local stress, and fracture can occur even when the mean stress is relatively low.

The stress distribution in an adhesive joint can be influenced by the design of the joint, *e.g.* by its shape. On the other hand, the properties of the adhesive may be such that large differences in stress can be compensated for by plastic deformation. This can be achieved in two ways. Firstly, the thermosetting base resin may be combined with thermoplastic resins, as in the combination of phenolic resins with polyvinyl compounds such as polyvinyl alcohols, polyvinyl chlorides, polyvinyl acetate, or polyvinyl formal. These thermoplastics exhibit steric effects that prevent tight crosslinking of the condensate, and partly react with the hydroxymethyl groups of the phenol-formaldehyde resol. They also reduce the viscosity of the mixture before curing, and so improve its wetting properties. In some cases, the thermoplastic component also sets, but prevents the complete formation of a three-dimensional network, which would be brittle because of its "molecular bracing" [7]. Similar types of modification have proved suitable for other types of resin, as is illustrated by the modification of epoxide resins with polyamides. Moreover, the resins preferred for use as adhesives are those that have a low tendency toward "crystallization", *i.e.* toward micelle formation, during crosslinking, owing to the presence of bulky side chains or lack of symmetry. These types include polyvinyl esters, polymethacrylic acid, and epoxide and phenolic resins.

Secondly, the ease of deformation of a plastic can be influenced by the use of plasticizers. These are monomers that do not take part in crosslinking, prevent complete three-dimensional crosslinking, and facilitate movement between the macromolecules in the solid state by acting as "lubricants". They must form stable mixtures with the base resin and contain long hydrocarbon chains to provide the "lubricating action", while at the same time reducing the volatility and diffusibility, and in plastics with dipoles, the plasticizers must also contain dipoles. An example of a useful plasticizer is butyl adipate *(1)* [8].

$$CH_3-(CH_2)_3-OOC-(CH_2)_4-COO-(CH_2)_3-CH_3 \qquad (1)$$

Flexible plastics are basically weaker, and tend to creep under a permanent load. It must therefore be decided in each individual case whether flexibility is more important than strength.

The flexibility of adhesives, which also depends on the temperature, can be determined by the torsional vibration test, from which it is possible to calculate the damping of the adhesive as a function of temperature as well as its shear modulus. The shear modulus at a given temperature is characteristic of the state of the adhesive. It is possible in this way to find the width of the freezing-in and softening ranges, in which the maximum damping occurs, as well as that of the rubbery-elastic range. A comparison of the temperature-dependent rigidity modulus with the strength of adhesive joints shows that the strength decreases considerably in the rubbery-elastic state [9] To obtain adhesives having a high heat resistance, the occurrence of this state must be postponed to higher temperatures by modification of the structure.

The existing experimental results do not, however, provide a sound basis for definite conclusions. Secondary damping maxima that occur at high temperatures and disappear after prolonged heating suggest that the thermosetting and thermoplastic components of an adhesive retain their independence

[4] *G. Sandstede, E. Robens,* and *G. Walter* in: Internationaler Kongress für grenzflächenaktive Stoffe. Universitätsdruckerei Mainz 1961, Vol. III.

[5] *L. Dimter,* Dissertation, Universität Leipzig, 1963.

[6] *A. F. Lewis* and *L. J. Forrestal* in: Adhesion, ASTM Special Technical Publication. American Society for Testing and Materials, Philadelphia 1964, p. 59.

[7] *L. Dimter* and *K.Thinius,* Plaste u.Kautschuk *11,* 328 (1964).

[8] *F. Nerdel:* Organische Chemie. 2nd Edit., de Gruyter, Berlin 1964.

[9] *W. Althof,* Kunststoffe *56,* 750 (1966).

when combined, so that the torsional vibration test can also provide information about the degree of crosslinking.

As a result of the development of synthetic adhesives, high-strength materials such as thermosetting polymers, glass fiber reinforced plastics, and metals can now be bonded with adhesives as well as the materials such as wood, paper, and textiles that have been bonded in this way since ancient times. Substances of the first group are far superior to most adhesives in their strength and, as far as the metals are concerned, in their heat resistance.

In order to take advantage of the high strength of these materials with the weaker adhesives, the joints should be designed in such a way that when the cross sections of the adherends are very small, relatively high stresses are transferred by large joint areas. The joint area for adherends having a given cross section may be of any size if it is parallel to the load. The adhesive is then subject to a shear stress (Fig. 1). The strengths of adhesive joints are therefore usually given

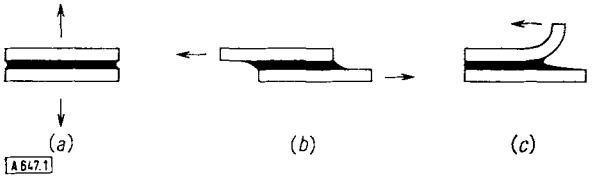


Fig. 1. Loading of adhesive joints: (a) tensile ,(b) shear, (c) peel.

as shear strengths, while tensile strengths (Fig. 1a) are important only when the adherends have a low internal strength, since the joint areas in this case cannot be greater than the cross sections of the adherends.

Another type of loading, which places great demands on the plasticity and tensile strength of the adhesive, is peeling (Fig. 1c). Adhesives are generally very sensitive to peeling forces (to which structural components are frequently subjected), since the stress acts along a line, and is therefore very highly concentrated. The peel strength of an adhesive is consequently of great importance [10].

The strength and heat resistance of synthetic adhesives depend on their chemical composition. Adhesives that set in a few minutes at room temperature are important. These adhesives play a valuable part *e.g.* in mass production processes.

3. Types of Adhesives

Practically any high polymer may be used as a base resin for adhesives. The substances listed in Table 1 are particularly suitable because of their adhesive properties coupled with relatively high cohesive strength, adequate heat resistance, and considerable resistance to aggressive media, as well as their ease of use.

The problem of increasing the strength and heat resistance of macromolecules can only be solved if as

[10] *U. Draugelates* and *W. Brockmann*, Adhäsion *10*, 11 (1966).

Table 1. Base resins suitable for industrial use in adhesives [11].

Epoxide resins	Cellulose esters
Unsaturated polyester resins	Cellulose ethers
Phenolic resins (PF)	Polyvinyl alcohol (PVA)
Resorcinol resins	Polyvinyl acetals
Urea resins (UF)	Polyvinyl ethers
Melamine resins (MF)	Polystyrene (PS)
Organopolysiloxanes	Polyisobutylene
Polyurethanes	Polybutadiene
Polyvinyl acetate (PVAc)	Butadiene-acrylonitrile copolymers
Polyvinyl chloride (PVC)	Polychloroprene
	Polysulfide
Vinyl chloride-vinyl acetate copolymers (PVCAc)	Polyaromatic resins
Polyacrylates	
Polymethacrylates	

many chemical bonds and hydrogen bonds as possible are allowed to form, since, owing to their high bond energy, these bonds are better able to withstand high mechanical and thermal stresses than are intermolecular van der Waals forces.

The maximum strength that can theoretically be attained by a high polymer bound exclusively by chemical bonds is easy to calculate. If polyethylene chains are packed together as densely as possible and parallel to one another, approximately 5×10^{14} chains can be fitted into each square centimeter. When a bundle of chains packed in this way is broken by a longitudinal stress, each C–C bond passing through the cross section contributes about 5×10^{-4} dyne to the tensile strength, giving a total of 25×10^{10} dyne/cm^2. In practical terms, this corresponds to a tensile strength of 2500 kg/mm^2, which is far greater than that actually found for crystalline polyethylene. This difference is due to defects, which lead to stress peaks and premature failure.

If the chemical bonds are replaced by hydrogen bonds, which have a strength of about 10^{-5} dyne, the stress required to cause breakage in the model is 50 kg/mm^2. This corresponds approximately to the values found for highly oriented fibers. Thus in these fibers, the hydrogen bonds are broken before the stresses destroy the stronger covalent bonds [12].

These considerations are important if a high polymer is to be stable above 300 °C and to exhibit a useful strength, since the van der Waals forces no longer contribute to cohesion in this temperature range, their bond energy then being less than the kinetic energy of the chain segments [12].

Owing to the need for heat resistance, the molecular chains must be made so rigid between the nodes of the three-dimensional network that very little rotational energy can accumulate in them. This rigidity can be achieved *e.g.* by the incorporation of cyclic structures [12].

3.1. Phenolic Resins

The phenolic resins were among the earliest of the modern high-strength adhesives. Owing to the large number of possible modifications, they are suitable for the bonding of nearly all materials. They are formed by the reaction of phenol with formaldehyde to give hydroxymethylphenol, which condenses with elimination of water. Phenols can be linked by CH_2 or CH_2-O-CH_2 groups. The products are resols, self-

[11] *L. Dimter*: Klebstoffe für Plaste. VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1966.

[12] *H. E. Mark* in: Haftsysteme und Haftfestigkeit. Dechema Monograph No. 51. Verlag Chemie, Weinheim 1966.

curing resins, or novolacs, which can be cured by substances that remove formaldehyde [11].

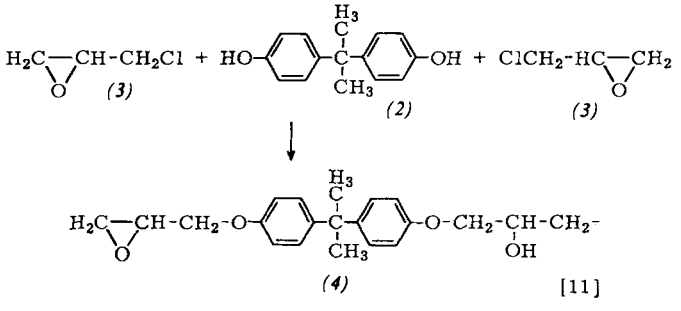
A more important group within this class of adhesives is formed by the polyvinyl formal-, polyvinyl acetal-, and polyvinyl butyral-modified types. Polyvinyl formal-modified phenolic resins were the first metal adhesives to be used in aircraft construction. They are characterized by high strength and aging resistance. Their tensile strength is between 8 and 10 kg/mm² and their shear strength about 3.5 kg/mm². Above 80 °C, however, the strength decreases very rapidly.

About 70 % of the joints in the fuselage and wings of the Fokker F 27 "Friendship", a light-metal aircraft, are bonded in this way. Some 400 of these machines have been in use over a period of more than eight years in countries with widely different climates. Despite this long service, the adhesive joints have retained their strength in full [13].

Phenolic resins can also be modified with elastomers such as rubber to give good deformation properties and strength at low temperatures. Similar results are obtained by modification with polyamides, which increase the impact strength and improve adhesion to many materials. The hot strength of phenolic resins, however, was improved only when they were combined with a second group of resins, *i.e.* epoxide resins.

3.2. Epoxide Resins

Epoxide resins *(4)* are formed by the condensation of polyfunctional phenols, such as bisphenol A *(2)*, with epichlorohydrin *(3)*.

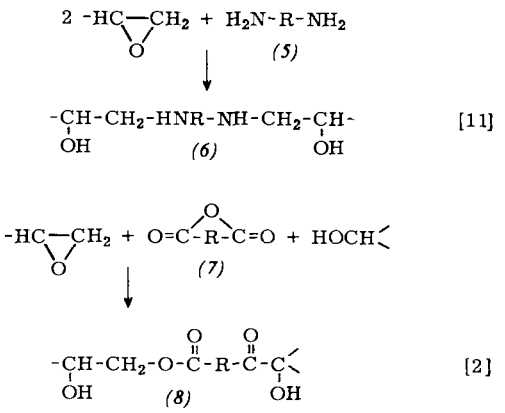


[11]

The most important characteristic of these resins, which is responsible for many of their properties, is the presence of terminal, extremely reactive epoxy groups.

The epoxide resins are cured by addition of polyamines *(5)* or acid anhydrides *(7)*, which add to the epoxy groups to form *(6)* and *(8)*.

Their low shrinkage on curing is an important advantage in adhesive and casting applications. Since their OH groups also react, the molecules not only become larger on curing, but are also crosslinked to form three-dimensional networks. Amine-based curing agents react even at room temperature, and epoxide resins can therefore be used in two-component cold-setting adhesives. Curing agents based on acid anhydrides can be added to epoxide resins by the manufacturer, since the curing reaction begins only above 100 °C. The resulting products are one-component thermosetting adhesives, which can be supplied in the form of solids, powders, or pastes [14].



[11]

[2]

The strong adhesion of epoxide resins to nearly all materials was utilized in adhesive technology as long ago as 1948 [15]. This adhesion is due, not only to the polarity of the resins, but also to the presence of "unused" epoxy groups, which form chemical, and therefore extremely strong, bonds with the molecules on the surfaces of the adherends, *e.g.* metal oxides and hydroxides, or even polyamides.

The versatility of the epoxide resin adhesives, which can be modified in many ways, is too well known to need further elaboration here. They are generally inferior to phenolic resins in their strength and aging resistance, particularly in unfavorable climates, and their strength decreases rapidly above 80 to 100 °C. On the other hand, in addition to good adhesion, they are distinguished by ease of handling.

It has recently been found that the hot strength and stability of the epoxide resins can be appreciably improved, firstly by increasing the epoxide content to allow higher crosslink densities, *i.e.* more chemical bonds per unit volume, and secondly by the synthesis of resins containing aromatic glycidylamines or glycidyl tetraphenylglyoxal resins as stable chain segments. Systems have also been tried in which alicyclic epoxide resins are formed by reaction of peroxy acids with unsaturated cyclic compounds [14]. In these cases the epoxy groups are directly attached to the ring. Heat-resistant epoxide resins, when used to bond metals, still have shear strengths of 0.9 kg/mm², *i.e.* 70 % of the strength at room temperature, at temperatures of up to 250 °C.

The second way in which the good adhesive properties of the epoxide resins can be utilized for heat-resistant adhesives is by combination with other polymers, such as phenolic resins.

3.3. Epoxide-Phenolic Resin Combinations

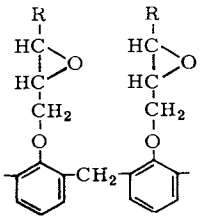
Epoxide-phenolic resin combinations provided an early solution to the problem of producing joints having satisfactory shear strengths between −200 and

[13] *R. J. Schiekelmann* in: Fachtagung Schweissen und Kleben im Luft- und Raumfahrzeugbau. Technische Presse der Deutschen Messe- u. Ausstellungs-AG. Hannover 1966, p. 25.

[14] *B. J. Hayes*, Adhäsion *11*, 97 (1967).

[15] *E. Preiswerk*, Technica *1965*, 247.

+300 °C. The principal component of these resins [*e.g. (9)*] is phenolic resin.



(9) [11]

The curing in these resins, which have a low epoxide content, is assumed to be due only to reaction of the phenol component, the epoxy groups playing no part in the crosslinking [16].

Another group of epoxide-phenolic resin adhesives, which have a much higher content of epoxide groups, are crosslinked by the addition of a curing agent for epoxides. Their strength and heat resistance are better than those of the first group. However, they are difficult to handle, and their shelf life at room temperature is short; prolonged storage is possible only at −10 to −20 °C. The peel strength of adhesives of this type is often unsatisfactory.

3.4. Nylon-Modified Epoxide Adhesives

Nylon-modified epoxide adhesives have proved advantageous where high strength and toughness, and particularly high peel strength between −250 and +60 °C are required. Owing to their cohesive strength, coupled with good flexibility, they possess excellent properties at low temperatures and in dynamic stress situations. They are therefore used for the production of highly stressed joints, particularly in aircraft construction.

The types of nylon that are suitable for use in these adhesives can absorb up to 20 % of water in a moist atmosphere. They must therefore be stored and used only in air-conditioned rooms. They are sensitive to moisture even when set. Until the development of nylons that dissolve in epoxide resins and also do not absorb much moisture, it will be necessary to paint over nylon-modified epoxide adhesive films to protect them against the penetration of water vapor [14].

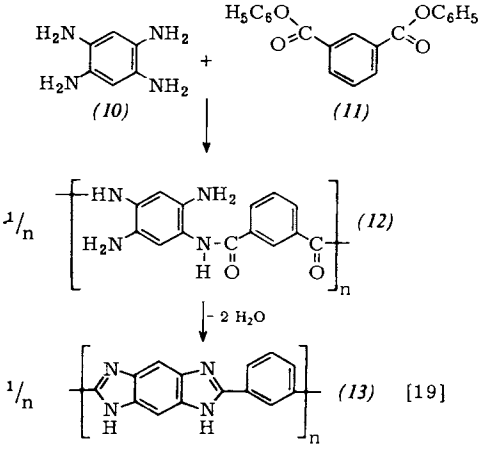
The thermal stability of adhesives based on common organic polymers can also be increased by the addition of amphoteric inorganic oxides such as As_2O_5 [17]. It does not, however, appear possible to use these adhesives above 300 °C. Moreover, the high hot strength is gained in most cases at the expense of flexibility, and hence of the technological characteristics at low temperatures.

Adhesives based on new polymers first prepared only in the past few years offer greater promise. The use of these substances as adhesives will depend on their existence in the form of prepolymers that finally set only in the adhesive joint.

[16] *K. W. Humphreys* in *D. J. Alner*: Aspects of Adhesion. University of London Press, London 1965, p. 66.

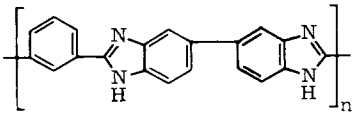
[17] *H. H. Levine*, Brit. Plastics *34*, 395 (1961).

Because high hot strength in adhesives can be obtained, not only by introducing as many chemical bonds or hydrogen bonds as possible into the crosslinked substance, but also by introducing thermally stable chain segments between the nodes of the network, interest was turned to base resins consisting of fully aromatic and in some cases linear, polymers. The chains of these polymers are so rigid and absorb so little rotational energy that the crosslinking points need not be situated close together, with the result that the flexibility is greatly improved. Adhesives based on polybenzimidazoles have already been extensively tested [18]. Aromatic polybenzimidazoles *(13)* are formed by melt condensation of aromatic tetramines *(10)* with diphenyl esters *(11)* of aromatic dicarboxylic acids [19].



(10) *(11)* *(12)* *(13)* [19]

The reaction leads initially, at 220 to 260 °C, to a polyamino amide *(12)*, from which the polybenzimidazole *(13)* is formed on setting above 300 °C. Another polybenzimidazole, which has the formula *(14)*, can also be cast into films, since it is soluble in dimethyl sulfoxide and formic acid.



(14) [19]

Adhesives having the same shear strength (≈ 2.0 kg/mm²) at 260 °C as at room temperature are obtained from polybenzimidazoles stabilized with inorganic arsenic compounds. As the temperature is raised to 420 °C, the strength falls to a value of 1.5 kg/mm², which is still of practical use.

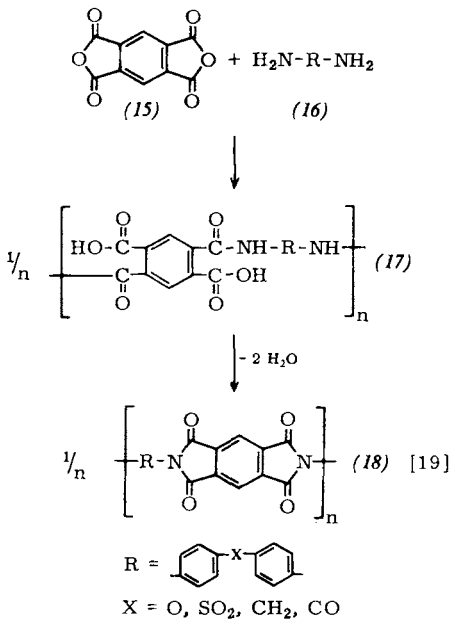
The polybenzimidazoles are sensitive to prolonged storage at 260 to 300 °C. At 310 °C, the shear strength decreases to 0.52 kg/mm² in only 100 hours. These adhesives are cured at about 320 °C. Since volatile components are eliminated, heated presses are required for curing [18].

[18] *R. B. Krieger* and *R. E. Politi*, American Cyanamid Co. Bloomingdale Dept., unpublished experiments (1965).

[19] *F. T. Wallenberger*, Angew. Chem. *76*, 484 (1964); Angew. Chem. internat. Edit. *3*, 460 (1964).

3.6. Polyimide Adhesives

The adhesive properties can be considerably improved by the use of polyimides *(18)* as the base resins instead of polybenzimidazoles. The polyimides can be prepared by the reaction of pyromellitic dianhydride *(15)* with aromatic diamines *(16)* in a ratio of 1:1 in dimethylformamide or diethylacetamide [19].



The intermediate pyromellitamidic acid *(17)* can be cast. On subsequent heating, intramolecular cyclodehydration leads to insoluble, infusible polyimide *(18)*.

The shear strength of adhesive joints between stainless steel adherends with polyimide adhesives is ≈ 2.0 kg/mm² at room temperature, ≈ 0.73 kg/mm² at 420 °C, and ≈ 0.42 kg/mm² at 530 °C; its value at −196 °C is greater than 2.8 kg/mm².

The aging resistance of polyimide adhesives can be seen from the following values: Storage of titanium adhesive joints at 310 °C for more than 4000 h led to a decrease in shear strength from the original value of ≈1.41 kg/mm² to 0.88 kg/mm², while storage at 260 °C for more than 2000 h resulted in no loss of shear strength [18]. The aging properties of polyimide adhesives, like those of the polybenzimidazoles, can be improved by the addition of arsenic compounds [19].

The mechanical properties of the polyaromatic adhesives at high temperatures are compared in Figures 2 and 3 with those of heat-resistant adhesives based on conventional resins. Figure 2 shows the variation of the shear strength with the testing temperature, while Figure 3 shows a plot of the shear strength against storage time at 260 °C [20].

The outstanding properties of these polyaromatic adhesives, particularly at high temperatures, make them suitable for use *e.g.* in the construction of aircraft for speeds of two to three times the speed of sound. During flight, the outer skins of

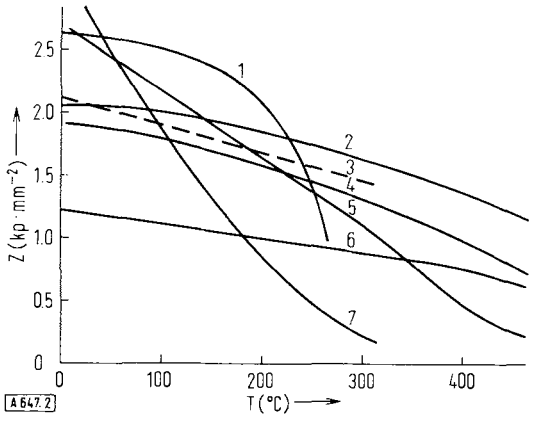


Fig. 2. Shear strength (Z) of joints between metal adherends with different adhesives as a function of temperature. 1: Modified epoxides; 2: polybenzimidazoles; 3: amides, imides; 4: polyimides; 5: epoxide-phenolic; 6: epoxide-silicone; 7: nitrile-phenolic.

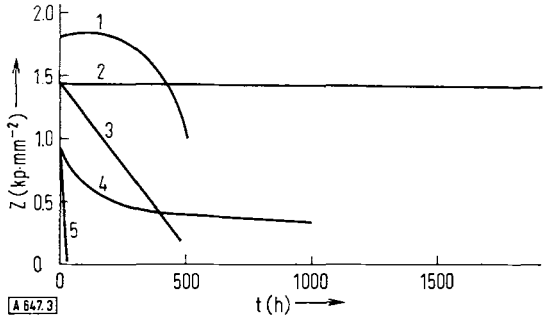
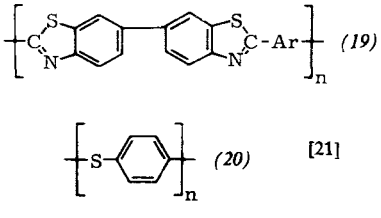


Fig. 3. Shear strength (Z) of joints between metal adherends at 260 °C as a function of storage time at 260 °C. 1: Polybenzimidazoles; 2: polyimides; 3: epoxide-phenolic; 4: epoxide-silicone; 5: modified epoxides.

such aircraft heat up to 200 to 260 °C because of friction with the air and the intense solar radiation at altitudes above about 25000 ft. Light alloys based on aluminum fail at these temperatures, and it is necessary to use materials based on titanium or high-strength steel, which are difficult to weld. The joints are therefore made with adhesives, which have the added advantage that they permit the production of structural elements having large smooth surfaces. New construction methods such as sandwich and laminated constructions are totally dependent on adhesive techniques.

3.7. Further Development of Polyaromatic Adhesives

The use of adhesives based on aromatic polymers has only started. Of the many aromatic polymers, mention should be made of two such substances, that are likely to become important as adhesives, not only for metals, but also for high-temperature plastics. The polybenzothiazoles *(19)* exhibit outstanding resistance to oxidative deterioration up to about 600 °C, while the phenylene sulfide polymers *(20)* should be thermally stable up to 900 °C.



[21]

[20] *E. Loechelt*, Lecture at the Conference on "Bonding of Metals" in the Haus der Technik, Essen, February 1967.

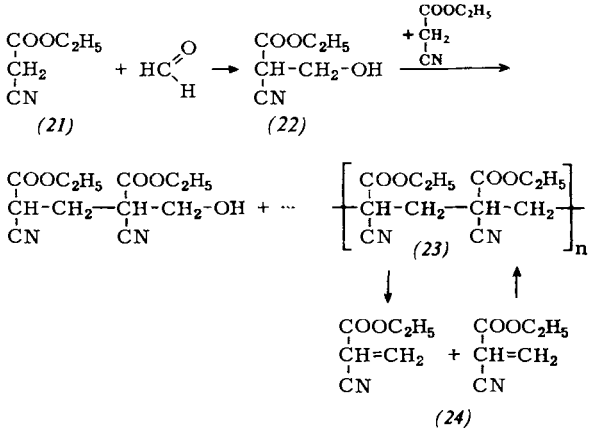
[21] *R. C. Kausen*, Mater. Design Engng. *60*, 108 (1964).

No details of the technological behavior of these materials as adhesives are yet available.

4. One-Component Adhesives as Blocked Polymer Systems

In the use of adhesives, the required operations to start the crosslinking process often present difficulties in practice (see also Section 2.1.1.). The difficulties relate to the mixing of two-component adhesives and the long setting times at room temperature. One-component systems that crosslink by condensation are expensive to use because of the cost of heated presses or autoclaves. There is therefore considerable interest in adhesives that need not be mixed and that set between the adherends, whenever possible without the application of heat or pressure. This requirement can be satisfied if chemically or mechanically blocked polymer systems are used as adhesives.

Typical examples of chemically blocked polymers are the cyanoacrylates *(23)*, which can be prepared from alkyl cyanoacetates *(21)* and formaldehyde *(22)* in the presence of basic catalysts.



The resulting polymers *(23)* are pyrolyzed to form cyanoacrylate monomers *(24)*, which repolymerize in the presence of weak bases, *e.g.* water (which is adsorbed on the surface of the adherends) or alcohols [2]. The polymerization is probably initiated by the strongly electron-attracting nitrile and ester groups situated very close to ethylenic double bonds. When these double bonds are polarized by weak bases, fast polymerization takes place, and the originally liquid adhesive sets within a few minutes.

To suppress spontaneous setting during storage, inhibitors are added to the cyanoacrylates. Mixtures of this type give bonds as strong *e.g.* as those obtained with epoxide resins. The disadvantage of these adhesives is that they cost about ten times as much as commercial epoxide resins. Since the monomers are very fluid and set only in the vicinity of the interfaces, cyanoacrylate adhesives are only suitable for joints with thin adhesive film thicknesses. Their thermal stability is also poor, since the polymerized substance is thermoplastic.

Other chemically blocked adhesives are diacrylates such as tetraethylene glycolyl dimethacrylate [22]. This adhesive sets with cumene hydroperoxide as the catalyst and benzenesulfimide as an accelerator to give a polymer. The monomer remains liquid in air. This is an advantage in the bonding of rings and wheels to shafts and in the fixing of ball bearings or screw joints.

A promising alternative to the chemical blockage of the reactants in cold-setting one-component adhesives appears to be mechanical separation of the reactive polymer from the catalyst. This can be achieved with the aid of molecular sieves, *e.g.* aluminum silicates (zeolites) [23]. The adhesive components in the cavities can be displaced by water, which is more strongly adsorbed in the crystals, or liberated by heat. The thermal energy must be greater than the adsorption energy in the cavities.

For example, benzoyl peroxide, which is a common catalyst for the curing of polyester resins, may be "accommodated" in molecular sieves and added to the resin by the manufacturer. The resulting one-component adhesive can be stored for long periods, and can be cured by the addition of water or by heating. The toxicity and flammability of these products before and during use are also reduced.

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German version: Angew. Chem. *80*, 641 (1968)
Translated by Express Translation Service, London

[22] *H. W. Coover* in *I. Skeist*: Handbook of Adhesives. Reinhold, New York 1962, p. 409.
[23] *J. R. Neddenriep*, Adhäsion *10*, 356 (1966).

$S_E(P)$: Electrophilic Substitution at Phosphorus[**]

BY S. G. WARREN[*]

Reactions belonging to the formal category of electrophilic substitutions at phosphorus are classified according to mechanism and the coordination number of the phosphorus atom.

1. Introduction

Nucleophilic substitution at carbon, at the more familiar hetero elements, and even in metal complexes presents a well organized, useful array of mechanisms. The reactions which belong to the formal category of electrophilic substitution, however, do not normally form a conceptual entity. Electrophilic substitution in an aromatic system is rarely compared with the reactions of Grignard reagents or with the decarboxylation of acetoacetic acid; this is perhaps sensible since there seems little similarity between these mechanisms.

Electrophilic substitution at phosphorus is rather different. Phosphorus rarely forms more than one double bond and unsaturated systems involving phosphorus are normally attacked at the phosphorus atom by nucleophiles. The reactions corresponding to S_E(Aryl) are thus absent or unimportant in organophosphorus chemistry. Most electrophilic substitutions at phosphorus involve changes in the σ bond structure about the phosphorus atom. Electrophilic substitution at phosphorus therefore provides a unifying classification for certain well known reactions (*e.g.* the reactions of dialkyl phosphites with electrophiles) and some "anomalous" reactions (*e.g.* P–C bond cleavage in phosphonates).

This article is intended to supplement the many reviews of nucleophilic substitution at phosphorus, and nucleophilic attack by phosphorus[1,2], with a survey of the reactions from the literature under a reasonable classification of electrophilic substitutions. In most cases there is no precise mechanistic evidence.

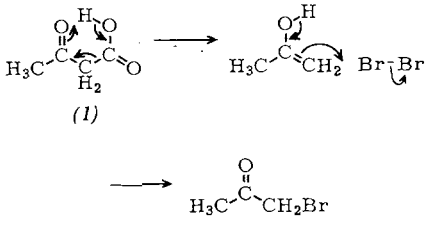
2. Electrophilic Substitution

Electrophilic substitution is the replacement of one group by another at the *substrate atom* (A) in which the *leaving group*[2a] (X) departs without its bonding electrons and the *electrophile* (Y) accepts electrons into an empty orbital to form the new bond with the substrate atom:

$$A{-}X + Y^{\oplus} \rightarrow A{-}Y + X^{\oplus}$$

An example from carbon chemistry is the decarboxylation of acetoacetic acid *(1)* with bromine.

The substrate atom (A) is the carbon (methylene) of acetoacetic acid, the leaving group (X) is CO_2, and the electrophile ($Y^{\oplus}$) is bromine. The reaction is in fact a two-step process with the enol form of acetone as an intermediate[4].

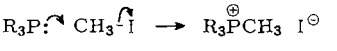


(1)

There are fundamentally, four types of mechanism possible for each valency state: S_E1, S_E2, addition-elimination, and elimination-addition.

3. S_E(P-3) Reactions

The trivalent phosphorus atom has a lone pair of electrons which may react with electrophiles[5]. Normally the first step is addition; the reaction may stop at this stage:



The addition step may alternatively be followed by an expansion of the valency shell of the phosphorus atom to form *(2)*.

Neither of these reactions is a substitution at the phosphorus atom: this is the third alternative in which

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Cambridge (England)

[**] The following notation is used in this article: S_E1 and S_E2 for monomolecular and bimolecular electrophilic substitution respectively. The symbol and number in brackets after these symbols denote substrate atom and its coordination number: P-3 is X_3P, P-4 is $X_3P{=}Y$, $P^{\oplus}$-4 is (phosphonium) $X_4P^{\oplus}$, P-5 is X_5P; X can be any atom or group of atoms and Y is normally O, S, Se, NR, or CR_2.

[1] *R. F. Hudson*: Structure and Mechanism in Organo-Phosphorus Chemistry. Academic Press, London, New York 1965.

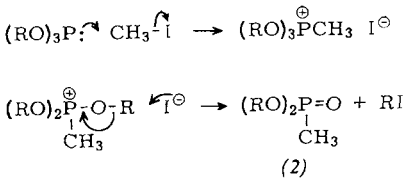
[2] *A. J. Kirby* and *S. G. Warren*: The Organic Chemistry of Phosphorus. Elsevier, Amsterdam 1967.

[2a] *Grob* and *Schiess* [3] refer to X as the *electrofuge*.

[3] *C. A. Grob* and *P. W. Schiess*, Angew. Chem. *79*, 1 (1967); Angew. Chem. internat. Edit. *6*, 1 (1967).

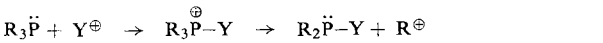
[4] *B. R. Brown*, Quart. Reviews (Chem. Soc., London) *5*, 131, (1951); *F. H. Westheimer*, Proc. chem. Soc. (London) *1961*, 253.

[5] Ref. [1], Chapters 5 and 6; ref. [2], Chapter 3.

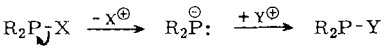


(2)

the trivalency is regenerated by the loss of an electrofugal substituent:

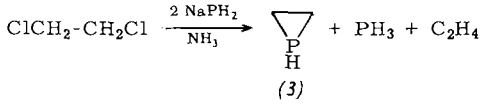


3.1. S_E1(P-3) Reactions



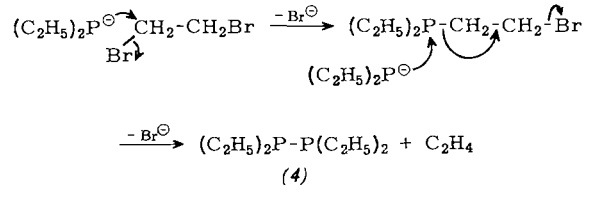
Alkali metals remove a hydrogen atom from primary or secondary phosphines to give salts [6]. These salts react readily in dry organic solvents with alkyl or acyl halides [7] to give secondary or tertiary phosphines in good yield.

Phosphirane has recently been prepared in this way by the action of sodium hydrogen phosphide in liquid ammonia on 1,2-dichloroethane [8]. Two electrophilic substitutions by the S_E1(P-3) mechanism are presumably involved.



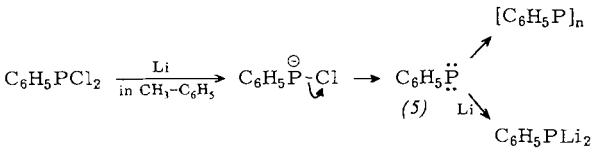
(3)

1,2-Dihaloethanes also react with dialkylphosphide anions. Ring formation is not, of course, possible and the second mole of $R_2P^{\ominus}$ ion apparently prefers the hard P-3 electrophile to the softer sp^3 carbon atom. A diphosphine is formed with the elimination of ethylene [9].



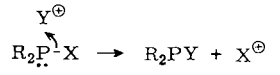
(4)

Salts may also be prepared from halophosphines and alkali metals [10] but if the anion bears a nucleofugal substituent (*e.g.* another halogen atom), an alternative reaction – elimination – occurs with formation of *(5)* [11]. These highly reactive intermediates either polymerize or combine with nucleophiles.

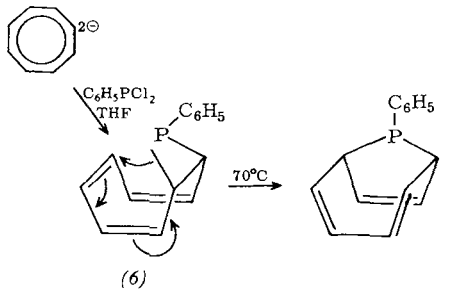


Phosphide anions react readily with other electrophiles such as epoxides [12], carbon dioxide [13], the halogens [14], and protic solvents [14].

3.2. S_E2(P-3) Reactions

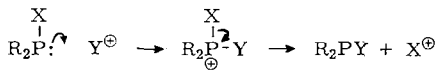


This mechanism seems unlikely since electrophiles will presumably prefer the lone pair electrons on the phosphorus atom to the relatively inaccessible electrons in a σ bond. The only reported example of a S_E2(P-3) reaction is the isomerization of the phenylphosphinecyclooctatetraene adduct *(6)* [15]. This is probably better described as a valence tautomerism.



(6)

3.3. Addition-Elimination



This mechanism is followed by the majority of S_E(P-3) reactions – not surprisingly, since the initial interaction between the lone pair of electrons and the electrophile must be particularly favorable. This step is well known, well documented [5], and mechanistically straightforward. The second step, the loss of the electrofugal substituent, has not been studied in detail but it may be inferred in many cases.

[6] *K. Sasse:* Organische Phosphor-Verbindungen, Methoden der Organischen Chemie (Houben-Weyl). Georg Thieme Verlag, Stuttgart 1963, Vol. 12, Part 1, p. 21.

[7] *K. Issleib* and *H. Anhoeck*, Z. Naturforsch. *16b*, 37 (1961).

[8] *R. I. Wagner, L. D. Freeman, H. Goldwhite,* and *D. G. Rowsell*, J. Amer. chem. Soc. *89*, 1102 (1967).

[9] *K. Issleib* and *D.-W. Müller*, Chem. Ber. *92*, 3175 (1959).

[10] Ref. [6], Part 1, p. 17ff.

[11] Ref. [2], p. 243.

[12] *K. Issleib* and *H.-M. Möbius*, Chem. Ber. *94*, 102 (1961).

[13] *W. Kuchen* and *H. Buchwald*, Chem. Ber. *92*, 227 (1959).

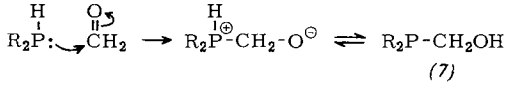
[14] Ref. [6], Part 1, p. 17ff.

[15] *T. J. Katz, C. R. Nicholson,* and *C. A. Reilly*, J. Amer. chem. Soc. *88*, 3832 (1966).

3.3.1. P–H Compounds

3.3.1.1. Addition of Phosphines to Carbonyl Compounds

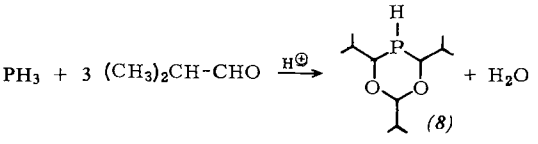
Phosphine, and substituted phosphines, react with most carbonyl compounds. The initial substitution gives an hydroxyalkylphosphine *(7)* [16].



(7)

This reaction is often followed by further additions (if phosphine or a primary phosphine is used) or further reactions with the carbonyl group since even trisubstituted phosphines are still nucleophilic, and complex cyclic products are usually formed [17].

Thus, when gaseous phosphine and liquid isobutyraldehyde are simultaneously introduced into a mixture of tetrahydrofuran and concentrated hydrochloric acid, the cyclic acetal *(8)* is obtained in 85% yield [18]. Presumably by condensation of the bis-hydroxyalkylphosphine which is first formed with a further molecule of aldehyde.



(8)

3.3.1.2. The Formation of P–P Bonds

Phosphines attack a P-3 atom which bears a nucleofugal substituent (*e.g.* a halogen atom) forming diphosphines *(9)* [19]. Even a disubstituted amine is expelled in this way, the equilibrium being 89 % to the

$$(CH_3)_2P{-}N(CH_3)_2 + (CH_3)_2PH \rightleftharpoons (CH_3)_2P{-}P(CH_3)_2 + (CH_3)_2NH$$

(9)

right at room temperature. The diphosphine *(9)* may be obtained more quickly by heating (yield up to 85 %).

3.3.1.3. Other Reactions

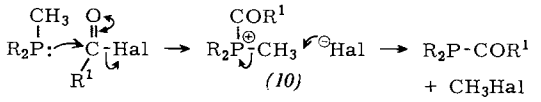
Trivalent P–H compounds react with most electrophiles including halogens [20], epoxides [21], carbon disulfide [22], acyl halides [23], isocyanates [24], oxidizing agents [25], and sulfur [20].

3.3.2. P–C Compounds

P–C bond cleavage is often regarded as anomalous. It is, however, an expected consequence of electrophilic attack on the phosphorus atom of a P–C compound if the carbon atom is electrofugal.

3.3.2.1. sp^3-Carbon as Leaving Group

The methyl group acts as an electrofugal leaving group when a methyl phosphine is attacked by an acyl halide, since nucleophilic attack by the phosphine on the halide generates a phosphonium compound *(10)*, and the methyl group is then attacked by the halide ion released in the first stage of the reaction [26].



(10)

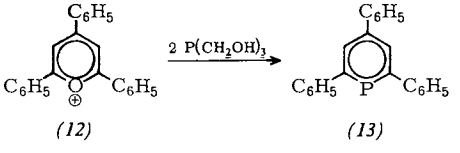
An oxygen substituent makes an sp^3 carbon atom a leaving group even without nucleophilic attack. Hydroxymethylphosphines, such as *(11)*, decompose in acidic solution and react with a number of electrophiles with loss of formaldehyde [27].

$$(HOCH_2)_3P + 3\,(CH_2{=}CHCN \rightarrow P(CH_2CH_2CN)_3 + 3\,CH_2O$$

(11)

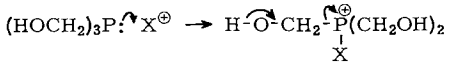
Tris(hydroxymethyl)phosphine is used to insert a phosphorus atom into electrophilic molecules. Thus, pyrylium salts *(12)* are converted into phosphabenzenes *(13)* with the loss of three molecules of formaldehyde [28, 29].

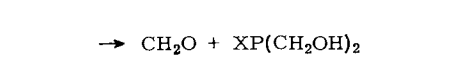
These reactions must involve a series of electrophilic substitutions in which a hydroxymethyl group is lost.



(12) *(13)*

$$+ 3\,CH_2O + O{=}P(CH_2OH)_3$$





3.3.2.2. sp^2 Carbon as Leaving Group

Nucleophilic attack on the carbonyl group provides the driving force for the decomposition of α-ketophosphines *(14)*. Oxygen, nitrogen, and phosphorus nucleophiles all react in this way [30].

The electrophile in these reactions, $H^{\oplus}$, is generated by the initial nucleophilic attack on the carbonyl group.

[16] *E. I. Grinshtein, A. B. Bruker,* and *L. Z. Soborowskii,* Doklady Akad. Nauk SSSR *139,* 1359 (1961); Chem. Abstr. *56,* 1475 (1962).

[17] Ref. [6], Part 1, pp. 29ff.

[18] *S. A. Buckler* and *V. P. Wystrach,* J. Amer. chem. Soc. *83,* 168 (1961).

[19] *A. H. Cowley,* Chem. Reviews *65,* 617 (1965).

[20] Ref. [6], Part 1, p. 70.

[21] *A. B. Naselow,* Dissertation Abstracts *24,* 1400 (1963).

[22] Ref. [6], Part 1, p. 72.

[23] Ref. [6], Part 1, p. 73.

[24] *M. Halmann* and *L. Kugel,* J. chem. Soc. (London) *1962,* 3272.

[25] *S. A. Buckler,* J. org. Chemistry *24,* 1460 (1959).

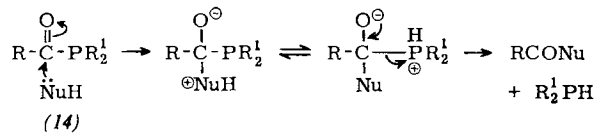
[26] *K. Issleib* and *E. Priebe,* Chem. Ber. *92,* 3183 (1959); *K. Issleib* and *H. O. Fröhlich,* Z. Naturforsch. *14b,* 349 (1959).

[27] Ref. [6], Part 1, pp. 50ff.

[28] *K. Dimroth* and *P. Hoffmann,* Angew. Chem. *76,* 433 (1964); Angew. Chem. internat. Edit. *3,* 384 (1964).

[29] *G. Märkl,* Angew. Chem. *78,* 907 (1964); Angew. Chem. internat. Edit. *5,* 846 (1966).

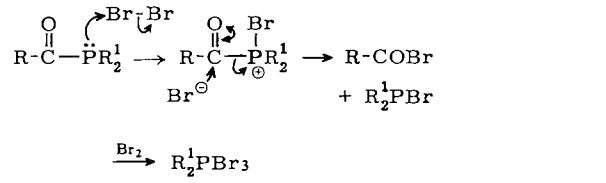
[30] *K. Issleib* and *O. Löw,* Z. anorg. allg. Chem. *346,* 241 (1966).



(14)

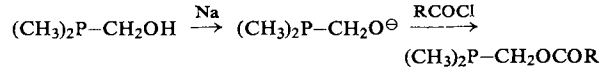
NuH = H_2O, C_2H_5OH, $(C_2H_5)_2NH$, $(C_6H_5)_2PH$

Ketophosphines also decompose with reagents such as bromine whose initial electrophilic attack at phosphorus generates a nucleophile for attack at the carbonyl group [30]. A quantitative yield of $R^1_2PBr_3$ is obtained from *(14)* in carbon tetrachloride solution at room temperature.

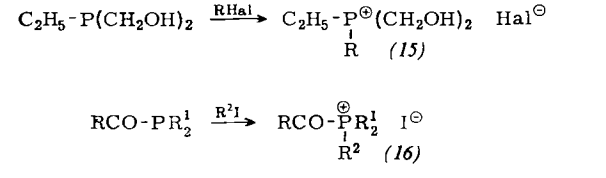


3.3.2.3. Other Reactions with Electrophiles

The reaction of a P-3 compound bearing an electrofugal substituent with an electrophile does not always lead to electrophilic substitution. Many electrofugal substituents are nucleophilic and may react with the electrophiles themselves – thus, hydroxymethylphosphines react with sodium and acid chlorides at oxygen and not at phosphorus [31].



Even when the electrophile does attack the phosphorus atom, the leaving group does not always depart; hydroxymethyl- *(15)* [31] and α-ketoalkylphosphonium [30] salts *(16)* may be prepared by the alkylation of the respective phosphines. The phosphine and alkyl halide are briefly heated under reflux in acetone [30].

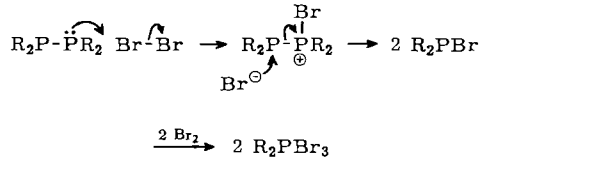


(15)

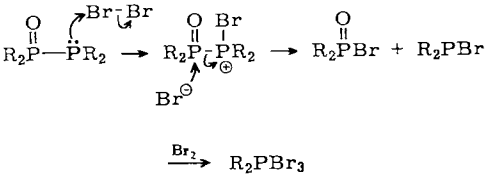
(16)

3.3.3. P–P Compounds [19]

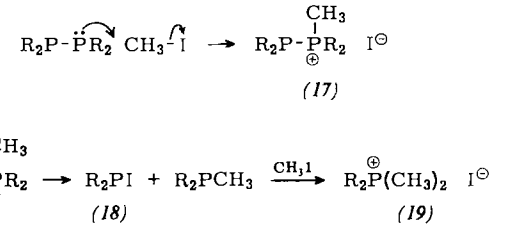
Diphosphines and diphosphine monoxides are susceptible to electrophilic substitution reactions since electrophilic attack on the lone pair electrons of one phosphorus atom may be followed by nucleophilic attack at the other phosphorus atom. Bromine, for example, cleaves diphosphines quantitatively in carbon tetrachloride solution at room temperature [32,33].



Diphosphine monoxides are attacked by the electrophile at the P-3 atom and by the nucleophile at the P-4 atom; for example, an equimolar mixture of the bromides is produced [34].



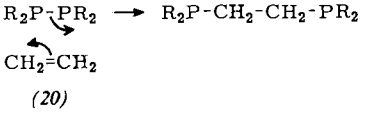
Even alkylation can lead to P–P bond cleavage. Tetramethyl and tetraethyl diphosphines give phosphonium salts *(17)* with methyl iodide but tetracyclohexyldiphosphine [32] and other diphosphines with bulky [32], aromatic, or electron-withdrawing substituents [35–37] are cleaved by alkylation; compounds *(18)* and *(19)* are formed.



(17)

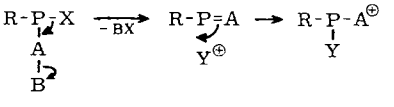
(18) *(19)*

A few reactions of diphosphines with electrophiles follow different courses: although oxidation with 2 M nitric acid does give rapid P–P cleavage of tetraalkyl diphosphines with the production of phosphinic acids, dry air bubbled through a benzene solution of the diphosphine gives the dioxide [35]. P–P cleavage may also be a cyclic process; with olefins, diphosphines insert two carbon atoms into the P–P bond in a reaction which seems best described as a cycloaddition *(20)* [38].



(20)

3.4. Elimination-Addition



This mechanism probably does not occur since the indications are that intermediates of the structure

[31] *E. I. Grinstein, A. B. Bruker*, and *L. Z. Soborowskii*, Ž. obšč. Chim. *36*, 302 (1966).

[32] *K. Issleib* and *W. Seidel*, Chem. Ber. *92*, 2681 (1959).

[33] *W. Kuchen* and *H. Buchwald*, Chem. Ber. *91*, 2871 (1958).

[34] *J. McKechnie, D. S. Payne*, and *W. Sims*, J. chem. Soc. (London), *1965*, 3500.

[35] *H. Hoffmann, R. Grünewald*, and *L. Horner*, Chem. Ber. *93*, 861 (1960).

[36] *W. R. Cullen*, Canad. J. Chem. *38*, 439 (1960).

[37] *K. Issleib* and *A. Tzschach*, Chem. Ber. *92*, 1397 (1959).

[38] *A. B. Burg*, J. Amer. chem. Soc. *83*, 2226 (1961).

R–P=A react with nucleophiles rather than with electrophiles [39].

4. $S_E(P^{\oplus}\text{-}4)$ Reactions

It would be surprising if positively charged atoms were readily attacked by electrophiles, and indeed the only mechanism whereby the positively charged phosphorus atom substitutes electrophilically appears to be the $S_E1(P^{\oplus}\text{-}4)$ mechanism in which the positive charge is lost *before* electrophilic attack occurs. This mechanism is in fact simply the addition-elimination mechanism for $S_E(P\text{-}3)$ with the two steps in the reverse order

$$R_3\overset{\oplus}{P}\text{-}X \longrightarrow R_3P: \curvearrowright Y^{\oplus} \longrightarrow R_3\overset{\oplus}{P}Y$$

The one important example of this mechanism is the reaction of hydroxymethylphosphonium salts *(21)*. These compounds lose formaldehyde on treatment with base to give a phosphine which may then be alkylated before another mole of formaldehyde is in turn removed by treatment with base. In this way asymmetrically substituted phosphines may be synthesized [40].

$$HO^{\ominus} \curvearrowright H\text{–}O\text{–}CH_2\text{–}\overset{\oplus}{P}(CH_2OH)_3 \longrightarrow (HOCH_2)_3P + CH_2O$$

(21)

$$(HOCH_2)_3P \xrightarrow{RI} (HOCH_2)_3P^{\oplus}RI^{\ominus} \xrightarrow{NaOH} (HOCH_2)_2PR + CH_2O$$

$$(HOCH_2)_2PR \xrightarrow{R^1I} (HOCH_2)_2P^{\oplus}RR^1\ I^{\ominus} \longrightarrow \textit{etc.}$$

Tetrakis(hydroxymethyl)phosphonium salts *(21)* react with dimethylamine to give tris(dimethylaminomethyl)phosphine *(22)* in an interesting variation of this reaction. Here the liberated formaldehyde combines with the phosphine and the dimethylamine in a Mannich reaction [41].

$$(HOCH_2)_4P^{\oplus}X^{\ominus} \xrightarrow{(CH_3)_2NH} (HOCH_2)_3P + CH_2O + (CH_3)_2NH_2^{\oplus}\ X^{\ominus}$$

(21)

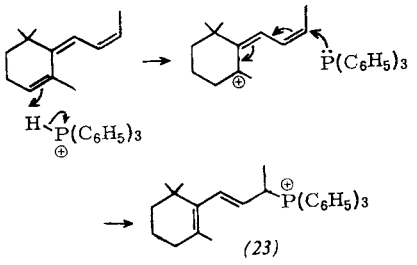
$$CH_2O + (CH_3)_2NH \longrightarrow (CH_3)_2\overset{\oplus}{N}{=}CH_2$$

$$(CH_3)_2\overset{\oplus}{N}{=}CH_2 \curvearrowleft :P(CH_2OH)_3 \longrightarrow$$

$$(HOCH_2)_3\overset{\oplus}{P}\text{-}CH_2\text{-}N(CH_3)_2 \longrightarrow\longrightarrow\longrightarrow 3\ CH_2O + [(CH_3)_2N\text{-}CH_2]_3P$$

(22)

One route to Wittig reagents uses this mechanism: olefins add protonated phosphines to give phosphonium salts *(23)* [42]. Subsequent treatment with strong base generates a Wittig reagent.



(23)

5. $S_E(P\text{-}4)$ Reactions

The range of reactions which are formally $S_E(P\text{-}4)$ is very large and contains representatives of most classes of electrophiles and leaving groups. In a few cases mechanistic studies have been attempted and for one mechanism at least (the "tautomerism" mechanism) it is possible to present well documented examples.

5.1. $S_E1(P\text{-}4)$ Reactions

$$R_2\overset{O}{\overset{\|}{P}}\text{-}X \longrightarrow R_2\overset{O}{\overset{\|}{P}}{}^{\ominus} \curvearrowright Y^{\oplus} \longrightarrow R_2\overset{O}{\overset{\|}{P}}\text{-}Y$$

Phosphite diesters are useful synthetic reagents and many reactions are known in which their anions react with electrophiles. Secondary phosphine oxides are less well known but react in much the same way. (A full account of these reactions is given in Houben-Weyl [43].) Leaving groups other than the proton are known. It is assumed that $S_E\text{-}(P\text{-}4)$ reactions that occur in strong bases have an anion as an intermediate.

5.1.1. Reactions of P–H Compounds with Base and Electrophile

Dialkyl and diaryl phosphites react with alkali metals in inert organic solvents to give the anions $(RO)_2PO^{\ominus}$, which combine with most electrophiles. Their alkylation and acylation are standard synthetic procedures [43].

These anions also attack phosphorus atoms. Attack is possible through phosphorus or oxygen and a mixture of compounds is normally formed [44]. This remains, however, the best method of preparing hypophosphates since yields of up to 60% may be obtained by adding cold (0–5 °C) phosphorohalidate to a solution of the anion in benzene. The hypophosphate *(24)* is collected by distillation. Higher yields are obtained by generating the phosphorohalidate in the presence of the anion with a reagent such as sulfuryl chloride [45].

[39] *G. M. Burch, H. Goldwhite,* and *R. N. Haszeldine,* J. chem. Soc. (London) *1964,* 572; *H. Goldwhite, R. N. Haszeldine,* and *D. G. Towsell,* J. chem. Soc. (London) *1965,* 6875.

[40] *H. Hellmann* and *O. Schumacher,* Angew. Chem. *72,* 211 (1960).

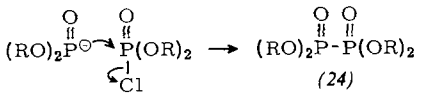
[41] *H. Coates* and *P. A. T. Hoye,* Ger. Pat. 1077214 (1960), Brit. Pat. 842593 (1960). Chem. Abstr. *55,* 4363 (1961).

[42] *H. Pommer,* Angew. Chem. *72,* 811 (1960).

[43] Ref. [6], Part 2, pp. 39ff.

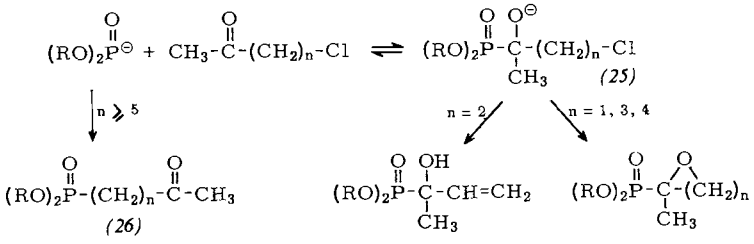
[44] *J. Michalski* and *A. Zwierzak,* Bull. Acad. polon. Sci. Sér. Sci. chim. *13,* 253, 677 (1965); *J. Michalski* and *A. Zwierzak,* Proc. chem. Soc. (London) *1964,* 80.

[45] *J. Michalski* and *T. Modro,* Chem. and Ind. 1570 (1960); Roczniki Chem. (Ann. Soc. chim. Polonorum) *36,* 483 (1962).



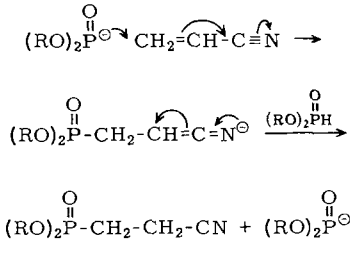
(24)

Phosphite anions are hard bases and prefer the hard electrophiles [46] (such as the carbonyl group) to the softer sp^3 carbon atoms. Halo ketones are therefore normally attacked first at the carbonyl group and the intermediate *(25)* trapped by displacement of the halide ion with the negatively charged oxygen atom produced. If the chain is sufficiently long, however, reversible addition to the carbonyl group allows the thermodynamically favored product, oxophosphonate *(26)*, to be formed [47].

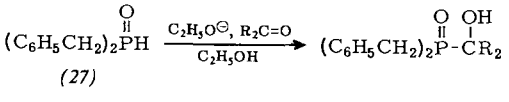


(25) *(26)*

Only a trace of base is needed to catalyze the addition of dialkyl phosphites to electrophilic olefins [48], since the dialkylphosphite anion is continuously regenerated by protonation of the product. The reactions are normally carried out in alcohol with a trace of alkoxide as catalyst. Secondary phosphine oxides also form anions which react with electrophiles and oxidizing agents [49], *e.g.* $R_2P(O)^{\ominus}$ reacts with H_2O_2 or R^1Hal to give $R_2PO_2^{\ominus}$ or $R_2P(O)R^1$.

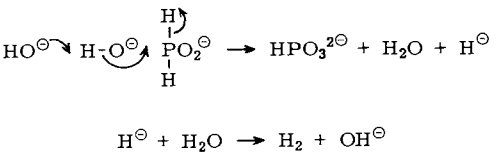


The phosphine oxides *(27)* also undergo base-catalyzed additions to aldehydes [49], ketones [50], and α,β-unsaturated ketones [50]. These reactions are again carried out in alcohol with a trace of alkoxide as catalyst.



(27)

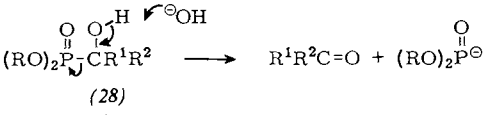
Strong hard bases [46], such as hydroxide ion in water, attack the phosphorus atom in $H_2PO_2^{\ominus}$ directly, expelling hydride ions as hydrogen gas [51]. This reac-



tion even occurs with hypophosphorous acid [52] although kinetic work shows that catalysis is needed since the rate is proportional to the *square* of the hydroxide ion concentration.

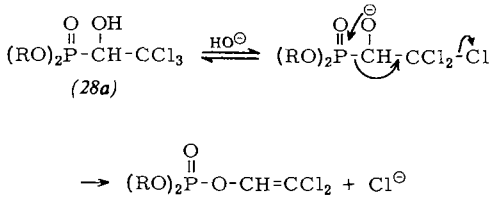
5.1.2. P–C Bond Cleavage

α-Hydroxyphosphonates *(28)* are cleaved by strong base in aqueous solution to a carbonyl compound and a phosphite [53, 54]. The hydroxide ion presumably removes a proton from the hydroxyl group with consequent P–C cleavage and elimination of a phosphite anion. This is the reversal of the formation of α-hydroxyphosphonates which is normally carried out in non-aqueous solvents with a weak base (tertiary amine) or only a trace of strong base as catalyst [55].



(28)

The phosphorus atom is an alternative site for nucleophilic attack and side reactions include the elimination of the carbon atom as an alcohol [*(28)*, R = R^1 = C_6H_5, R^2 = H] [49] or even the evolution of hydrogen gas [*(28)*, R = C_6H_5, R^1 = R^2 = CH_3] [51].



(28a)

[46] *R. G. Pearson* and *J. Songstad*, J. Amer. chem. Soc. *89*, 1827 (1967).

[47] *G. Sturz*, Bull. Soc. chim. France *1964*, 2334.

[48] *A. N. Pudovik* and *B. A. Arbuzov*, Ž. obšč. Chim. *21*, 282 (1959); Chem. Abstr. *45*, 7517 (1951); *A. N. Pudovik* and *D. Kh. Yarmukhametova*, Izvest. Akad. Nauk SSSR Otdel. chim. Nauk 1952, *902*; Chem. Abstr. *47*, 10468 (1953).

[49] *L. Horner*, *P. Beck*, and *V. C. Toscano*, Chem. Ber. *94*, 1317, 1323 (1961).

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[51] *I. G. M. Campbell* and *I. D. R. Stevens*, Chem. Commun. *1966*, 505.

[52] *A. Sieverts* and *F. Loessner*, Z. anorg. allg. Chem. *76*, 1 (1912).

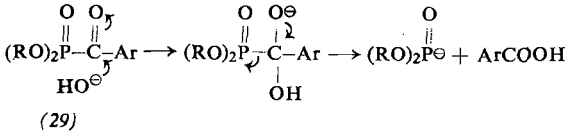
[53] *V. S. Abramov*, *L. P. Semenova*, and *L. G. Semenova*, Doklady Akad. Nauk SSSR *84*, 281 (1952); Chem. Abstr. *47*, 3227 (1953).

[54] *W. F. Barthel*, *B. H. Alexander*, *P. A. Giang*, and *S. A. Hall*, J. Amer. chem. Soc. *77*, 2424 (1955).

[55] Ref. [6], Part 1, p. 475.

When the β carbon atom of the phosphonate *(28a)* has a nucleofugal substituent, a rearrangement occurs producing a phosphate ester with elimination of the nucleofuge [54,56] as an anion.

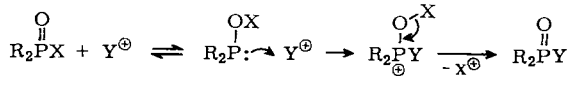
α-Ketophosphonates *(29)* are also cleaved by aqueous base, since addition of hydroxide ion to the carbonyl group provides a good leaving group [57].



(29)

Very strong bases are not needed for this reaction; benzoyl phosphonates are used as benzoylating agents for such nucleophiles as thiophenolate anion [58]. Uncharged nucleophiles such as hydrazine, hydrogen sulfide, hydrogen cyanide, or dialkyl phosphites, however, add to the carbonyl group without C–P cleavage since no anion is generated [59].

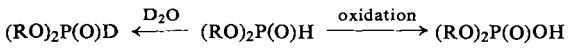
5.2. Tautomerism Mechanism



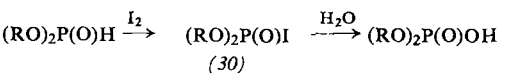
This mechanism is particularly favorable when X = H and is probably correct for most reactions of dialkyl phosphites and phosphine oxides which are not catalyzed by strong base. The phosphite-phosphonate tautomerism, which forms the first step, is essentially completely to the left. The rate determining step is often the formation of the phosphite-tautomer.

5.2.1. Oxidation and Exchange of the P(O)H Group [60]

Compounds with a P(O)H group, such as dialkyl phosphites, react with oxidizing agents to give the P(O)OH group, and with deuterium oxide to give the P(O)D group.

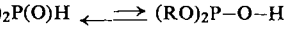


Hydrogen-deuterium exchange in dialkyl phosphites is catalyzed both by acids [61] and by bases [62]. The rate expression has terms for uncatalyzed, base-catalyzed, and both general and specific-acid catalyzed reactions. Oxidation (with iodine, for example) gives an identical rate expression and the rate constants for oxidation and exchange are very similar [63,64] (see Table 1). Oxidation with iodine must involve the formation of a phosphoroiodate intermediate *(30)* which is rapidly hydrolyzed to a phosphate diester. The rate, however, is independent of the iodine concentration. These facts suggest that there is a common



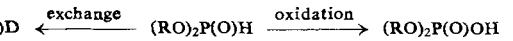
(30)

rate-determining step for oxidation and exchange and that this is the phosphonate-phosphite tautomerism:



Deuterium isotope effects for the oxidation reaction confirm this conclusion since the rate of oxidation of $(RO)_2P(O)D$ is substantially lower than that of the proton equivalent (see Table 1) [63].

Table 1. Oxidation and exchange with dialkyl phosphites [61–64].



acid catalyzed: rate = $(k_w + k_{H\oplus}[H^\oplus])[(RO)_2P(O)H]$

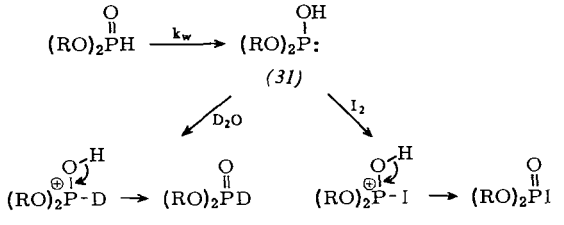
base catalyzed:

rate = $(k_w + k_{AcO\ominus}[AcO^\ominus] + k_{AcOH}[AcOH])[(RO)_2P(O)H]$

Catalyst	Rate Constants [a]		k_H/k_D $((RO)_2P(O)D)$
	Exchange	Oxidation	
$H^\oplus$	$k_{H\oplus} = 6\times10^{-2}$ $k_w = 8\times10^{-3}$ (23 °C)	3×10^{-2} 5×10^{-3} (20 °C)	4 1.7
$AcO^\ominus$	$k_{AcO\ominus} = 0.52$ (21 °C)	0.32 (20 °C)	–

[a] $k_{H\oplus}$, $k_{AcO\ominus}$ in $l\cdot mol^{-1}\cdot mm$; k_w in mm^{-1}.

The mechanism for the uncatalyzed reaction may therefore be written



Similar results have been obtained with phosphorous acid [65], hypophosphorous acid [66–68], phenyl hydrogen phosphinic acid $(C_6H_5)P(O)H\cdot(OH)$ [69], phosphites [70], and secondary phosphine oxides [71].

[56] *I. S. Bengelsdorf*, J. org. Chemistry *21*, 475 (1956).

[57] *K. D. Berlin* and *H. A. Taylor*, J. Amer. chem. Soc. *86*, 3862 (1964).

[58] *A. Takamizawa*, *Y. Sato*, and *S. Tanaka*, J. pharm. Soc. Japan *85*, 298 (1965); Chem. Abstr. *63*, 9940 (1965).

[59] Ref. [6], Part 1, p. 511.

[60] *D. Samuel*, Pure. appl. Chem. *8*, 449 (1964).

[61] *Z. Luz* and *B. Silver*, J. Amer. chem. Soc. *83*, 4518 (1961).

[62] *Z. Luz* and *B. Silver*, J. Amer. chem. Soc. *84*, 1095 (1962).

[63] *B. Silver* and *Z. Luz*, J. Amer. chem. Soc. *84*, 1091 (1962).

[64] *P. Nylen*, Z. anorg. allg. Chem. *235*, 161 (1938).

[65] *A. D. Mitchell*, J. chem. Soc. (London) *1920*, 1322; *1921*, 1266; *1922*, 1624; *1923*, 629, 2241.

[66] *W. A. Jenkins* and *D. M. Yost*, J. inorg. nuclear Chem. *11*, 297 (1959); J. chem. Physics *20*, 538 (1952).

[67] *R. L. Carroll* and *L. B. Thomas*, J. Amer. chem. Soc. *88*,1376 (1966).

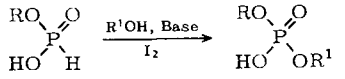
[68] *J. R. Van Wazer*: Phosphorus and its Compounds. Interscience, New York 1950, Vol. 1, p. 359ff.

[69] *J. Reuben*, *D. Samuel*, and *B. Silver*, J. Amer. chem. Soc. *85*, 3093 (1963).

[70] *P. Nylen*, Svensk. kem. Tidskr. *48*, 2 (1936); Chem. Abstr. *30*, 3702 (1936).

[71] *B. B. Hunt* and *B. C. Saunders*, J. chem. Soc. (London) *1957*, 2413.

The final stage in the oxidation of phosphorous acid [72,73] or its monoesters [74] is nucleophilic attack by water. If the oxidation is carried out in an alcohol, phosphorylation of the alcohol then occurs [72,73] and a high yield of mono- or diester of phosphoric acid is obtained.



R = H or Alkyl

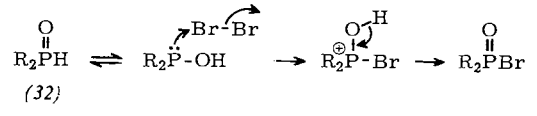
5.2.2. Other Reactions of P(O)H Compounds

5.2.2.1. Dialkyl Phosphites

No other quantitative work has been done on the reactions of dialkyl phosphites with electrophiles but very many such reactions are known. They are summarized in Houben-Weyl [75].

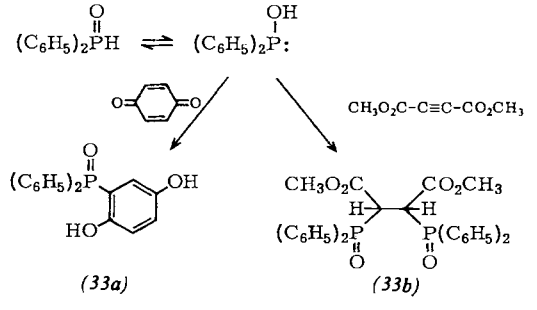
5.2.2.2. Secondary Phosphine Oxides [76]

Dialkyl- [50,76] and diaryl- [71] phosphine oxides *(32)* react with halogens, oxidizing agents such as nitric acid or hydrogen peroxide [77], and sulfur without base catalysis. The mechanism is presumably the same as that for the phosphite diesters.



(32)

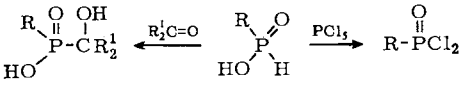
Addition to unsaturated compounds also occurs: diphenylphosphine oxide, for example, gives 1:1 and 2:1 adducts, *(33a)* and *(33b)*, respectively, with quinone and acetylenedicarboxylic ester [51].



(33a) *(33b)*

5.2.2.3. Hydrogen Phosphinates RP(O)(OH)H

These acids *(34)* are readily oxidized to phosphonic acids, react with halogenating agents to give phosphonic dihalides, and add to carbonyl groups to give phosphinic acids [78,79]. Phosphorous and hypophosphorous acids (R = OH and H respectively) behave similarly [80].



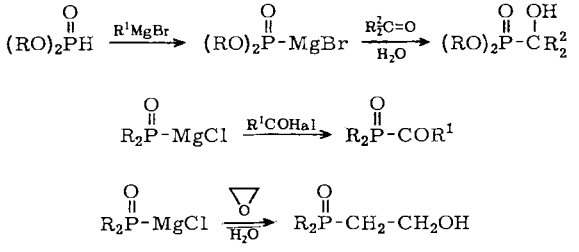
(34)

5.3. S_E2(P-4) Reactions

Base-catalyzed S_E(P-4) reactions have been assumed to be S_E1(P-4) (Section 5.1.) while those with $H^{\oplus}$ as leaving group (not base catalyzed) have been treated under the tautomerism mechanism (Section 5.2.). Other reactions will be treated here.

5.3.1. Organometallic Compounds

The substituted metal atom, one of the classical electrofugal leaving groups in carbon chemistry [81], is also known in organophosphorus chemistry. Grignard reagents, for example, can be prepared from dialkyl phosphites [82], and dialkyl- [50] or diaryl-phosphine oxides [71]. They are powerfully nucleophilic and react with ketones, acyl halides, and epoxides to give good yields of a variety of P–C compounds.



5.3.2. Phosphorus Migrations

There are a number of reactions which are very difficult to explain without a 1,2 Wagner-Meerwein type of migration of a phosphorus atom along a σ bond. The reaction of diethyl benzoylphosphonate *(35)* with diazomethane [82] is an example. The reaction product *(36)* has a methylene group "inserted" between the carbonyl group and the phosphorus atom. This is a well-known reaction in carbon chemistry leading to ring expansion in cyclic [83] or migration in acyclic ketones [84].

---

[72] *A. J. Kirby*, Chem. and Ind. *1963*, 1877.

[73] *N. G. Feschenko* and *A. V. Kirsanov*, Ž. obšč. Chim. *36*, 157 (1966); *T. Obata* and *T. Mukaiyama*, J. org. Chemistry *32*, 1063 (1967).

[74] *G. M. Blackburn*, *J. S. Cohen*, and Lord *Todd*, J. chem. Soc. (London) *C 1966*, 239.

[75] Ref. [6], Part 2, pp. 44ff.

[76] *K. D. Berlin* and *G. B. Butler*, Chem. Reviews *60*, 243 (1960).

[77] *R. H. Williams* and *L. A. Hamilton*, J. Amer. chem. Soc. *74*, 5418 (1954).

[78] Ref. [6], Part 1, pp. 229 and 301ff.

[79] Ref. [6], Part 1, pp. 368ff.

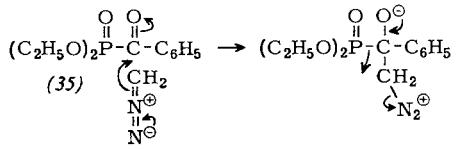
[80] Ref. [6], Part 1, pp. 360ff., 448; *M. C. Marie*, Ann. Chimie (8), *3*, 335 (1904).

[81] *B. Capon*, *M. J. Perkins*, and *C. W. Rees*: Organic Reaction Mechanisms, Interscience, London 1965, p. 81ff., 1966, p. 95 ff.

[82] *B. A. Arbuzov*, *V. S. Vinogradova*, *N. A. Polezhaeva*, and *A. K. Shamsutdinovoa*, Izvest. Akad. Nauk SSSR Otdel. chim. Nauk *1963*; 675; Chem. Abstr. *59*, 11551 (1963).

[83] *E. Mosettig* and *A. Burger*, J. Amer. chem. Soc. *52*, 3456 (1930).

[84] *D. W. Adamson* and *J. Kenner*, J. chem. Soc. (London) *1939*, 181.



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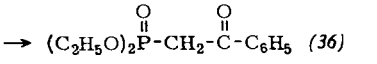
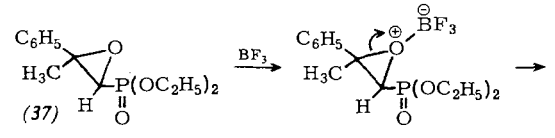


(36)

If this mechanism is correct, the $(C_2H_5O)_2P(O)$ group migrates better than the phenyl group. The same group apparently migrates when α,β-epoxy phosphonates are heated or treated with boron trifluoride in ether [85].



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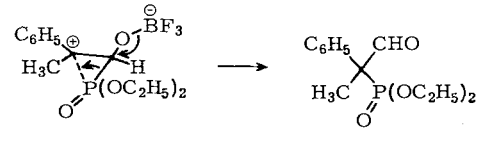
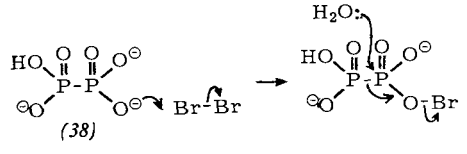
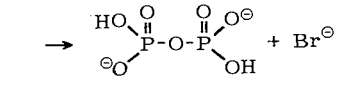


5.3.3. The Oxidation of Hypophosphoric Acid

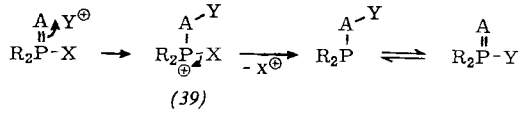
Hypophosphoric acid *(38)* reacts with bromine water at pH = 7 to give pyrophosphoric acid in 97% yield [86]. The pH-rate profile for the reaction is bell shaped: the two inflections correspond to the third dissociation constant of hypophosphoric acid and the reaction of bromine with hydroxide ion. The reaction is thus one between the trianion of the acid and bromine. The very high yield suggests that the reaction is not one of cleavage to phosphate and a phosphorylating fragment since the latter would be expected to phosphorylate the solvent. A better explanation is phosphorus migration:



(38)



5.4. Addition-Elimination

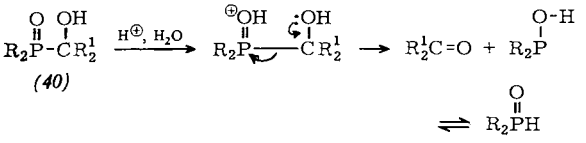


(39)

This mechanism involves the same steps as the tautomerism mechanism but in the reverse order. The first step is attack by the electrophile on the phosphoryl oxygen (or sulfur *etc.*) atom (A), the expected site for electrophilic attack in a P-4 compound. The intermediate phosphonium compound *(39)* can react in many ways however, and only if X is a good electrofuge will substitution occur. The mechanism is especially favored if X = H since the last stage, the phosphite-phosphonate tautomerism, is then rapid.

5.4.1. α-Hydroxyphosphonates

The P–C bond of an α-hydroxyphosphonate *(40)* [87] (or phosphine oxide) [50] is quantitatively cleaved in aqueous acidic solution to form a carbonyl compound and a phosphite. The reaction is reversed in the absence of water and with base catalysis. The cleavage reaction is presumably initiated by protonation of the phosphoryl oxygen atom.

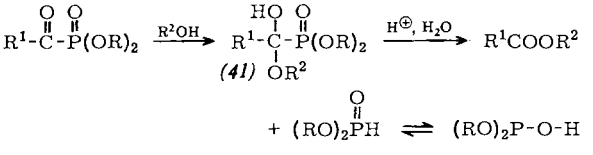


(40)

Other electrophiles, such as acid chlorides or anhydrides, attack the OH group without P–C bond cleavage [88].

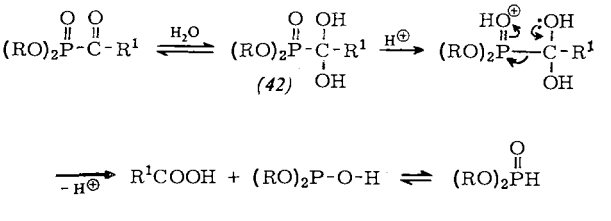
5.4.2. α-Ketophosphonates

When an α-ketophosphonate is dissolved in an alcohol, the carbonyl adduct may be isolated. This adduct decomposes to a carboxylic ester and a phosphite when treated with aqueous acid [89].



(41)

Ketophosphonates are also hydrolyzed by aqueous acid; the same mechanism presumably applies. The hemiacetal *(41)* and the diol *(42)* are stable until protonated, whereupon a good leaving group (phosphite) is formed [57,90].



(42)

[85] *R. H. Churi* and *C. E. Griffin*, J. Amer. chem. Soc. *88*, 1824 (1966).

[86] *B. Blaser* and *P. Halpern*, Z. anorg. allg. Chem. *215*, 33 (1933).

[87] Ref. [6], Part 1, pp. 385, 523.

[88] Ref. [6], Part 1, p. 508.

[89] *M. I. Kabachnik* and *P. A. Rossiyskaya*, Izvest. Akad. Nauk. SSSR Otdel. chim. Nauk *1945*, 597; Chem. Abstr. *41*, 88 (1947).

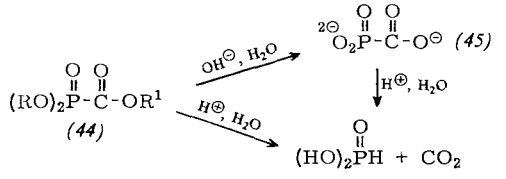
[90] *B. Ackermann*, *T. A. Jordan*, *C. R. Eddy*, and *D. Swern*, J. Amer. chem. Soc. *78*, 4444 (1956).

In the absence of water, treatment with acid removes only the esterifying groups to give pure ketophosphonic acid *(43)* (70–100 % yield)[91].

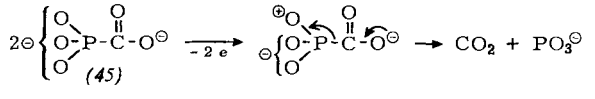
$$(RO)_2P(O)-COR^1 \xrightarrow[2.\ H_2O]{1.\ HBr} (HO)_2P(O)-COR^1 + 2\ ROH$$

5.4.3. Phosphonoformates

Phosphonoformate esters *(44)* hydrolyze rapidly in aqueous alkali to give the trianion *(45)* of phosphonoformic acid. In aqueous acidic solution, however, both the ester and the acid decarboxylate to give phosphorous acid[92–94].

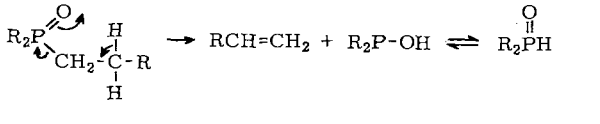


The decarboxylation of the acid shows uncatalyzed and acid catalyzed reactions[82,83]. The trianion also reacts with oxidizing agents with loss of carbon dioxide and formation of phosphate in aqueous solution[96] or alkyl phosphate in alcoholic solution[95]. This reaction, represented formally, is the removal of two electrons from the trianion *(45)* leading to the loss of CO_2 and the generation of a phosphorylating agent – probably metaphosphate[95].



5.4.4. Phosphonates and Phosphine Oxides

The thermal decomposition of alkyl phosphonates and phosphine oxides is not acid catalyzed but the elimination of olefin as one product suggests an electrocyclic process in which a hydrogen atom is transferred from the β carbon atom to the phosphoryl oxygen atom[97].



[91] *V. F. Cooke, W. Gerrard,* and *W. J. Green,* Chem. and Ind. *1953,* 351; *V. F. Cooke,* and *W. Gerrard,* J. chem. Soc. (London) *1955,* 1978.

[92] *P. Nylen,* Ber. dtsch. chem. Ges. *57 B,* 1023 (1924).

[93] *A. E. Arbuzov* and *A. A. Dunin,* Ber. dtsch. chem. Ges. *60 B,* 291 (1927).

[94] *P. Nylen,* Z. anorg. allg. Chem. *235,* 33 (1937).

[95] *S. G. Warren* and *M. R. Williams,* unpublished observations.

[96] *P. Nylen,* Z. anorg. allg. Chem. *218,* 304 (1934).

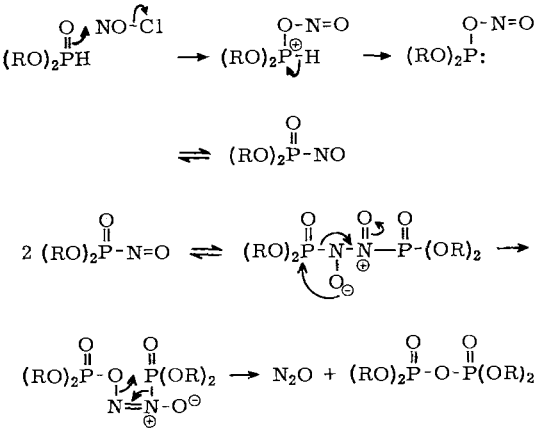
[97] *W. J. Bailey, M. W. Muir,* and *F. Marktscheffel,* J. org. Chemistry *27,* 4404 (1962).

5.4.5. Phosphites

The Michalski reaction between a dialkyl phosphite and nitrosyl chloride, which, in benzene, gives up to 90 % of tetraalkyl pyrophosphate[98] has aroused some mechanistic speculation[99].

$$2\ (RO)_2P(O)H \xrightarrow{2NOCl} (RO)_2P(O)-O-P(O)(OR)_2 + N_2O + 2\ HCl$$

The reaction is first order in both reagents; ^{18}O studies show that the pyrophosphate oxygen atom comes exclusively from the nitrosyl chloride and there is a negligible deuterium isotope effect when $(RO)_2P(O)D$ is used. The tautomerism- and S_E2-mechanisms are excluded by these facts and the most likely mechanism seems to be initial attack on the phosphoryl oxygen atom followed by a series of rearrangements:



The dimerization of nitroso compounds, the three-membered cyclic rearrangement at phosphorus[53], and the four-membered electrocyclic process (like the Wittig reaction[100]) are all well established reactions. Another example of this mechanism is the acid catalyzed deuterium exchange and oxidation of dialkyl phosphites discussed above (Section 5.2.1.).

5.4.6. P–P Compounds

Hypophosphoric acid[101] and its esters[44], diphosphine dioxides[102] and their thiono analogs[103,104], are all attacked by electrophiles with P–P bond cleavage. The reactions are satisfactorily explained by initial electrophilic attack at phosphoryl oxygen or sulfur (which generates a phosphonium center) and subsequent nucleophilic attack at the other phosphorus

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[99] *D. Samuel* and *B. Silver,* J. chem. Soc. (London) *1963,* 3582.

[100] Ref. [2], Chapter 6.

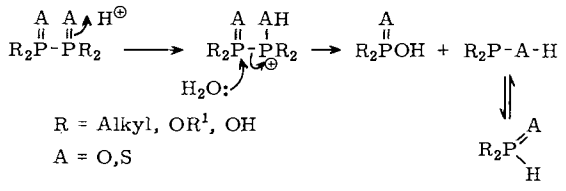
[101] *R. G. Van Name* and *W. J. Huff,* Amer. J. Sci. *45,* 91, 103 (1918); *A. Rosenheim* and *H. Zilg,* Z. physik. Chem. *139 A,* 12 (1928).

[102] *L. D. Quin* and *H. D. Anderson,* J. Amer. chem. Soc. *86,* 2090 (1964).

[103] *J. Michalski, W. Stec,* and *A. Zwierzak,* Bull. Acad. polon. Sci. Sér. Sci. chim. *13,* 680 (1965).

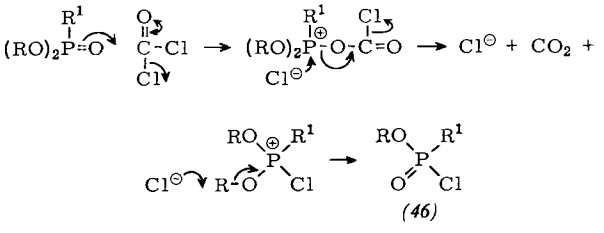
[104] *R. Cölln,* German Pat. 1054453 (1959); Chem. Abstr. *55,* 6375 (1961); *W. Kuchen* and *H. Buchwald,* Angew. Chem. *71,* 162 (1959).

atom releasing the phosphite tautomer of the product. Acids, halogens, and sulfuryl chloride all react in this way.



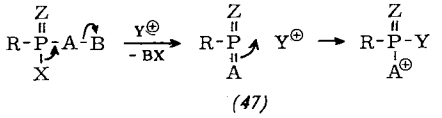
5.4.7. Electrophilic Attack on Phosphoryl Oxygen

Phosphates and phosphonates are attacked electrophilically at the P=O group by many reagents without *electrophilic* substitution at the phosphorus atom. Thus phosgene converts phosphonate diesters to phosphonochloridates by electrophilic attack at P=O followed by *nucleophilic* substitution at the phosphorus atom [105].



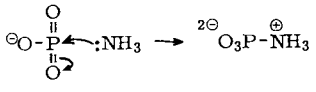
(46)

5.5. Elimination-Addition



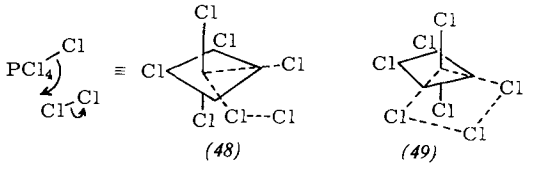
(47)

This mechanism has not yet been reported and it seems rather unlikely since metaphosphate reacts with nucleophiles rather than electrophiles.



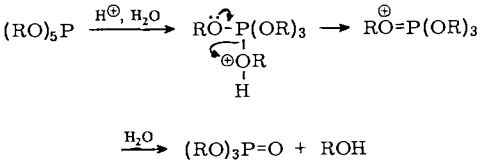
6. S_E(P-5)

The reaction of PCl_5 with radioactive chlorine [106] is the only S_E(P-5) reaction so far reported. Three chlorine atoms are replaced, presumably the three equatorial chlorine atoms, which precludes any ionic mechanism since the generation of $PCl_4^{\oplus}$ or $PCl_6^{\ominus}$ would make four chlorine atoms equivalent. A transition state such as *(48)* or *(49)*, which preserves the asymmetry of the trigonal bipyramid, is suggested.



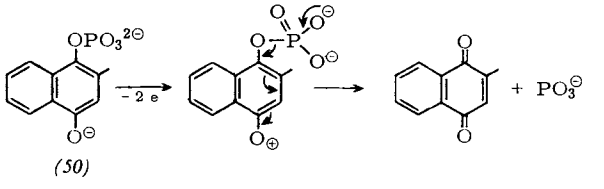
(48) *(49)*

Most P-5 compounds react with electrophiles with a change in coordination number [107].



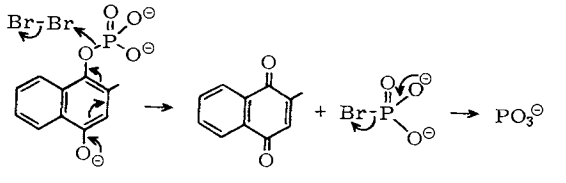
7. Oxidative Phosphorylation

One of the most intriguing biological-chemical problems is that of the reactions in the electron oxidation and cytochrome chain in which inorganic phosphate and ADP are converted into ATP under oxidizing conditions [108]. A chemical model for one of these steps is the oxidation of a quinol phosphate [109]. The usual description of such reactions is as



(50)

nucleophilic substitutions at the phosphorus atom [110]; they can, however, be interpreted as S_E(P-4) reactions.



Models for this process are the phosphorylation of alcohols by the oxidation of phosphorous acid [72] or phosphonoformate trianion [95]. Other oxidative phosphorylations include the treatment of thiol esters with iodine [111], the

[105] Ref. [2], p. 228.

[106] *J. Downs* and *R. E. Johnson*, J. chem. Physics *22*, 143 (1954).

[107] Ref. [2], p. 264.

[108] *H. R. Mahler* and *E. H. Cordes*: Biological Chemistry. Harper and Row, New York 1966, p. 597ff.

[109] *V. M. Clark*, *D. W. Hutchinson*, *G. W. Kirby*, and Sir *Alexander Todd*, J. chem. Soc. (London) *1961*, 715.

[110] *V. M. Clark*, *D. W. Hutchinson*, *A. J. Kirby*, and *S. G. Warren*, Angew. Chem. *76*, 704 (1964); Angew. Chem. internat. Edit. *3*, 678 (1964).

[111] *T. Wieland* and *R. Lambert*, Chem. Ber. *89*, 2467 (1956); *S. Åkerfeldt*, Acta chem. scand. *14*, 1980 (1960); *A. L. Nussbaum*, and *R. Tiberi*, J. Amer. chem. Soc. *87*, 2513 (1965).

oxidation of nitrone-phosphate adducts[112], and of phosphate esters of ascorbic acid[113].

In any event there must be at least two stages in an oxidative phosphorylation reaction: (i) the incorporation of inorganic phosphate into some organic molecule and (ii) the phosphorylation of ADP by this organophosphorus compound. One at least of these stages must be an oxidation. Naturally, there could be more stages between incorporation and phosphorylation.

There are three separate points in the cytochrome chain at which oxidative phosphorylation occurs, each presumably involving different metabolites[114]. Yet more reactions are involved in the analogous photosynthetic phosphorylations[115].

Received: September 4, 1967 [A 649 IE]
German version: Angew. Chem. *80*, 649 (1968)

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[113] *V. M. Clark, J. W. B. Hershey*, and *D. W. Hutchinson*, Experientia (Basel) *13*, 425 (1966).

[114] *A. Asano* and *A. F. Brodie*, J. biol. Chemistry *240*, 4002 (1965); *E. C. Slater*, Advances in Enzymol. *20*, 147 (1958); *R. S. Harris, I. G. Wool*, and *J. A. Loraine*: Vitamins and Hormones. Academic Press, New York 1966, Vol. 24.

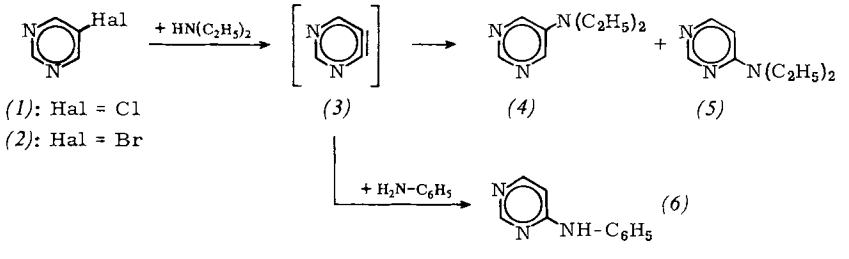
[115] *F. L. Crane* and *M. D. Heminger* in *R. S. Harris, I. G. Wool*, and *J. A. Loraine*: Vitamins and Hormones. Academic Press, New York 1966, Vol. 24, p. 489; *H. T. Witt, B. Rumberg, P. Schmidt-Mende, V. Siggel, B. Skerra, J. Vater*, and *J. Weikard*, Angew. Chem. *77*, 821 (1968); Angew. Chem. internat. Edit. *4*, 799 (1965).

COMMUNICATIONS

The Third Mechanism (AE_a) of Nucleophilic Aromatic Substitution[1]

By *Th. Kauffmann, R. Nürnberg*, and *K. Udluft*[*]

Reaction of the 5-halopyrimidines *(1)* or *(2)* with diethylamine at 130 °C (autoclave) affords 4-diethylaminopyrimidine *(5)* as well as the 5-isomer *(4)*; in the reactions with piperidine the *cine*-substitution product *(7a)* is formed[3,4]. The *EA* mechanism, involving *(3)*, which is thus indicated is supported by the observation that, in analogous reactions of *(1)* and *(2)* with diethylamine + aniline or with piperidine + aniline (in all cases 1:1), compound *(6)* is formed (yield 20–35%) in addition to the products named above, whereas aniline alone does not react with *(1)* or *(2)* under the same conditions.



Since the reaction of *(1)* and *(2)* with diethylamine gives the substitution products *(4)* and *(5)* [yield of *(4)* + *(5)* from *(1)* 29%, and from *(2)* 43%] in quite different molar proportions (82:18 and 40:60, respectively), a pure *EA* reaction by way of *(3)* is excluded and a mixture of *EA* and AE_n[3] is probable. The base-competition method was used to clarify the situation[2]. In separate experimental series at 130 °C compounds *(1)* and *(2)* were treated simultaneously with piperidine and diethylamine, which were used in various defined proportions. In each case the *cine*-substitution products *(5)* and *(7a)* were formed alongside the 5-substituted pyrimidines *(4)* and *(7b)*.

In a mixed EA/AE_n reaction, *(5)* and *(7a)* would be formed exclusively by way of *(3)*. Their relative amounts must thus remain constant if the halogen atom of the starting material is varied. As shown in Figure 1, this is not the case. *(5)* and *(7a)* thus certainly do not arise by way of *(3)* alone; some other *cine*-substitution mechanism must be operative. This mechanism, like the AE_n mechanism and unlike the *EA* mechanism[3], is not suppressed on addition of a good proton donor, so that it can hardly be other than the anomalous addition-elimination mechanism (AE_a)[3], with formulation by way of *(8)* and *(9)* being particularly probable.

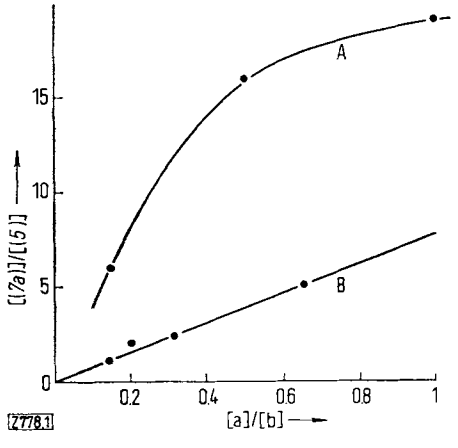
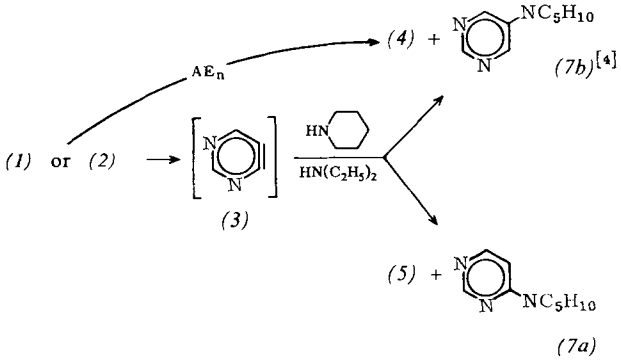
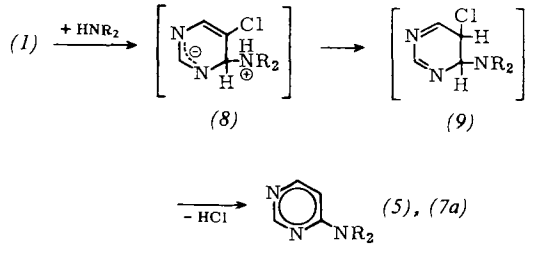


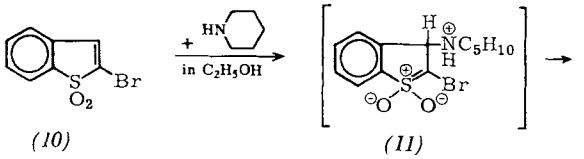
Fig. 1. Results of base-competition experiments with *(1)* (A) and *(2)* (B). *(5)* and *(7a)* were determined by gas chromatography [5] [a]/[b] = [piperidine]/[diethylamine].



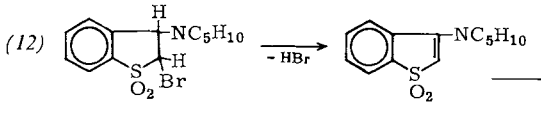


We assume that the AE_a mechanism is concerned with *cine*-substitution of *(1)* but not of *(2)*. This is because the experimental points lie on a curve for the competition experiments with *(1)* but on a straight line for those with *(2)*; in our experience – admittedly only for *EA* and AE_n substitutions – a mixed mechanism is displayed by non-linear dependence of the molar proportions of the substitution products on the molar proportions of the competing bases, whereas a pure mechanism leads to linear dependence[2,6,7]. Further, reaction of *(1)* with piperidine to yield *(7a)* is not inhibited by ethanol whereas the corresponding reaction with *(2)* is wholly suppressed on addition of ethanol, facts which indicate participation of the AE_a mechanism only in the competition experiments with *(1)*. The change from chloride *(2)* to bromide *(1)* apparently favors the AE_a mechanism over the *EA* mechanism[8].

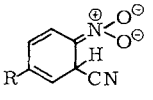
The AE_a mechanism was previously demonstrated only for the reaction of piperidine with *(10)*[9]. This reaction, in which intermediate *(12)* was isolated, can be formulated as



(10) *(11)*



(12)



(13)

proceeding by way of *(11)* [cf. *(8)*]. The close resemblance to the "von Richter carboxylation reaction"[10] (nucleophile: $CN^{\ominus}$; anionic leaving group: $NO_2^{\ominus}$; hypothetical intermediate: *(13)*; solvent: ethanol) should be pointed out.

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[4] 5-Piperidinopyrimidine is probably formed as well as the 4-isomer but escapes detection because of its great tendency to decomposition.

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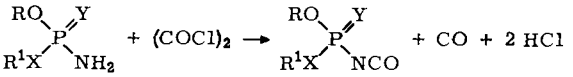
Phosphorus(v) Isocyanates

By *L. I. Samaraj, O. I. Kolodjažnij,* and *G. I. Derkatsch*[*]

Recently we reported[1] a simple synthesis of diester isocyanates of phosphoric and thiophosphoric acid *(2)* by the action of oxalyl chloride on the corresponding diester amides *(1)*. The reaction is effected at 0 °C in an inert solvent such as carbon tetrachloride or benzene.

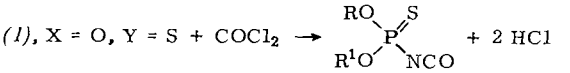


(1) X, Y = O, S *(2)*

We have now found that isocyanates *(3)* are also formed by the action of phosgene on diaryl thiophosphoramidates in boiling toluene or chlorobenzene[2].

Diaryl phosphoramidates do not react under these conditions. Dialkyl phosphoramidates and thiophosphoramidates do react, even at 0 °C, but the isocyanates are then formed in only poor yield.

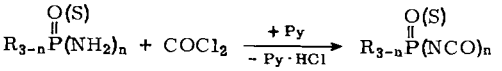
Finally we have used organic bases (pyridine, triethylamine) as HCl acceptors in the reaction of phosphorus(v) amides



(3)

	R	R^1	Yield (%)	B.p. (°C/torr)	n_D^{20}	d_4^{20}	Ref.
(3a)	C_6H_5	C_6H_5	50	130–134/0.09 m.p. = 49–51 °C	–	–	[1]
(3b)	C_6H_5	*p*-$CH_3C_6H_4$	53	127–129/0.07	1.5688	1.2388	–
(3c)	*p*-$CH_3C_6H_4$	*p*-$CH_3C_6H_4$	50	137–138/0.07	1.5645	–	[1]

with phosgene. This reaction, in an inert anhydrous medium at low temperature, affords varied types of phosphorus(v) isocyanates.



n = 1, 2 *(4)*

(4)	Yield (%)	B.p. (°C/torr)	n_D^{20}	d_4^{20}
$(CH_3O)_2P(S)NCO$	75	58–59/8	1.4718	1.2706
$(C_2H_5O)_2P(O)NCO$	73	91–93/14	1.4175	1.1820
$(C_6H_5O)_2P(O)NCO$ [3]	80	140–142/0.1	1.5450	–
$(C_6H_5O)P(S)(NCO)_2$	45	85/0.8	1.5640	1.3562
$ClCH_2(p\text{-}CH_3C_6H_4O)P(O)NCO$	71	126/0.25	1.5294	1.3273

Reaction of phosphorus(v) isocyanates with amines, alcohols, or thiols affords substituted ureas, urethanes, and thiourethanes.

The elemental analysis and IR spectra of all the new compounds conformed with the expected results.

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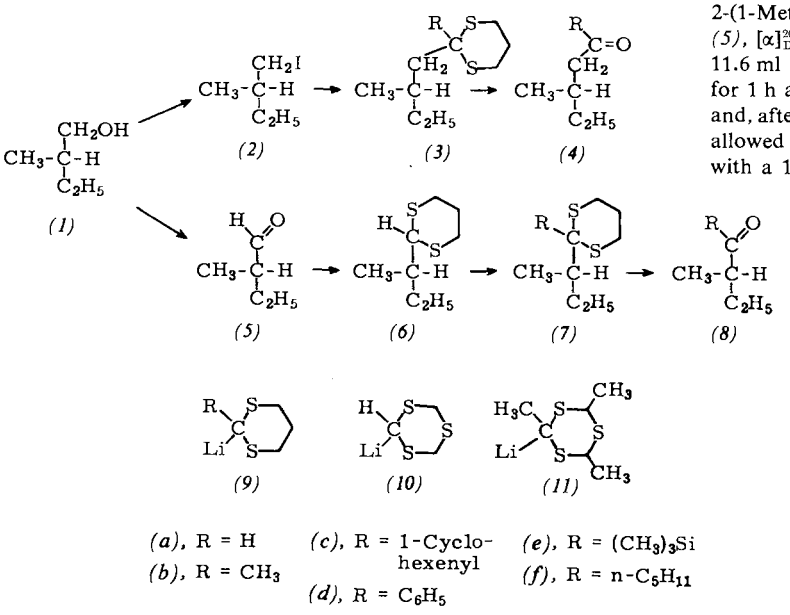
Preparation of (*S*)-2-Methylbutyl and (*S*)-*sec*-Butyl Ketones from Optically Active 2-Methyl-1-butanol by the Dithiane Method

By *D. Seebach* and *D. Steinmüller* [*]

Since optical resolution of aldehydes and ketones is difficult, optically active members of these series are usually prepared from other optically active compounds. Thus the carbonyl compounds *(4)* can be prepared from fermentation alcohol (2-methyl-1-butanol) *(1)* by way of *(2)* and its metal derivatives [yield *(2)*→*(4)* < 50%] [1].

The dithiane method [2] offers a suitable means for replacement of the halogen atom in *(2)* by an acyl group. For example, with 2-lithio-1,3-dithiane *(9a)* the iodide *(2)* gives a 65% yield of compound *(3a)* (b.p. 74 °C/0.3 torr) and thence by hydrolysis the aldehyde *(4a)*. The optically active ketones *(4b)*–*(4e)* can be obtained similarly. The lithio derivatives *(10)* [2b] and *(11)* were also used as "masked" acyl anions.



(a), R = H *(c)*, R = 1-Cyclohexenyl *(e)*, R = $(CH_3)_3Si$
(b), R = CH_3 *(d)*, R = C_6H_5 *(f)*, R = $n\text{-}C_5H_{11}$

Starting materials [a]	Product	Yield [b] (%) (% lit.)	$[\alpha]_D$ ($c \approx 5$, ether) exp.	calc. [c]	$[\alpha]_{D100}$ [c]
(10) + *(2)*	*(4a)*	60 [d] (40 [1a])	− 4.5	− 5.3	− 5.2 (heptane) [1a]
(11) + *(2)*	*(4b)*	50 (17–30 [1b])	+ 6.3	+ 7.4	+ 7.9 ($CHCl_3$) [1a] +9.9 (pure liquid) [1b]
(3), R = Li, + Cyclohexene epoxide	*(4c)*	40	+ 9.8	+11.5	—
(9d) + *(2)*	*(4d)*	70 [40 [1a])	+16.7	+19.6	+19.0 (pure liquid)[1c]
(3), R = Li, + $(CH_3)_3SiCl$	*(4e)*	60	+ 5.0	+ 5.9	—
(7), R = Li, + CH_3I	*(8b)*	55 (15 [1a])	+14.6 [e]	+24.4	+27.4 ($CHCl_3$) [1a] +30.0 (pure liquid)[1d]
(7), R = Li, + $n\text{-}C_5H_{11}I$	*(8f)*	50	+13.4	+22.4	—

[a] *(2)*: $[\alpha]_D^{23} = +4.8$ (pure liquid) (*ca.* 85% opt. pure); *(6)*: see experimental section.

[b] The crude products *(3)* and *(7)* were hydrolyzed directly. Yields refer to once distilled carbonyl compound.

[c] Calculated on optically pure starting material *(1)*, *(2)*, *(6)*, or *(8)*, R=OH; cf. experimental section.

[d] Hydrolysis affords first the dimethyl acetal of *(4a)* in 80% yield; b.p. 72 °C/50 torr, $n_D^{20} = 1.4073$, $[\alpha]_D^{19} = +4.3$ ($c = 11$, ether). This was hydrolyzed to the free aldehyde.

[e] In $CHCl_3$.

Optically active ketones of type *(8)* containing acidic hydrogen at the center of asymmetry racemize readily through the enol form. Since acidic or basic conditions cannot be avoided in the methods conventionally used for synthesis and resolution, preparation of such ketones presents particular problems. We have found that *(8f)* [3] and even *(8d)* [1d, 3], which has an enolizable H atom only on the asymmetric C atom, lose less than 5% of their optical activity when their aqueous-methanolic solutions are boiled for one to three hours with 2 molecular equivalents of $HgCl_2$ and one of HgO [2] or $CdCO_3$ [4] (these being conditions for neutral hydrolysis of the dithianes). Further, (*S*)-2-methylbutyraldehyde, which is readily prepared from the alcohol *(1)*, is converted by 1,3-propanedithiol into the dithiane *(6)*, whence hydrolysis [5b] regenerates the aldehyde with only 20% loss of activity (an average of 10% in each step).

The aldehyde *(5)* can thus be converted by way of *(6)* and its Li derivative into the dithianes *(7)* and thence into (*S*)-ketones such as *(8b)* and *(8f)*. Since compounds *(6)* and *(7)* cannot racemize, danger of racemization is confined to preparation of *(6)* and the hydrolysis *(7)*→*(8)*. From the experiments outlined it can be concluded that the loss of activity in passing from the aldehyde to the ketones *(8)* is probably less than 20%.

Owing to the manifold reactivity of the readily accessible Li derivatives of *(3a)* and *(6)* the dithiane method is superior to the methods previously customary for synthesis of compounds of type *(4)* and *(8)* [3].

Experimental:

2-(1-Methylpropyl)1,3-dithiane *(6)*: A solution of 10.0 g of *(5)*, $[\alpha]_D^{20} = +21.0$ (pure liquid) (60% optical purity [5a]) and 11.6 ml of 1,3-propanedithiol in 350 ml of $CHCl_3$ is stirred for 1 h at room temperature. The solution is cooled to 0 °C and, after passage of a fast stream of dry HCl gas for 2–3 min, allowed to stand in a refrigerator for 4 h. It is then washed with a 10% aqueous solution of KOH, dried over K_2CO_3, and distilled to yield 14–17 g of *(6)*, b.p. 67–70 °C/0.6 torr, $n_D^{20} = 1.5387$; $[\alpha]_D^{20} = -0.50$ ($c = 15$, ether).

Alkylation of *(6)* to give 2-(1-methylpropyl)-2-pentyl-1,3-dithiane *(7f)*: 3.85 g of *(6)* is metalated in 70 ml of THF with a 5% excess of butyllithium [2a]. After addition of 3.6 ml of 1-iodopentane, the mixture is allowed to stand for 3 days at −30 °C and then for another 3 days at 0 °C. Working up [2a] and distillation affords 4.20 g of *(7f)*, b.p. 105 °C/0.6 torr, $n_D^{20} = 1.5222$, $[\alpha]_D^{23} = -15.4$ ($c = 16$, ether).

Hydrolysis of *(7f)* to yield 3-methyl-4-nonanone *(8f)*: A mixture of *(7f)* (4.00 g, 16.4 mmole), HgO (32.5 mmole), $HgCl_2$ (32.5 mmole), H_2O (18 ml), and CH_3OH (180 ml) is

stirred vigorously at 20 °C for 16 h, and then at 65 °C for 1.5 h. The mixture is filtered while hot and the residue is washed with CH_3OH. The filtrate is diluted with water and extracted with pentane[2a]. Crude yield of *(8f)* 2.05 g, $[\alpha]_D^{22} = +13.6$ (c = 4, ether). Distillation affords 1.67 g of *(8f)* (overall yield calculated with respect to *(6)*, 51.4 %), b.p. 65–68 °C/7 torr, $n_D^{20} = 1.4232$, $[\alpha]_D^{23} = +13.4$ (c = 5, ether) [corresponds to +22.4 calculated with respect to optically pure *(6)*].

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[4] *M. L. Wolfrom*, *M. Konigsberg*, and *D. I. Weisblat*, J. Amer. chem. Soc. *61*, 574 (1939).

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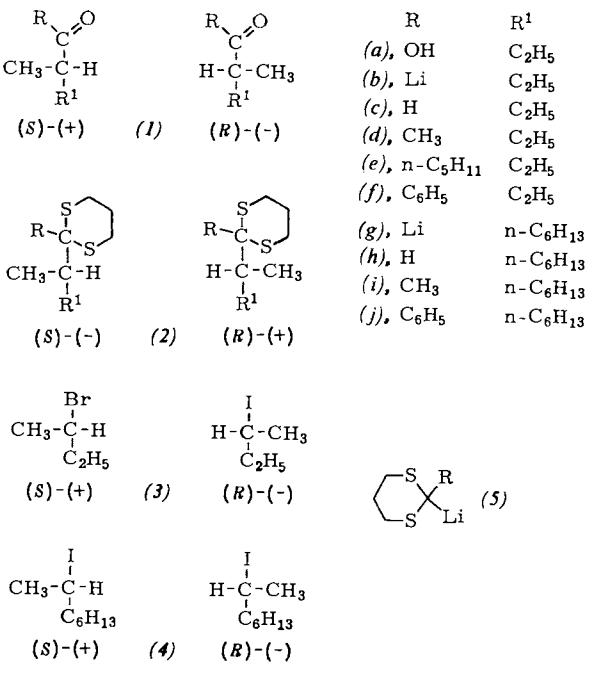
Synthesis of (*R*)- and (*S*)-Aldehydes and -Ketones from Chiral *sec*-Alkyl Halides

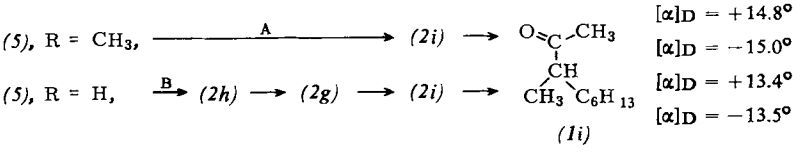
By *D. Seebach*, *D. Steinmüller*, and *F. Demuth* [*]

Ketones and aldehydes of type *(1)* are valuable for mechanistic studies and as reactive starting materials for the synthesis of other optically active compounds but they have not hitherto been simple to prepare[1]. We describe here a new method by which secondary alcohols, which are available easily and in large variety by resolution of racemates[2], can be converted into the compounds *(1)* by way of the halides[3] such as *(3)*[4] or *(4)*[5]. Alkylation of 2-lithio-1,3-dithianes *(5)* with optically active bromides or iodides involves inversion of configuration at the asymmetric C atom and leads to dithianes *(2)*, whose hydrolysis affords the carbonyl compounds *(1)*. The antipodes (*R*)-(−)-*(1)* and (*S*)-(+)-*(1)* can both be obtained in this way. Configurational assignment of the products *(1)* and thus also of the intermediate dithianes is effected by comparison with compounds of known absolute configuration[1,6] [for *(1c)*–*(1f)* and *(2c)*–*(2f)*] and by the fact that the sign of rotation is not changed when $R^1 = C_2H_5$ in substances of this type is replaced by $R^1 = C_6H_{13}$[7] [for *(1h)*–*(1j)* and *(2h)*–*(2j)*].

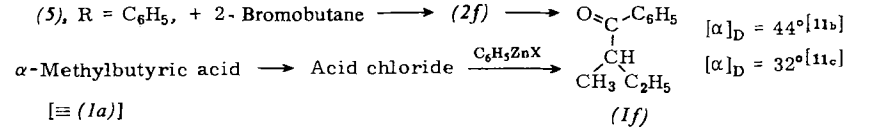


	R	R^1
(a)	OH	C_2H_5
(b)	Li	C_2H_5
(c)	H	C_2H_5
(d)	CH_3	C_2H_5
(e)	$n\text{-}C_5H_{11}$	C_2H_5
(f)	C_6H_5	C_2H_5
(g)	Li	$n\text{-}C_6H_{13}$
(h)	H	$n\text{-}C_6H_{13}$
(i)	CH_3	$n\text{-}C_6H_{13}$
(j)	C_6H_5	$n\text{-}C_6H_{13}$

The degree of inversion (proportion of the S_N2 reaction with Walden inversion) on alkylation of lithiodithianes with (*S*)-bromobutane *(3)*[4a] exceeds 85 %, as is seen by comparison of the numerical rotations of the resulting (*R*)-dithianes *(2c)*–*(2e)* with those of the (*S*)-dithianes[1] prepared from the (*S*)-aldehyde *(1c)*[8] [since the rotations of the optically pure iodides *(3)*[4b] and *(4)*[5] are not known, a corresponding statement cannot yet be made for their reaction with *(5)*]. We found that the amount of inversion depended on the structure of the lithiodithiane used. Treatment of *(5)*, R = CH_3, with optically active 2-iodooctane and subsequent hydrolysis afforded 3-methyl-2-nonanone *(1i)*[9] (route A), which was prepared also from the unsubstituted Li compound (route B). The rotation of the ketone obtained by route B was



about 10 % lower than that obtained by route A. This result was reproducible within experimental error (average error of the mean value ±0.1) for both antipodes (see Table), even when the conditions (temperature, molar proportions, reaction time, concentration) were purposely varied both in the alkylation step and in the hydrolysis. Thus the degree of inversion must be slightly higher in the reaction of the methyl derivative than in that of the unsubstituted compound[10] (cf. the higher yield on alkylation in the former case). From the rotation of the phenone *(1f)* prepared by the dithiane method it follows that the optical yield in the reactions bromobutane



→ ketone is in this case 40 % greater than when this compound is prepared from methylbutyric acid[6] by the usual methods. The overall chemical yields (alkylation of the anions and hydrolysis) lie between 30 and 60 % (Table).

Starting materials [a] and reaction steps [b] (excluding hydrolysis)	Products (1)	Yields (%) Step 1.	2.	Hydrolysis	Total	$[\alpha]_D$ ($c \approx 5$, ether) Exp. [d]	max. [11a] (calc. [11b])
1. (5), R = H, + (S)-(3)	(R)-(1e)	45	70	70	22	− 8.6	(23)
2. (R)-(2b) + n-$C_5H_{11}I$							
1. (5), R = n-C_5H_{11} + (R)-(3)	(S)-(1e)				30	+ 9.9	17
1. (5), R = C_6H_5, + (S)-(3)	(R)-(1f)	66		70	46	−16.9	(44)
1. (5), R = C_6H_5, + (R)-(3)	(S)-(1f)	78		80	62	+16.2	28
1. (5), R = H, + (S)-(4)	(R)-(1i)	42	97	77	31	−11.9	13.5
+ (R)-(4)	(S)-(1i)	40	98	79	31	+ 9.5	13.4
2. (2g) + CH_3I							
1. (5), R = CH_3, + (S)-(4)	(R)-(1i)	65		75	49	−13.2	15.0
+ (R)-(4)	(S)-(1i)	75		70	52	+10.5	14.8
1. (5), R = C_6H_5, + (S)-(4)	(R)-(1j) [c]	80		69	55	−21.5	24.5

[a] (S)-(3) [3a], $[\alpha]_D^{20} = +15.1$, (R)-(3) [3b] −19.3, (S)-(4) [3c] +44.9, (R)-(4) [3d] −36.2 (all pure liquids).

[b] For experimental methods see the literature cited in [1].

[c] B.p. 100 °C/0.01 torr, $n_D^{20} = 1.4990$.

[d] Rotations of the ketones purified by several molecular distillations; no activity is lost during the distillation.

The scope of the method is further extended if the reactive Li compounds (2b) and (2g) are used whose carbonyl groups are "masked" so that the center of asymmetry is protected against racemization.

Experimental:

(R)-(−)-3-Methyl-2-nonanone: 17.1 mmole of (4), $[\alpha]_D$ = +44.7 (pure liquid) is added to a solution of 20 mmole of (5), R = CH_3, in 35 ml of THF at −60 °C; the reaction vessel is sealed under argon and allowed to stand at −30 °C for 72 h, and then at −10 °C for 24 h. The reaction mixture is poured into water, extracted with pentane, and distilled to yield 5.8 mmole of (5), R = CH_3, H in place of Li, and 11.2 mmole of (2i), b.p. 120 °C/1 torr, $[\alpha]_D^{21} = +42.7$ (c = 12, ether). A mixture of (2i) (2.71 g, 11.0 mmole), $HgCl_2$ (24.3 mmole), HgO (12.2 mmole), and 85 % aqueous methanol (140 ml) is stirred vigorously under reflux for 3 h. The mixture is filtered and the filtrate is treated with water and extracted with pentane. The pentane solution is washed with a solution of NH_4Cl and with water, dried over Na_2SO_4, and distilled. Yield: 1.29 g of (R)-(−)-3-methyl-2-nonanone [75 % from (2i), 49 % from (4)], b.p. 65–66 °C/3 torr[9], n_D^{20} = 1.4248, $[\alpha]_D^{22} = -13.2$ (c = 5, ether).

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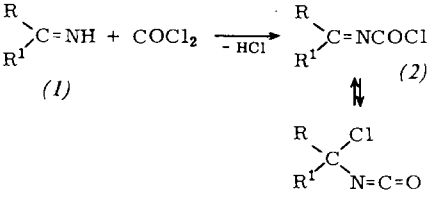
1-Halogenoalkyl Isocyanates

By L. I. Samaraj, O. W. Wischnewskij, and G. I. Derkatsch[*]

In our studies of organic isocyanates[1] we found that reaction of ketimines (1) with phosgene (100–110 °C, in inert solvents) or oxalyl dichloride (50–60 °C) usually gives N-(chloroformyl)-ketimines (2) (cf. ref. [2]).



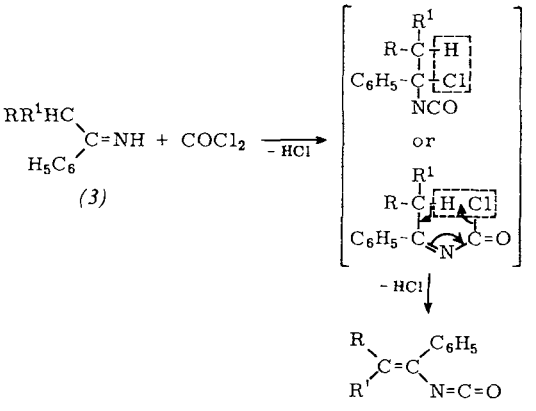
	R	R^1	Yield (%)	B.p. (°C/torr)	M.p. (°C)	n_D^{20}
(2a)	tert-C_4H_9	C_6H_5	85	118/9	—	1.5243
(2b)	C_6H_5	C_6H_5	87	135/0.1	42–45	—
(2c)	C_6H_5	p-$CH_3C_6H_4$	75	141/0.06	—	1.6170
(2d)	C_6H_5	α-$C_{10}H_7$	80	183/0.05	73–75	—

However, alkenyl isocyanates (4) are obtained from ketimines (3) and phosgene, probably by way of 1-chloroalkyl isocyanates as intermediates.

Reaction of bisketimines with phosgene affords diisocyanates.

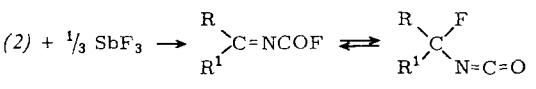
Treatment of the ketimine (3), R = H, R^1 = n-C_3H_7, with oxalyl dichloride leads to 4-isopropyl-5-phenylpyrrole-2,3-dione (5), as dark red prisms, m.p. 143–144 °C (from benzene), in 49 % yield.

1-Halogenoalkyl isocyanates (2) are very reactive. We have studied their reactions with water, alcohols, ammonia, primary and secondary amines, alkoxides, silver cyanate, and sodium azide. That with antimony trifluoride at 120–140 °C gives N-(fluoroformyl)-ketimines (6).



(3) (4)

	R	R¹	Yield (%)	B.p. (°C/torr)	n_D^{20}	d_4^{20}
(4a)	H	n-C_3H_7	70	115–117/7	1.5420	1.0767
(4b)	CH_3	CH_3	75	97–98/8	1,5455	1.0373



(2) + 1/3 SbF_3 → (6)

	R	R¹	Yield (%)	B.p. (°C/torr)	M.p. (°C)
(6a)	C_6H_5	C_6H_5	40	115/0.1	57–59
(6b)	C_6H_5	p-$CH_3C_6H_4$	30	120/0.01	44–46

The IR spectra of compounds (2) and (6) contain pronounced bands at 2260 cm^{-1}, 1640 cm^{-1}, and 1770 cm^{-1}, which indicate the presence of N=C=O, C=N, and a halogenoformyl group. The spectra show that compound (2a) exists wholly in the isocyanate form, but that (2d) exists almost wholly in the *N*-(chloroformyl) form. The other compounds exist as an equilibrium mixture of the isocyanate and the *N*-(halogenoformyl) form. Triethylamine shifts the equilibrium towards the isocyanate form.

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Synthesis of Dipotassium Difluorodiphosphate by Thermal Reaction of Tetraphosphorus Decaoxide with Potassium Fluoride

By *H. Falius* [*]

Salts of difluorodiphosphoric acid $H_2[P_2O_5F_2]$ were first prepared from the corresponding ester[1] by a multi-step synthesis starting from $POCl_2F$. By contrast, the thermal reaction between P_4O_{10} and KF is complete within a short time (*ca.* 1 h) and affords $K_2[P_2O_5F_2]$ (1) directly.

$$P_4O_{10} + 4\,KF \xrightarrow{\Delta} 2\,K_2[P_2O_5F_2]$$

When an intimate mixture (prepared with exclusion of moisture) of the two components in stoichiometric proportions is heated to relatively low temperatures spontaneous reaction takes place, the mixture suddenly becoming liquid; heating is then stopped immediately. The melt solidifies to a brittle glass, which, when crushed, readily dissolves in water to give an almost neutral solution. Compound (1) is readily obtainable in crystalline form by fractional precipitation with ethanol.

The reaction does not proceed exclusively according to the equation given; approximately equal quantities of $[PO_2F_2]^-$ (2), $[PO_3F]^{2-}$ (3), $[P_3O_{10}]^{5-}$, $[P_3O_9]^{3-}$, and $[P_4O_{12}]^{4-}$ are formed alongside the difluorodiphosphate. Thus, such reactions as $P_4O_{10} + 4\,KF \rightarrow 2\,K[PO_2F_2] + 2/n(KPO_3)_n$ (where $n = 3,4$) also occur. However, isolation of (1) presents no difficulties because it is the only product to crystallize during work-up of the reaction mixture; the polyphosphates form oils and fluoromonophosphates remain is solution.

The properties of compound (1) have not hitherto been documented. The colorless, doubly refracting crystals ($d_4^{20} = 2.34$) decompose on heating to give (2), (3), $[P_2O_7]^{4-}$ (4), and $[(PO_3)_n]^{n-}$. The anion is stable in neutral aqueous solution. On warming in acid solution, hydrolysis takes place to give $[PO_4]^{3-}$ and (4); in alkaline solution (3) is formed. Difluorophosphate does not form a difficultly soluble precipitate with any metal cation, nor with nitrone.

The ^{31}P–NMR spectrum of an aqueous solution of (1) shows a 1:1 doublet with $J_{PF} = 943$ Hz and $\delta = +17.8 \pm 1.0$ ppm (85% H_3PO_4 as external reference); the ^{19}F–NMR spectrum also has the structure expected for an AA'XX' system with $J_{PF} = 940$, $J_{PP'} = 2.5$, $J_{PF'} = -8$, and $J_{FF'} = 0$ Hz and $\delta = +72.6$ ppm ($CFCl_3$ as external reference). IR spectrum: 1295 s, 1160 s, 1120 m, 1045 (sh), 1007 vs, 869 vs, 834 vs, 736 vs, 530 vs, 490 m, 463 m, 397 m, 307 s, 163 w (br), 145 w (br), 134 w (br), 98 m, 84 m. (For assignments and couplings, see reference[2].) Elemental analysis and molecular-weight determination correspond to the composition (1).

Representative procedure:

P_4O_{10} (14.2 g, 0.05 mole) and KF (11.6 g, 0.2 mole) are heated as described above. On slow addition of 50 ml of ethanol to a solution of the reaction product in water (25 ml), an oil is precipitated. Further addition of 30 ml of ethanol to the decanted solution causes precipitation of a small volume of oil and a few crystals. A third precipitation with 75 ml of ethanol affords crystals that can be reprecipitated with ethanol from a small volume of water. The yield (1 g = 4%) is not high but this is not a great disadvantage because the starting materials are cheap.

The solubility of the sodium salt thwarted attempts at its preparation from NaF by an analogous procedure.

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[2] *C. Stölzer* and *A. Simon,* Z. anorg. allg. Chem. *339*, 30, 38 (1965).

Structure of the Anion $[O_3P-P(O_2)-PO_3]^{5-}$ in Pentasodium Triphosphate(IV,III,IV)-14-water

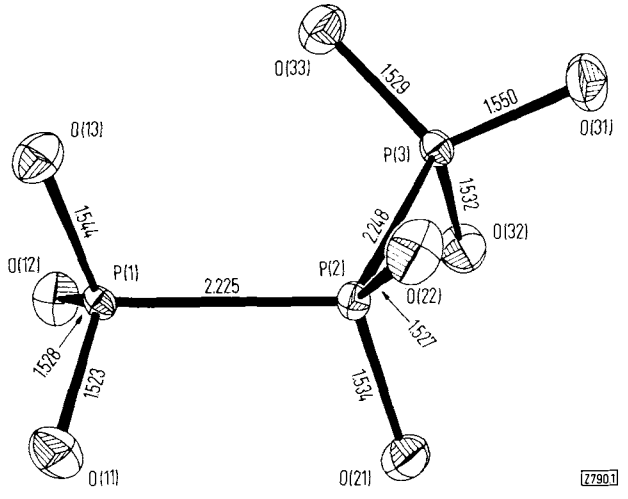
By *D. Mootz* and *H. Altenburg* [*]

Pentasodium triphosphate(IV,III,IV)-14-water, $Na_5P_3O_8 \cdot 14\,H_2O$ (1), which contains a chain of three contiguous phosphorus atoms, was first prepared by *Blaser* and *Worms*[1]. *Falius* described a more simple isolation from the reaction mixture produced on oxidation of red phosphorus with chlorite in an acid medium[2]. An incomplete crystal-structure

analysis[3] of a salt, $Cs_6[(PO_2)_6]\cdot xH_2O$ *(2)*, of the P_6 cyclic acid, and a more detailed one[4] for diammonium dihydrogen hypophosphate $(NH_4)_2H_2P_2O_6$ *(3)*, have been published and it seemed of interest to determine also the structure of *(1)* by X-ray methods.

Compound *(1)* crystallizes in the triclinic system with the space group $P\bar{1}$ with two formula units in the unit cell. The structure analysis (3332 independent data; precession camera with molybdenum radiation) was carried out according to the usual methods (Patterson function, Fourier syntheses, least-squares refinement, location of hydrogen atoms by the difference Fourier technique) and gave an *R* factor of 0.082.

The figure shows the structure of the anion with the atomic thermal vibration ellipsoids and bond lengths[5]. The estimated standard deviations are *ca.* 0.005 Å for P–P and 0.010 Å for P–O. Thus both P–P distances do not deviate significantly from their mean value 2.237 Å, although the observed difference could be correlated with the almost staggered conformation (see Figure) of the shorter bond



and the almost eclipsed conformation of the longer one. A P–P bond length of 2.20 ± 0.05 Å (mean value) was found in *(2)*, and 2,170 ± 0.003 Å in *(3)*. The relative lengthening in *(1)* may arise from the higher electric charge of the anion ($^5/_3$ electrons per P atom in *(1)* against 1 electron in *(2)* and *(3)*).

Within the limits of accuracy, the P–O distances are all equal and have a mean value of 1.533 Å. The bond angles are 109.9 ± 0.2° for P–P–P, 103.3 to 111.1° for P–P–O, and 110.8 to 115.8° for O–P–O. The Na^+ ions form puckered layers by corner-, edge-, and, in one case, face-linkage of more or less distorted NaO_6 octahedrons. Eight of the fourteen water molecules participate in three hydrogen bonds each and the other six are involved in two hydrogen bonds each; all the protons are involved in hydrogen bonding.

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We thank Dr. *Falius* for a sample of this substance.

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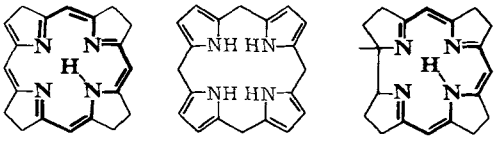
[5] We are grateful to Dr. *R. D. Rosenstein* for calculation of the data shown in the figure, with the ORTEP program by *C. K. Johnson*, ORNL-3794, Oak Ridge National Laboratory, Tennessee (1965).

Corphin, a Corrinoid-Porphinoid Ligand System

By *A. P. Johnson, P. Wehrli, R. Fletcher*, and *A. Eschenmoser*[*] [**]

The structural details of the formation of the corrin nucleus of vitamin B_{12} in nature are still unclear[1]. From a purely chemical point of view the question may be raised in this connection as to what the properties of compounds of type *(1)* would be. This hitherto unknown ligand system[2] is in the oxidation state of a hexahydroporphin; it is thus isomeric with the known structural type *(2)* of porphinogen and differs formally from the corrin structure *(3)* by a reductive ring contraction. In order to study the chemistry of this system we have been concerned with the development of methods for its synthesis; we describe here the preparation of the palladium complex *(9)* and a preparatively remarkable difference in the topological control of a reaction by nickel(II) and palladium(II) ions.



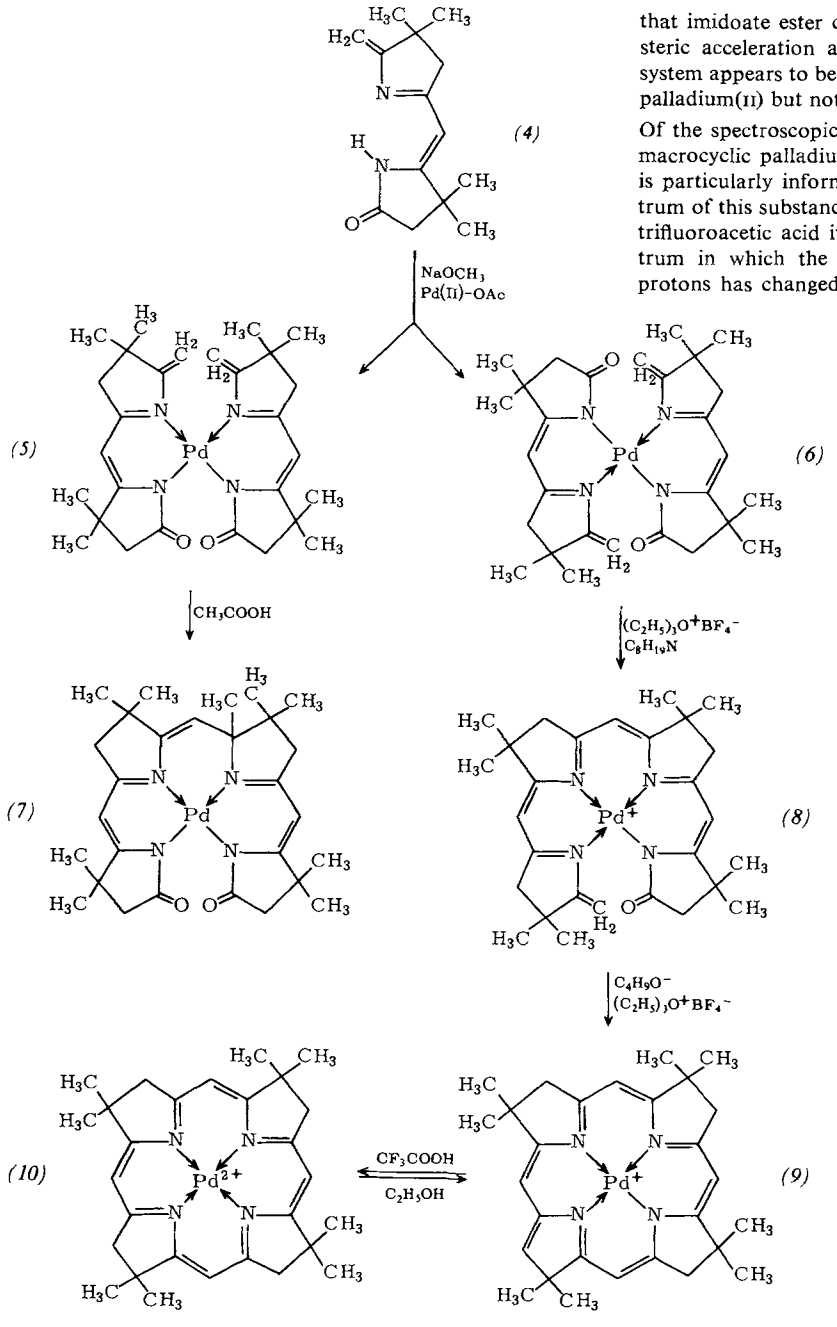
(1) *(2)* *(3)*

Complex formation from the sodium salt of the known bicyclic lactam *(4)*[3], *e.g.* by anhydrous palladium(II) nitrate (or acetate[4]) in acetonitrile (RT/*ca.* 15 min), leads to the diastereoisomeric, diamagnetic and therefore clearyl planoid complexes *(5)* and *(6)*; they are differentiated on thin-layer chromatography and can be separated by fractional crystallization (yields 26 and 24 %). The *cis*-configuration of the isomer *(5)* follows from the fact that under the influence of acetic acid at room temperature the compound is converted into a condensation product of structure *(7)*; in contrast, the centrosymmetric *trans*-isomer *(6)* is unchanged under these conditions (1.0 equivalent of CH_3COOH in CH_2Cl_2/RT/24 h). After treatment of the *trans*-isomer *(6)* with triethyloxonium tetrafluoroborate-diisopropylethylamine[5] in methylene chloride at room temperature the complexes *(8)* and *(9)* can be isolated as crystalline perchlorates in yields of *ca.* 20 % and 40–45 %, respectively. The mono-condensed complex *(8)* can be cyclized very easily by triethyloxonium tetrafluoroborate to give *(9)*; preliminary deprotonation of the positively charged lactam complex ion being necessary[8].

The changes *(6)* → *(8)* and *(8)* → *(9)* involve base-catalyzed imidoyl ester condensations of the type previously described in the synthesis of corrin complexes[3,9]. The intramolecular condensation steps occur very rapidly and intermediate imidoyl ester derivatives could not be observed.

All our attempts to achieve condensation between two molecules of the bicyclic lactam *(4)* by treatment of the corresponding free alkyl imidoate derivatives[3,9,10] with bases or acids failed. Equally unsuccessful were attempts to achieve with nickel(II) or cobalt(II) complexes what was finally accomplished with palladium(II). Treating the potassium salt of *(4)* with 1 equivalent of anhydrous nickel(II) or cobalt(II) perchlorate in acetonitrile leads in each case to a complex of structure *(11)*[11], which can be isolated in crystalline form in yields of 80–90 %. These products are homogeneous on thin-layer chromatography, paramagnetic in $CHCl_3$ solution, and presumably tetrahedroid in structure. The corresponding imidoate diperchlorates *(12)*[12] can be isolated in crystalline form and are also paramagnetic in $CHCl_3$; no intramolecular cyclization of these complexes could be detected by UV spectroscopy when they were subjected to thermal treatment or exposed to various basic conditions.

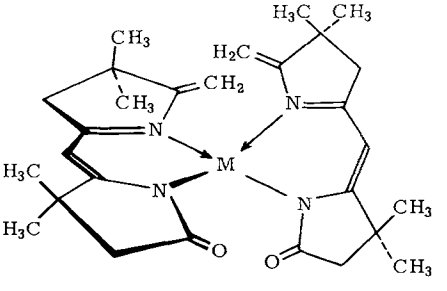
The palladium(II) ion is known to have a stronger tendency than nickel(II) to planoid coordination[13]. The difference in



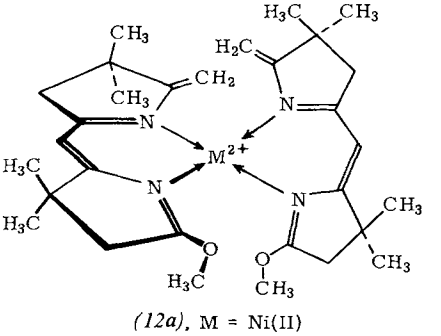
that imidoate ester condensations in this system do require steric acceleration and the necessary strain in the ligand system appears to be provided by the "planarity pressure" of palladium(II) but not by that of nickel(II).

Of the spectroscopic data that support the structure of the macrocyclic palladium(II) complex *(9)*, the NMR spectrum is particularly informative. In deuteriochloroform the spectrum of this substance consists of 12 separate singlets, but in trifluoroacetic acid it appears as a sharp three-singlet spectrum in which the intensity ratio of the vinyl:methylene protons has changed from 5:6 to 4:8. In deuteriotrifluoroacetic acid the intensity of the CH_2 singlet at 3.05 ppm[16] is time-dependent, the signal disappears almost completely within a few hours at room temperature. Thus, in trifluoroacetic acid the compound exists as the protonated centrosymmetric tetraketimine complex *(10)*; in agreement therewith, the UV spectrum in ethanol, but not in trifluoroacetic acid, has the character of a bathochromically shifted corrin

behavior of the complexes *(6)* and *(11a)* serves as a drastic preparative illustration of this property. However, failure of the imidoate ester condensation with the nickel complexes *(11a)* and *(12a)* should not be ascribed to any resistance of the nickel ion to a flattening of the ligand system since *(11a)* is converted into a diamagnetic nickel complex of type *(7)* under the influence of protic acids[10]; rather it seems



(11a), M = Ni(II)
(11b), M = Co(II)



(12a), M = Ni(II)
(12b), M = Co(II)

Table 1. Spectroscopic data for the palladium(II) complexes *(5)*—*(9)* [14].

(5)	
M.p.	*ca.* 220 °C (decomp.), from CCl_4-cyclohexane.
λ_{max} (nm) [log ε]	257 [shoulder/4.07],300 [3.87],380 [4.19] in C_2H_5OH.
ν_{max} (cm^{-1})	1685—1695s, 1645m, 1567s, 1497—1505s, *etc.*, in $CHCl_3$.
δ (ppm)	1.10/1.13/1.23/1.56 (4s/8 CH_3), 2.16/2.49 (AB system/$\|J\| \approx 17$ Hz/2 CH_2), 2.54 (s/2 CH_2), 4.20 (s, broad/2 H), 5.04 (s/4 H) in $CDCl_3$.
m^+/e	572 (39 %), 571 (31 %), 570 (74 %), 569 (46 %), 568 (92 %/M^+ ^{106}Pd), 567 (91 %), 566 (45 %), 553 (100 %/M^+-CH_3/ + corresponding companion peaks).
M (found)	in CH_2Cl_2 (25 °C): 573.
(6)	
M.p.	*ca.* 240 °C (decomp.), from $CH_2Cl_2/(C_2H_5)_2O$.
λ_{max} (nm) [log ε]	258 [4.06], 290 [3.93], 385 [4.15] in C_2H_5OH.
ν_{max} (cm^{-1})	1697s, 1640w, 1570s, 1497—1505s *etc.* in CH_2Cl_2.
δ (ppm)	1.11/1.21/1.28/1.33 (4s/8 CH_3), 2.17 (s/2 CH_2), 2.47/2.67 (AB system/$\|J\| \approx 18$ Hz/2 CH_2), 4.18 (s, broad/2 H), 5.00 (s/4 H) in $CDCl_3$.
m^+/e	572 (42 %), 571 (36 %), 570 (77 %), 569 (52 %), 568 (100 %/M^+ ^{106}Pd), 567 (94 %), 566 (51 %), 553 (87 %/M^+-CH_3/ + corresponding companion peaks)
M (found)	in CH_2Cl_2 (25 °C): 564.
(7)	
M.p.	240—250 °C, from C_2H_5OH.
λ_{max} (nm) [log ε]	312 [3.94], 371 [4.13], *ca.* 440 [shoulder/3.7] in C_2H_5OH.
ν_{max} (cm^{-1})	1686s, 1589s, 1568s, 1520 vs *etc.* in $CHCl_3$.
δ (ppm)	0.99/1.01/1.06/1.10/1.20/1.23/1.39/1.45 (8s, that at 1.23 ppm with double intensity/27 H), 2.0—2.9 ("m"/8 H), 4.62 (s/1 H), 4.91 (s/1 H), 5.00 (s/1 H) in $CDCl_3$.
m^+/e	568 (M^+/5 %), 557 (39 %), 556 (25 %), 555 (82 %), 554 (30 %), 553 (100 %/M^+-CH_3), 552 (77 %), 551 (35 %).
(8)	
M.p.	*ca.* 180 °C (decomp.), from CH_2Cl_2/C_2H_5OAc.
λ_{max} (nm) [log ε]	265 [4.20], 337 [4.41], 398 [3.79], 428 [3.82], 483 [4.06] in C_2H_5OH; 252 [4.25], 301 [4.36], 318 [shoulder/4.30], 333 [shoulder/4.14], 400 [3.62], 492 [3.93] in C_2H_5OH + 1 drop of 1 N ethanolic C_2H_5ONa per 50 ml.
ν_{max} (cm^{-1})	1748m, 1622m, 1598s, 1550s, 1510vs *etc.* in $CHCl_3$.
δ (ppm)	1.26/1.32/1.42/1.44/1.52/1.54 (6s/8 CH_3), 2.48/2.62 (AB system/$\|J\| \approx 17$ Hz/2 H), 2.98 (s/2 H), 3.33 (s/2 H), 3.40 (s/2 H), 4.66 (d/$\|J\| \approx 2$ Hz/1 H), 4.80 (d/$\|J\| \approx 2$ Hz/1 H), 6.09 (s/1 H), 6.40 (s/1 H), 6.46 (s/1 H) in $CDCl_3$.
(9)-ClO_4	
M.p.	*ca.* 160 °C (decomp.) from CH_2Cl_2/C_2H_5OAc.
λ_{max} (nm) [log ε]	a) in C_2H_5OH: 258 [4.06], 267 [4.07], 298 [4.36], 336 [4.52], 362 [4.06/weak shoulder], 400 [3.71/flat], 488 [4.09/broad], 552 [3.54/shoulder], unchanged in C_2H_5OH/CF_3COOH 4:1 and 3:2. b) in CF_3COOH: intense end absorption < 270nm, 310 [4.68/weak shoulder], 323 [4.77], 342 [4.95], 385 [4.21/shoulder], 400 [4.34/flat], 426 [4.89] [= spectrum of *(10)*]; mixed spectrum *(11)*:*(10)* *ca.* 1:1 in C_2H_5OH/CF_3COOH *ca.* 2:3.
ν_{max} (cm^{-1})	1680w, 1642m (shoulder), 1622s, 1587m, 1550s, 1526m, 1508s (ClO_4^-: 1090s broad) *etc.* in CH_2Cl_2.
δ (ppm)	a) in $CDCl_3$: 1.40/1.46/1.48/1.52 (4 s/8 CH_3), 3.23 (s/2 H), 3.30 (s/2 H), 3.40 (s/2 H), 6.19 (s/1 H) 6.29 (s/1 H), 6.41 (s/1 H), 6.53 (s/1 H), 6.57 (s broad/1 H). b) in CF_3COOH: 1.42 (s/24 H), 3.10 (s/8 H), 6.07 (s/4 H). c) in CF_3COOD: 1.42 (s/24 H), 3.05 (s broad/49 % of 6 H after 18 min at RT), 6.02 (s/4 H); Intensity of the ($-CH_2$)-signal: 25 % after 50 min 11 % after 78 min *ca.* 4 % after 115 min < 1 % after 49 h Intensity of the (=CH—) singlet: 90 % after 49 h 82 % after 72 h 53 % after 384 h
(9)-BF_4^- [15] m^+/e	536 (35 %), 535 (30 %), 534 (66 %), 533 (31 %), 532 (^{106}Pd/M^+-H/72 %), 531 (65 %), 530 (38 %), 517 (M^+-H-CH_3/100 %/ + corr. companion peaks), 502 (M^+-H-2 CH_3/71 %/ + corr. companion peaks), 487 (M^+-H-3 CH_3/35 %/ + corr. companion peaks), 472 (M^+-H-4 CH_3/28 %/ + corr. companion peaks).

spectrum. As expected, the tetraketimine complex *(10)* is extremely electrophilic; even in a 1:1 mixture of trifluoroacetic acid and ethanol it exists predominantly in the deprotonated form *(9)*.

We use the trivial name corphin for the ligand system *(1)* to hint at its structural relationships to both the porphin and the corrin system [17].

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[2] Compounds of this type are an objective of the work by *H. H. Inhoffen et al.* on "Gemini-Porphyrins"; see, *e.g. H. H. Inhoffen* and *W. Nolte*, Tetrahedron Letters *1967*, 2185. Derivatives of a 5,15-diaza analog have been synthesized by *R. Scheffold*, ETH Zürich (personal communication).

[3] *E. Bertele, H. Boos, J. D. Dunitz, F. Elsinger, A. Eschenmoser, I. Felner, H. P. Gribi, H. Gschwend, E. F. Meyer, M. Pesaro*, and *R. Scheffold*, Angew. Chem. *76*, 393 (1964); Angew. Chem. internat. Edit. *3*, 490 (1964); detailed directions for the preparation of *(4)* are contained in the Dissertations of *R. Scheffold* (1963) and *P. Wehrli* (1967) (ETH, Zürich).

[4] Cf. *T. A. Stephenson, S. M. Monehouse, A. R. Powell, J. P. Heffer*, and *G. Wilkinson*, J. chem. Soc. (London) *1965*, 3632. Use of anhydrous Pd(II) perchlorate in acetonitrile is not advisable (explosion in one of the preparative experiments).

[5] 0.05 equiv. of diisopropylethylamine [6] + 3.0 equiv. of triethyloxonium tetrafluoroborate [7], 2.5 h, then 3.0 equiv. each of base and oxonium salt added, and reaction allowed to proceed for a further 45 min (N_2 atmosphere). Working up with dilute $HClO_4$, $NaClO_4$, and CH_2Cl_2.

[6] *S. Hünig* and *M. Kiesel*, Chem. Ber. *91*, 380 (1958).

[7] *H. Meerwein, G. Hinz, P. Hofmann, E. Kroning*, and *E. Pfeil*, J. prakt. Chem. *147*, 17 (1937); Org. Syntheses *46*, 113 (1966).

[8] *E.g. (8)* + 1 equiv. of potassium *tert*-butoxide in *tert*-butyl alcohol; after removal of the solvent, reaction with *ca.* 8 equiv. of $(C_2H_5)_3O^+$ BF_4^- in CH_2Cl_2, RT, 25 min; yield *ca.* 70 %. Cf. UV spectrum of *(8)* in C_2H_5OH/C_2H_5ONa.

[9] *A. Eschenmoser*, Pure appl. Chem. *7*, 297 (1963); *A. Eschenmoser, R. Scheffold, E. Bertele, M. Pesaro*, and *H. Gschend*, Proc. Roy. Soc. (London), Ser. A *288*, 306 (1965).

[10] *P. Wehrli*, Dissertation, ETH Zürich (1967).

[11] Compare the chemical, analytical, and spectroscopic characterization of these complexes and some of their derivatives in ref. [10].

[12] Prepared by direct complexation of the methyl imidoate ester from *(4)* [10].

[13] Cf., for example, *D. P. Graddon*: An Introduction to Coordination Chemistry. Pergamon Press, London, 1961, pp. 29ff.

[14] IR: relative intensities s = strong, m = medium, w = weak; NMR: δ-values referred to $\delta_{TMS} = 0$. The complexes *(5)*—*(9)* gave correct analytical values.

[15] M.p. > 250 °C; the UV, IR, and NMR spectroscopic data correspond to those of the perchlorate.

[16] Remarkably the signals are not shifted to lower field.

[17] In a paper by *J. A. Hill, J. M. Pratt*, and *R. J. P. Williams*, J. theoret. Biol. *3*, 423 (1962), the designation "corphyrins" was used for vitamin B_{12} and its derivatives; however, for these compounds designation as derivatives of corrin has come to stay.

New Boron Heterocycles

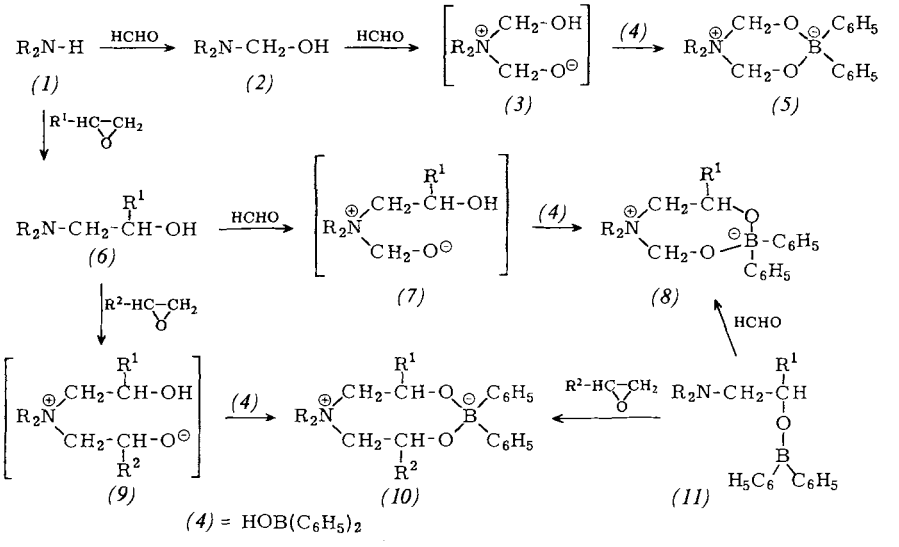
By *W. Kliegel*[*]

In the reaction of secondary amines *(1)* with formaldehyde the hypothetical[1] second reaction intermediate, the betaine-like formaldehyde adduct *(3)* of hydroxymethylamine *(2)*, can be trapped by esterification with hydroxydiphenylborane *(4)*. The free electrons of the negatively charged oxygen atom can go into the empty orbital of the boron atom, thus leading to fixation of the aldehyde molecule in the ring.

Ethanolic solutions of *(1)* are heated briefly to boiling with two molecular equivalents of formaldehyde in aqueous solution and one molecular equivalent of *(4)*[2]. The difficultly soluble[3] compound *(5)* crystallizes out of the reaction solution in analytically pure form.

In the same way, *N*-(2-hydroxyalkyl)dialkylamines *(6)* react with formaldehyde and *(4)* to give heterocyclic compounds having seven-membered rings *(8)*.

If the reaction is carried out with epoxides in place of formaldehyde, corresponding eight-membered rings *(10)* are formed.



(4) = $HOB(C_6H_5)_2$

		Decomp. point (°C)
5a)	$R_2 = -(CH_2)_3-$	157
5b)	$R_2 = -(CH_2)_4-$	135
5c)	$R_2 = -(CH_2)_5-$	125
5d)	$R_2 = -(CH_2)_2-O-(CH_2)_2-$	96
5e)	$R = C_2H_5$	114
5f)	$R = n\text{-}C_3H_7$	100

		Decomp. point (°C)
8a)	$R = C_2H_5$, $R^1 = H$	154
8b)	$R_2 = -(CH_2)_5-$, $R^1 = H$	106 [a]
8c)	$R_2 = -(CH_2)_5-$, $R^1 = CH_3$	164
10a)	$R = C_2H_5$, $R^1 = H$, $R^2 = CH_3$	203 [a]
10b)	$R = C_2H_5$, $R^1 = R^2 = H$	229

[a] Present as the hydrate.

Compounds *(8)* and *(9)* are also obtained when corresponding esters of *(4)* and amino alcohols *(11)*[4] are allowed to react with formaldehyde or epoxides, as was established with *(8a)* and *(10a)* – identical products were obtained by both routes. The yields vary between 30 and 70%. The colorless, highly stable compounds decompose on heating. Formaldehyde is liberated on pyrolysis of *(5)* and *(8)*[5].

The insolubility of the heterocycles in weakly polar solvents, their IR and NMR spectra[6], as well as their elemental analyses, are in accord with the betaine structure suggested.

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[1] *P. A. S. Smith*: Open-Chain Organic Nitrogen Compounds. W. A. Benjamin, New York 1965, Vol. 1, p. 27.

[2] Hydroxydiphenylborane was used in the form of: a) hydrate; see *H. J. Roth* and *H. N. El Din*, Arch. Pharmaz. *295*, 679 (1962); b) oxybis(diphenylborane); see *R. Neu*, Chem. Ber. *87*, 802 (1954); c) aminoethoxydiphenylborane: smooth transesterification; cf. *M. Umland*, Angew. Chem. *79*, 583 (1967); Angew. Chem. internat. Edit. *6*, 574 (1967); d) triphenylborane; diphenylation by the action of amino alcohols or chelating agents; see, *e.g.*, *H. J. Roth*, *R. Brandes*, and *Ch. Schwenke*, Arch. Pharmaz. *297*, 766 (1964); *R. Köster* and *G. W. Rotermund*, Liebigs Ann. Chem. *689*, 40 (1965).

[3] Soluble only in strongly polar solvents such as acetic acid and trifluoroacetic acid, also moderately soluble in warm pyridine or acetonitrile.

[4] *B. Skowronska-Serafinowa*, *B. Ustupska-Stefaniak*, and *M. Makosza*, Roczniki Chem. (Ann. Soc. chim. Polonorum) *35*, 723 (1961); Chem. Abstr. *55*, 23396 (1961).

[5] Gaseous pyrolysis products trapped in water; formaldehyde test with chromotropic acid, after *F. Feigl*: Spot Tests in Organic Analysis. Elsevier, Amsterdam 1960, p. 350.

[6] ^1H–NMR spectrum of *(5a)* in $CF_3COOH/CDCl_3/TMS$: the methylene protons of the acetal-like grouping $-O-CH_2-\overset{\oplus}{N}R_2-CH_2-O-$ give a four-proton singlet at $\delta = 5.13$ ppm; – of *(8a)* in the same solvent mixture: two-proton singlet for the methylene protons of the group $-O-CH_2-\overset{\oplus}{N}R_2-$ at $\delta = 5.15$ ppm.

Identification of the n-σ* Transition in the Electron Excitation Spectrum of 2-Butanone

By *H.-H. Perkampus*[*]

Three electronic transitions are to be considered for the carbonyl group[1]. The spectroscopic properties of one of these, the longwave n-π* transition, have been known for a long time[2]. In contrast, there is still some uncertainty surrounding the electronic transition in the range 50000–56000 cm^{-1}. In many monographs and books, this transition in the near vacuum-ultraviolet is assigned to an N–V transition, *i.e.* to a π-π* transition analogous to that of an ethylenic double bond[3]. However, according to *McMurry*[4] it is a permitted n-σ* transition, whose oscillator strength should be about 0.02. The π-π* transition then lies at higher wave numbers ($\tilde{\nu} > 60000\ cm^{-1}$)[1], as is evident from measurements in the vacuum ultraviolet[5].

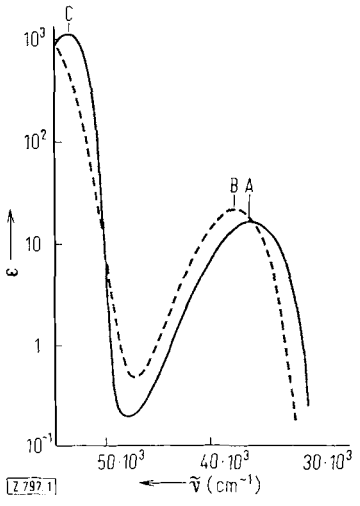

Fig. 1. Electron excitation spectrum of 2-butanone.
— *n*-Heptane; $c = 2.94 \times 10^{-3}$, 2.26×10^{-2}, and 2.26×10^{-1} M
----- Water; $c = 5.04 \times 10^{-3}$ and 5.04×10^{-2} M.
A: $\tilde{\nu} = 36100$ cm^{-1} ($\varepsilon = 17$), B: $\tilde{\nu} = 37500$ cm^{-1} ($\varepsilon = 21$),
C: $\tilde{\nu} = 53700$ cm^{-1} ($\varepsilon = 1250$).

The measurements were carried out with a Zeiss spectrophotometer PMQ II (double monochromator MM12 with CaF_2 prisms, Suprasil cuvettes of layer thicknesses 0.10 and 1.00 cm); a stream of dry nitrogen was passed through the instrument before and during use. The spectral resolving power was 70 cm^{-1} at 54000 cm^{-1}; the scattered light was below 1% at 55000 cm^{-1}.

It should be possible to decide whether the second transition is a n-σ^* or a π-π^* transition from the solvent dependence of the ultraviolet spectra[6]. The ultraviolet spectrum of 2-butanone in *n*-heptane and water as solvents (see Figure) clearly shows that the second electronic transition, like the n-π^* transition, undergoes a hypsochromic shift as the solvent changes from nonpolar to polar. Since a bathochromic shift is generally to be expected for a π-π^* transition[6], the assignment according to *McMurry*[4] is reasonable. In *n*-heptane the oscillator strength for this n-σ^* transition is found to be $f = 0.018$.

H. Wolf has recently reported similar hypsochromic shifts for the second electronic transition[7] in the CD spectra of saturated lactams.

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[4] *H. L. McMurry*, J. chem. Physics *9*, 231 (1941).

[5] *J. S. Lake* and *A. J. Harrison*, J. chem. Physics *30*, 361 (1959).

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[7] *H. Wolf*, personal communication.

A Generator System for 1-(2-Chloroethyl)-aziridine

By *H. M. Rauen, K. Norpoth*, and *H. Schriewer*[*]

Whereas aziridine is accessible in any amount desired for synthetic purposes, 1-(2-chloroethyl)aziridine has not yet been made on a preparative scale. We here describe a generator system by which a solution of this reactive compound may be obtained.

In buffered aqueous solution *N,N*-bis(2-chloroethyl)amine undergoes, as first reaction step, Cl^- heterolysis to 1-(2-chloroethyl)aziridine ($k = 5.0 \times 10^{-4}$ sec^{-1} at 10^{-3} M, 37 °C, pH = 7.2; $k = 12.3 \times 10^{-4}$ sec^{-1} at 10^{-3} M, 43 °C, and pH = 7.2; in each case 0.2 M phosphate buffer[1]). However, the reaction continues *via* hydrolytic ring opening to *N*-(2-chloroethyl)-*N*-(2-hydroxyethyl)amine, renewed Cl^- heterolytic ring closure to 1-(2-hydroxyethyl)aziridine ($k = 1.0 \times 10^{-4}$ sec^{-1} at 10^{-3} M, 37 °C, and pH = 7.2; $k = 2.7 \times 10^{-4}$ sec^{-1} at 10^{-3} M, 43 °C, and pH = 7.2; in each case 0.2 M phosphate buffer[1]), and hydrolytic ring opening to diethanolamine.

The rate constants of the hydrolytic ring opening reactions are probably lower than those of the Cl^- heterolytic ring closures. Since the ring opening reactions are rate-determining, the aziridine derivatives accumulate in a static reaction system. In the conditions given above, the yield of 1-(2-chloroethyl)aziridine increases rapidly at first, remains constant between 60 and 120 min (37 °C), and then falls less rapidly[2]. If the static reaction system is disturbed by a continuous stream of inert gas, then the gaseous 1-(2-chloroethyl)aziridine is carried over in the gas stream. The effluent is passed into an ice-cooled double trap (Normag No. 9213) containing equal volumes of chloroform and water. The entry tube terminates just above the boundary between the solvents. The water largely prevents the volatile chloroform being removed in the gas stream. The gaseous 1-(2-chloroethyl)-aziridine that passes over dissolves first in the water but then immediately goes into the chloroform, in which it is much more soluble (partition coefficient $H_2O/CHCl_3 = 0.13{:}1$). When the chloroform layer is removed it provides a solution of 1-(2-chloroethyl)aziridine suitable for preparative purposes.

Identification (proposal by *H. Arnold*): Add HBr-glacial acetic acid, keep at room temperature for 12 h, remove the solvent. *N*-(2-Bromoethyl)-*N*-(2-chloroethyl)amine crystallizes (analysis and comparison with an authentic product).

If the concentration of *N,N*-bis-(2-chloroethyl)amine is raised, so as to increase the yield of aziridine derivative, then it is advisable to use a pH-stat in spite of the presence of the phosphate buffer. Direct extraction of the incubation solution with chloroform (*i.e.* without transferring the gaseous products with a stream of inert gas) is not advisable since undecomposed starting material is also soluble in chloroform (partition coefficient $H_2O/CHCl_3 = 0.09{:}1$).

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A Novel Tricarbonylchlororhenium(I) and Reactions of Substituted Carbonylchlororheniums(I) with Water and Other Oxygen-containing Ligands

By *W. Hieber* and *W. Rohm*[*]

Continuing our work on replacement reactions of carbonylhalogenorhenium complexes $Re(CO)_5X$ and $[Re(CO)_4X]_2$ with organyl chalcogenides[1] we examined the thermal behavior of a binuclear complex containing diphenyl sulfide, namely $[Re(CO)_3S(C_6H_5)_2Cl]_2$[1].

$S(C_6H_5)_2$ is evolved when this compound is heated above 90 °C in a high vacuum; there remains a residue that contains chlorine but no sulfur and whose IR spectrum shows only the ν(CO) vibrations of three carbonyl groups. This material consists of a chlorotricarbonyl $[Re(CO)_3Cl]_x$. Starting material and products are in thermal equilibrium: treat-

ment of the solid product with diphenyl sulfide quantitatively regenerates the starting material:

$$[Re(CO)_3S(C_6H_5)_2Cl]_2 \overset{\Delta}{\rightleftharpoons} (CO)_3Re\begin{matrix}Cl\\ \diagup\ \diagdown\\ Cl\end{matrix}Re(CO)_3 \quad (1)$$
$$+\ 2\ S(C_6H_5)_2$$

In the cold the thermolysis product is soluble only in acetone, but when heated it dissolves without evolution of gas in polar solvents, *i.e.* in reagents containing a donor atom. From this fact, from the IR spectrum and elemental analysis, and above all from the reactivity, we conclude that we are dealing with a binuclear structure containing one free coordination position per rhenium atom; however, a higher polymer is not excluded.

The very hydrophobic substance *(1)*, wholly insoluble also in boiling benzene, dissolves on prolonged heating in ethers, alcohols, and even in water with formation of binuclear and mononuclear complexes[1] obtained by addition of solvent molecules, namely $[Re(CO)_3LCl]_2$ or $Re(CO)_3L_2Cl$. Specifically, pure crystalline compounds $[Re(CO)_3LCl]_2$ were obtained with ligands (L) = tetrahydrofuran *(2)*[1], ethanol *(3)*, and methanol *(4)*. Reaction with water affords an aqua complex that is indicated by preliminary work to be $Re(CO)_3(H_2O)_2Cl$ *(5)*.

The IR spectrum (KBr disk) of *(5)* shows two sharp ν(OH) stretching vibrations and the δ(HOH) band, whereas only one sharp ν(OH) absorption is observed for *(3)* and *(4)*.

	ν(CO) (cm^{-1})	ν(OH) (cm^{-1})	δ(HOH) (cm^{-1})
(5)	2018 vs, 1930 vs (sh)	3607 m, 3541 m	1603 m
(3)	2045 vs, 1931 vs, 1903 vs	3546 m	
(1)	2064 vs, 1946 vs (sh)		

In all the complexes, "ether-like"-bound (sp^3 hybridized) oxygen behaves as a donor atom. Hitherto the only known carbonylhalogenorhenium compounds containing oxygen-donor ligands of that type have been those with "ylide-like"-bound (sp-hybridized) ligands[2] such as pyridine 1-oxide, triphenylphosphine oxide, and the corresponding bidentate derivatives.

Whereas carbonyl complexes of several metals containing cyclic ethers (some of them unstable) are known[3], compounds *(3)–(5)* are the first in which it has been possible to introduce alcohols and even water as donor ligands into the carbonyl derivative. (In ionic reaction products of metal carbonyls with alcohols, *e.g.* $[V(CH_3OH)_6][V(CO)_6]_2$[4], the alcohol and carbon monoxide are not bound to one and the same metal atom.)

Meanwhile, starting with *(1)* we have isolated also carbonylchlororhenium complexes containing dioxane, diisopropyl ether, and acetone (with which *(1)* reacts even in the cold) and studied their IR spectra. Further, reactions with *sec*- and iso-butyl alcohol, ethylene glycol, benzophenone, benzil, and acetylacetone have been observed. Moreover, weakly basic nitrogenous compounds such as diphenylamine and triphenylamine react with *(1)*; but the substances formed in these reactions have not yet been investigated.

Experimental:

Di-μ-chlorohexacarbonyldirhenium(I) *(1)*:

$[Re(CO)_3S(C_6H_5)_2Cl]_2$ was heated in a sublimation apparatus at 120–130 °C in a high vacuum for one day. Diphenyl sulfide separated as drops on the cold finger. The pale yellow residue was digested several times with hot benzene, to remove undecomposed starting material, and then dried in a high vacuum. It contained a small proportion (*ca.* 4%) of insoluble, undefined decomposition products.

Preparation of complexes *(2)–(5)*:

Compound *(1)* is heated on a fritted filter (G 4) with tetrahydrofuran[1], ethanol, methanol, or water until dissolution has occurred, then a small residue is filtered off, and the solvent is removed in a vacuum. The products, usually first precipitated as oils, crystallize during a few hours' drying in a high vacuum and can be recrystallized from chloroform.

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[3] See, *e.g.*, *W. Strohmeier*, Angew. Chem. *76*, 873 (1964); Angew. Chem. internat. Edit. *3*, 730 (1964); *W. Strohmeier, C. Barbeau*, and *D. v. Hobe*, Chem. Ber. *96*, 3254 (1963); *C. Barbeau*, Dissertation, Universität Würzburg, 1963; *E. O. Fischer* and *M. Herberhold*, Experientia, Suppl. *9*, 259 (1964); *M. I. Bruce* and *F. G. A. Stone*, J. chem. Soc. (London) A *1967*, 1238.

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Degradation of Fructose Amino Acids to *N*-(2-Furoylmethyl)amino Acids. Intermediates in Browning Reactions[1]

By *K. Heyns, J. Heukeshoven*, and *K.-H. Brose*[*]

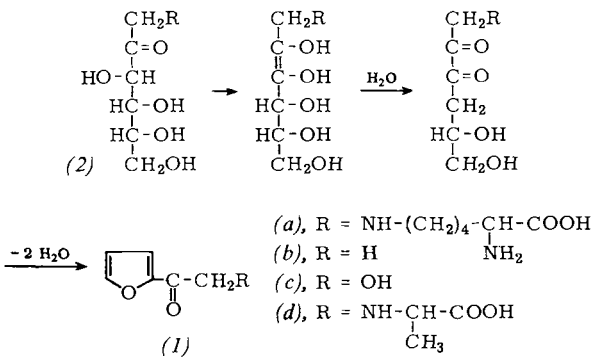
On ion-exchange chromatography of milk-powder hydrolyzates, *Erbersdobler* and *Zucker*[2,3] found the elution region of the basic amino acids to contain, besides arginine, a ninhydrin-positive substance X that was formed also on mere heating together of glucose with lysine or lysine-containing proteins and subsequent treatment with acid. These reactions occur also in browning reactions of Maillard type, and they decrease the biological value of the protein.

We obtained this substance X by heating ε-fructose-lysine *(2a)*[4] with 6 N HCl at 90 °C (1 h) and isolated it in a pure state by preparative ion-exchange chromatography. It is, however, not necessary to use pure *(2a)* for the acid hydrolysis; crude *(2a)*, which is prepared by heating glucose with lysine in methanol, leads to the same substance. Its analytical data indicate structure *(1a)*, that of a lysine-containing derivative of acetylfuran *(1b)*.

The IR, UV, and NMR spectra of the two compounds are very similar. IR (KBr) for *(1a)*: 3440 s, 2980 s, 1740 vs, 1682 vs, 1570 m, 1465 s, 1400 s cm^{-1}; for *(1b)*: 344 s, 2980 s, 1685 vs, 1565 m, 1455 s, 1390 m cm^{-1}. The strong band in the IR spectrum of *(1a)* at 1740 cm^{-1} is due to the carboxyl group of the lysine residue. The bands at 1682 and 1570 cm^{-1} are assigned to the conjugated carbonyl group. The UV bands are characteristic of the furan ring: for *(1a)* (dil. HCl): 281 and 227 nm; for *(1b)* (H_2O): 275 and 226 nm. The furan ring protons appear in the NMR spectra with fully corresponding chemical shifts and coupling constants, except that the signals for *(1a)* are shifted by 0.15–0.20 ppm downfield with respect to those for *(1b)* (in D_2O, tetramethylsilane as internal standard). For *(1a)*: H-3 τ = 2.35; H-4 τ = 3.20; H-5 τ = 2.05; $J_{3,4}$ = 3.7 Hz; $J_{5,4}$ = 1.5 Hz; $J_{3,5}$ = 0.5 Hz. For *(1b)*: H-3 τ = 2.57; H-4 τ = 3.35; H-5 τ = 2.21; $J_{3,4}$ = 3.7 Hz; $J_{5,4}$ = 1.6 Hz; $J_{3,5}$ = 0.7 Hz.

Vigorous treatment with acid degrades *(1a)* to lysine. Fluorodinitrobenzene converts *(1a)* into a mono(dinitrophenyl) derivative that is cleaved to α-(dinitrophenyl)lysine on vigorous action of acid, whereby it is proved that the ε-amino group of the lysine of *(1a)* is bound to the acetylfuran[5]. *(1a)* takes up 3 mol. equiv. of H_2 on catalytic hydrogenation.

Formation of *(1a)* from *(2a)* appears to parallel that of 1-(2-furyl)glycolaldehyde *(1c)* on acid treatment of fructose *(2c)* [6].



On treatment of fructose-alanine *(2d)* with acid an analogous series of reactions leads to *N*-(2-furoylmethyl)alanine *(1d)*. *N*-(2-Furoylmethyl)methylamine hydrochloride could be prepared as model substance from 1-methylamino-1-deoxy-fructose (yield 60 %).

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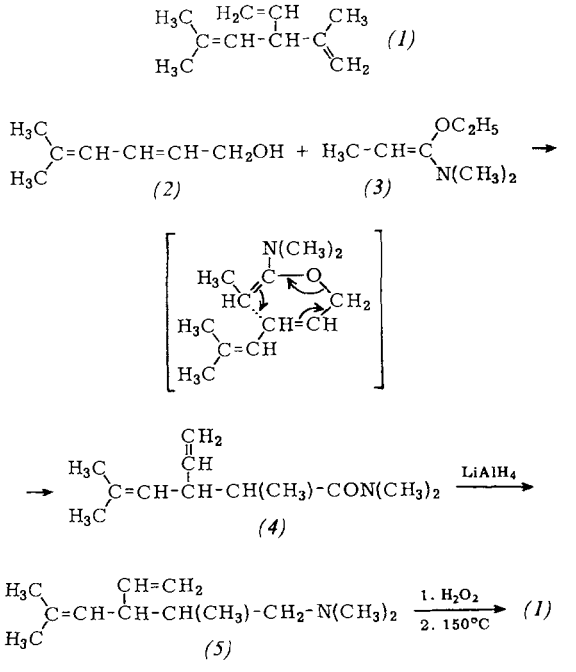
Synthesis of Santolinatriene

By *W. Sucrow* [*]

Santolinatriene was isolated by *Thomas* and *Willhalm* in 1964 from *Santolina chamaecyparissus* L. and was identified as 2,5-dimethyl-3-vinyl-1,4-hexadiene *(1)* [1].

Our work on preparation of 1,4-dienes from derivatives of *N,N*-dimethylpropionamide [2] suggested that the Claisen rearrangement of ketene *O,N*-acetals described by *Eschenmoser et al.* [3] might be useful for synthesis of a precursor of *(1)*.

When boiled with the 2.5-fold amount of 1-ethoxy-*N,N*-dimethylpropenylamine *(3)* [6] in xylene, 5-methyl-2,4-hexadien-1-ol *(2)* [4] (prepared by us by reducing 5-methyl-2,4-hexadienal [5] with $NaBH_4$), gives a 78 % yield of *N,N*-dimethyl-2,5-dimethyl-3-vinyl-4-hexenamide *(4)* [b.p. 80 °C (bath temp./0.1 torr. IR: $-CH=CH_2$ 3080, 992, 914; $-CON(CH_3)_2$ 1655 cm^{-1}. ^1H–NMR: $H_3C-C-CO$ (d) $\delta = 0.98$; $(H_3C)_2C=$ (d) 1.58, (d) 1.65; $>CH-CO$ (dq) 2.55; $-N(CH_3)_2$ (s) 2.83, (s) 2.99; $=C-CH-C=$ (m) about 3.1; $=CH_2$ (m) 4.88, (m) 5.02; $-CH=C<$ (m) about 4.9; $-CH=CH_2$ (ddd) 5.57 ppm]. Reducing *(4)* with $LiAlH_4$ in ether leads to *N,N*-dimethyl-*N*-(2,5-dimethyl-3-vinyl-4-hexenyl)amine *(5)* [b.p. 100 °C (bath temperature)/22 torr. IR: $=CH_2$ 3080, 1640, 998, 914 cm^{-1}) in 86 % yield. With 30 % hydrogen peroxide in methanol *(5)* affords the amine oxide (not further characterized), whose Cope degradation at 150 °C and 2 torr gives 57 % of *(1)*, which corresponds in all its properties to natural santolinatriene [1] [b.p. 143 °C. IR: 3085, 1670, 1643, 996, 916, 896 cm^{-1}. UV: $\lambda_{max}^{C_2H_5OH}$ = 202 nm, ε = 12700. ^1H–NMR and mass spectra are superposable on those of the natural *(1)* [1]; M^+ at *m/e* 136.1249, calc. 136.1252]. IR and NMR spectra were measured for CCl_4 solutions.



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Bis(chloromercuri)-2,4-pentanedione, an Unusual Acetylacetone Derivative

By *F. Bonati* and *G. Minghetti* [*]

Surprisingly, mercury(II) acetylacetone [1] does not dissolve in the usual solvents. Its structure is not yet fully clarified. In an attempt to prepare it by dropwise addition of 5.14 ml of acetylacetone to a saturated aqueous solution of mercury(II) chloride (6 g in 100 ml) [1], we obtained a chlorine-containing colorless crystalline compound (2.0 g; m.p. ~152 °C). This was filtered off from the now acid solution and washed with a little cold water, in which it is difficultly soluble. The ^1H–NMR spectrum, measured for a hexadeuterioacetone solution, contains only one signal, at τ = 7.10. In the IR spectrum C=O, Hg–Cl, and two Hg–C stretching vibrations were observed at 1690 vs, (broad), 343s, 521s, and 566 cm^{-1}. The compound is not an electrolyte in acetone or acetonitrile; its reaction with iron results in separation of mercury and in chloroform it consumes one molar equivalent of

bromine. The molecular weight in acetone is 228. (The compound is insoluble in other solvents; it attacks steel, the soluiton becoming immediately red.) All these facts can be accounted for by formula *(1)*.

(1) *(2)*

Formula *(2)* would require only one Hg–C stretching vibration and one Hg–Cl vibration at lower wave numbers; for Hg_2Cl_2 the latter is at 260, for C_6H_5HgCl at 331, and for $HgCl_2$ at 375 cm^{-1}. Organomercury derivatives with a Hg–Hg bond are not known.

Mercury(II) bromide, cyanide, and acetate do not react with acetylacetone under the above conditions; nor does mercury(I) chloride.

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N-Fluorosulfamidoyl Fluoride, Pentafluorosulfur *N*-Fluoro-*N*-(fluorosulfonyl)amide, and *N*-(Dichloromethylene)fluoroformamide [1]

By *H. W. Roesky* [*]

Sulfamidoyl fluoride *(1)* [2] reacts with elemental fluorine at room temperature, giving *N*-fluorosulfamidoyl fluoride *(2)*.

$$FSO_2NH_2 + F_2 \rightarrow FSO_2{-}NHF + HF$$
(1) *(2)*

(2) is a colorless liquid that decomposes appreciably in Pyrex glass vessels within one day, with formation of SiF_4. It can be considered as the first derivative of difluoroamine HNF_2 in which one fluorine atom has been replaced by the FSO_2 group. Reaction of *(2)* with an excess of fluorine gives *N,N*-difluorosulfamidoyl fluoride *(3)* [3].

$$(2) + F_2 \rightarrow FSO_2NF_2 + HF$$
(3)

Formation of sulfonyl fluoride SO_2F_2 was not observed during the fluorination.

Elemental analysis proves the composition of *(2)*. The ^{19}F–NMR spectrum shows a doublet at $\delta_F = -39.6$ ppm for the FSO_2 group and a doublet at $\delta_F = 91.8$ ppm for the NF group (referred to CCl_3F, external; intensity ratio 1:1; $J_{FF} = 7.7$ Hz). The ^1H–NMR spectrum contains a singlet at $\delta_H = -7.8$ ppm (referred to TMS, external).

The following absorptions appear in the NaCl and KBr regions of the IR spectrum (capillary film on AgCl plates): 3700s, 3250s, 3050m, 2780m, 1638m, 1472vs, 1370m, 1240vs, 1000vs, 820vs, 695vs, 575vs, 480s cm^{-1}. In this determination some *(1)* was probably also formed.

The mass spectrum shows, besides the molecular ion FSO_2NHF^+ 117 (62.9 %), fragments at *m/e* 98 (13.5 %) SO_2NHF, 85 (61.8 %) FSNHF, 83 (100 %) FSO_2, 67 (43.8 %) FSO, 64 (67.3 %) SO_2, 48 (35.9 %) SO, and 99 (33.7 %) FSO_2NH_2.

Difluorosulfur *N*-(fluorosulfonyl)imide *(4)*, prepared from *(1)* and tetrafluorosulfur [4], reacts with elemental fluorine, giving pentafluorosulfur *N*-(fluoro)-*N*-(fluorosulfonyl)amide *(5)*.

$$FSO_2N{=}SF_2 + 2\,F_2 \rightarrow FSO_2{-}NF{-}SF_5$$
(4) *(5)*

(5) is a clear liquid that can be kept in glass vessels. The NaCl and KBr regions of the IR spectrum contain absorptions at 1490vs, 1440w, 1303w, 1250vs, 1032w, 1010w, 925vs, 885vs, 862s, 810vs, 715w, 623w, 572vs, 524w, 490w cm^{-1}.

The mass spectrum shows fragments at *m/e* 227 (0.2 %) $FSONFSF_5$, 224 (0.6 %) FSO_2NFSF_4, 208 (0.2 %) $FSONFSF_4$, 205 (0.7 %) FSO_2NSF_4, 188 (0.13 %), 186 (1.6 %) SO_2NSF_4, 167 (0.3 %) SO_2NSF_3, 127 (100 %), 128 (1.1 %), 129 (6.4 %) SF_5, 108 (6.3 %), 110 (0.05 %) SF_4. Further fragments, SF_3, SO_2F, SF_2, SOF, SO_2, SF, SO, and SN, were also detected. The following chemical shifts were obtained from the ^{19}F–NMR spectrum: $\delta_{NF} = +23.2$ ppm, $\delta_{SO_2F} = -41.0$ ppm, $\delta_{SF} = -61.7$ ppm, $\delta_{SF_4} = -69.0$ ppm (referred to CCl_3F, external).

After the preparation of *N*-(fluoroformyl)iminosulfur dichloride [5] we succeeded in synthesizing *N*-(dichloromethylene)fluoroformamide *(7)* by fluorination of *N*-(dichloromethylene)chloroformamide [6] with silver monofluoride.

$$Cl{-}\overset{O}{\overset{\|}{C}}{-}N{=}CCl_2 + AgF \longrightarrow F{-}\overset{O}{\overset{\|}{C}}{-}N{=}CCl_2 + AgCl$$
(6) *(7)*

(7) is a liquid that has a pungent odor, b.p. 78–80 °C; its composition is proved by elemental analysis. The ^{19}F–NMR spectrum shows a singlet at $\delta_F = -12.65$ ppm (referred to CCl_3F, external).

The infrared spectrum of the liquid in the NaCl and KBr region shows bands at 2270m, 1850vs, 1730w, 1660vs, 1180vs, 1061m, 955vs, 908s, 778m, 742w, 637vs, 538s cm^{-1}. They are provisionally assigned to the following vibrations: ν(CO) 1850, ν(C=N) 1660, ν(CF) 1180, ν_{as}(CCl) 995, and ν_s(CCl) 908 cm^{-1}.

Experimental:

Synthesis of *(2)*:

Fluorine and nitrogen (F_2:N_2 = 1:2, *ca.* 60–70 bubbles/min) are led through 50 g of *(1)* in a quartz trap for 24 h; *(2)*, a little *(3)*, and some SiF_4 remain in the vessel. In an attached receiver (cooled in dry ice) 48 g of *(3)* is collected, and in a further trap (cooled by liquid air) SiF_4 separates. SiF_4 is formed by reaction of the HF with the glass. *(2)* is distilled from the reaction mixture in a vacuum into a precooled receiver: b.p. 29–30 °C/32 torr; yield 5 g.

Synthesis of *(5)*:

10 g of fluorine is condensed onto 33 g of *(4)* contained in a 100 ml nickel autoclave cooled to the temperature of liquid nitrogen. The mixture is then warmed to room temperature, kept there for 3 days, and then warmed at 70 °C for a further 3 days. The volatile products are removed; they can be identified by infrared spectroscopy as SO_2F_2, FSO_2NF_2, SOF_2, SF_4, and SF_6. The residue in the autoclave is distilled in a vacuum. 3 g of *(5)*, b.p. 30–31 °C is obtained alongside unchanged *(4)*.

Synthesis of *(7)*:

20 g of *(6)* is fluorinated by 60 g of AgF at 120–140 °C in a glass vessel. The volatile products are collected in a cooled receiver (acetone/dry ice). Then the trap is warmed to room temperature and the contents fractionated under atmospheric pressure. Unchanged *(6)* is then accompanied by 10 g of *(7)*, b.p. 78–80 °C.

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Organic Compounds in Fossil Plants (*Voltzia brongniarti*, Coniferales)[1]

By *H. Knoche, P. Albrecht*, and *G. Ourisson*[*]

We recently reported our work on a fossil horsetail recovered from a clay inclusion in the variagated sandstone of the Northern Vosges (Trias, 2×10^8 years old)[3]. The fossil plants *Voltzia brongniarti* (Coniferales) are also found in this same sandstone[3]. Pieces of this fossil plant, about 1–5 cm long, were collected in Hangviller (Moselle), care being taken during collection to obtain as pure specimens as possible and the working up being controlled by blank experiments. Inorganic analysis gave a content of 60% goethite, $Fe_2O_3\cdot H_2O$[4].

The dry fossil (2.6 kg) was ground and extracted with a 3:1 benzene-methanol mixture (3 l) under the action of ultrasound. After centrifugation, decantation, and removal of the solvent by distillation, there remained 42 mg (16 ppm) of residue. The hydrocarbon fraction (3 mg, 1.2 ppm) was isolated by column chromatography on silica gel; it was crystalline and was shown by its gas chromatogram[5] to consist almost wholly of one component. This substance was identified as *n*-$C_{28}H_{58}$ by gas chromatography on filled and capillary columns[6], by inclusion in molecular sieves (Linde 5 Å), and by the mass spectrum. *n*-Octacosane has not previously, to our knowledge, been found as chief component of the cuticular wax of a plant. As is well known, it is mainly the odd-numbered hydrocarbons that occur in such waxes, and furthermore as mixtures of homologs; in conifers nonacosane, $C_{29}H_{60}$, occurs most frequently, alongside hydroxy esters and alcohols[7,8].

We regard it as extremely unlikely that *Voltzia*, alone among the conifers, contained an almost homogeneous even-numbered hydrocarbon, and we conclude that we are dealing with a transformation product. It is not possible to study directly what its precursor in *Voltzia* was, since this plant is extinct. Of extant conifers the family Taxodiaceae is the most closely related[9]. We have therefore studied the wax of two members of this family in the hope of identifying possible precursors of the *n*-octacosane. In the wax of *Cryptomeria japonica* Don. only 10-nonacosanol was found – this is a widely distributed constituent of many conifer waxes; it can hardly be considered as precursor of the octacosane. However, the wax of *Taxodium distichum* Rich. contains 1-octacosanol as well as 10-nonacosanol. The former alcohol was previously found only in the wax of one other conifer, *Gingko biloba* L.[10]. We presume that *n*-$C_{28}H_{58}$ was formed in the fossil by reduction of the primary alcohol *n*-$C_{27}H_{55}$–CH_2OH; 10-nonacosanol either was not present or was degraded in an unknown way. In this connection it is interesting that, according to *Hoering*, octadecanol is reduced to octadecane simply by heating it with sedimentary rocks[11].

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[1] Part II. – Part I: [2]. This work was carried out as part of the research program D.G.R.S.T. No. 64-FR-058. – We thank *L. Grauvogel* and *J. C. Gall* for help in collecting the fossils, and Dr. *P. Witz* (Geigy, Basel) and *G. Teller* (Strasbourg) for measuring the mass spectra.

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[4] We thank S.N.P.A., Pau (France), for carrying out the analysis.

[5] Conditions: Perkin-Elmer 226 gas chromatograph, 1.5% SE-30 on Aeropack 30, 80/100 mesh, 1.80 m long, diam, 3 mm, program 6.25 °C/min, 100–290 °C, 30 ml He/min.

[6] Capillary column: 0.5 mm, SE-30, 240 °C, 6.2 ml He/min. Retention times: benzene 3.4 min; *n*-$C_{28}H_{58}$, 15 min.

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Bis(tricarbonylcyclopentadienylchromium), a Catalyst for Selective Hydrogenation

By *A. Miyake* and *H. Kondo*[*]

Tricarbonylcyclopentadienylhydridochromium *(1)* is converted by conjugated dienes at room temperature quantitatively into bis(tricarbonylcyclopentadienylchromium) *(2)*. The conjugated dienes are hydrogenated in the process, *e.g.* isoprene to 2-methyl-2-butene.

$$2\ C_5H_5(CO)_3CrH + CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}CH{=}CH_2 \longrightarrow$$

(1)

$$[C_5H_5(CO)_3Cr]_2 + CH_3{-}\overset{\overset{CH_3}{|}}{C}{=}CH{-}CH_3$$

(2)

We also obtained *(2)*, in *ca.* 80% yield from bis(cyclopentadienyl)chromium, by the following reaction, without the need to isolate *(1)*:

$$(C_5H_5)_2Cr \xrightarrow[70°C]{CO,\ H_2} (1) \xrightarrow[20°C]{\text{isoprene}} (2)$$

In contrast to dienes with conjugated double bonds, olefins with isolated –C=C– bonds are totally unreactive towards *(1)*. Since *(1)* is regenerated from *(2)* by hydrogen[1], *(2)* can with advantage be used as catalyst for selective hydrogenation. Some examples are given in Table 1. Characteristics for hydrogenation catalyzed by *(2)* are the following:

1. Isolated double bonds are not hydrogenated.

2. Double bonds do not migrate.

3. Hydrogenation occurs smoothly above 70 °C and at H_2 pressures > 50 atm, but also slowly at room temperature or atmospheric pressure.

4. Except for sterically hindered dienes, the hydrogen is added preferentially at the ends of the conjugated system.

Experimental:

Preparation of *(2)*:

A solution of bis(cyclopentadienyl)chromium (5.57 g) in benzene (50 ml) is transferred under argon to a 100 ml autoclave. The solution is heated under H_2 (p_{H_2} = 50 atm) and CO (p_{CO} = 150 atm) with constant shaking for 20 h at 70 °C.

Table 1. Selective hydrogenation of polyenes catalyzed by *(2)*.

Polyene	Hydrogenation products (mole-%)		
[a]	(95)	(3)	(2) [b]
	(100)	(*trans* 88, *cis* 12)	
	(78)	(22)	
	(100)		
	(74)	(26)	
	(66)	(34)	
	(46)	(29)	(25)
	(51)	(29)	(20)

[a] Conditions of hydrogenation: isoprene 2.0 g and *(2)* 0.15 g in benzene 10 ml, p_{H_2} = 90 atm, 70 °C, 5 hr. Approximately the same conditions also for the other polyenes.

[b] No isoprene and only traces of 2-methylbutane were observed in gas chromatograms.

After cooling the excess gas is released and the reaction mixture is treated at 20 °C with isoprene (5 ml); the initial pale green mixture turns deep green in color. The solvent is distilled off under vacuum at room temperature. On sublimation of the dark green residue in high vacuum at 90–110 °C, 4.80 g (78 %) of compound *(2)* (color: blue green) is obtained.

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Cycloheptasulfur, S_7, and Cyclodecasulfur, S_{10} — Two New Sulfur Rings

By *Max Schmidt, B. Block, H. D. Block, H. Köpf*, and *E. Wilhelm* [*]

The first successful experiments designed to yield thermodynamically unstable compounds containing only one kind of atom (element modifications) led [1] to the preparation of cyclohexasulfur, S_6, and cyclododecasulfur, S_{12}, by kinetically controlled "metathetic reactions" according to the equation:

$$H_2S_x + Cl_2S_y \rightarrow 2\ HCl + S_{x+y}\ (x + y = 6 \text{ or } 12)$$

In the meantime S_{12} also was isolated from sulfur melts [3] in clear contradiction to predictions [2] of its instability, and this induced us to study further the experimentally difficult reactions of sulfanes with chlorosulfanes in the hope of obtaining new sulfur rings.

We have meanwhile succeeded in our purpose by two different processes: Bis(π-cyclopentadienyl)titanium(IV) pentasulfide, $(C_5H_5)_2TiS_5$ *(1)*, which was recently described [4], reacts with lower chlorosulfanes quantitatively under mild conditions, according to the equation:

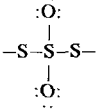
$$\underset{(1)}{(C_5H_5)_2TiS_5} + S_xCl_2 \rightarrow \underset{(2)}{(C_5H_5)_2TiCl_2} + \frac{1}{n}\ S_{(5+x)n}$$

From *(1)* and SCl_2 (x = 1) we obtained almost 100 % of *(2)* and sulfur that could be separated into 87 % of pure S_6 (n = 1) and 11 % of pure S_{12} (n = 2).

Reaction of *(1)* with S_2Cl_2 (x = 2) is also quantitative. From the sulfur formed thereby we have, up to the present, isolated a 23 % yield of the hitherto unknown cycloheptasulfur, S_7 (n = 1).

This, the first odd-numbered sulfur ring, is of particular interest because it is inconceivable [5] that a seven-membered ring should have the same atomic distances, bond angles, and dihedral angles and thus the same energy content of all the sulfur atoms (if the unlikely flat ring, with dihedral angles of 180 °, is excluded by reasons of bonding theory). S_7 crystallizes from toluene in centimeter-long, intensely yellow needles, which, unlike the much paler S_8, retain their color on cooling. S_7 melts reversibly at 39 °C and becomes successively highly viscous by polymerization at ~ 45 °C, mobile at ~ 115 °C, highly viscous at 159 °C, and mobile on further heating. Under the influence of light and also storage at room temperature it changes readily into S_8 by way of a polymer; however, it can be kept unchanged for weeks in the cold and the dark. X-rays rapidly decompose S_7 at room temperature, but good single-crystal photographs were obtained at −80 °C (space group: Cmma. Lattice constants: a = 21.77 Å, b = 20.97Å, c = 6.09 Å, 112 atoms = 16 formula units in the orthorhombic unit cell; the structure is being calculated) [6].

Because of the instability of the group [7]



reaction of sulfuryl chloride with *(1)* also leads quantitatively to sulfur rings, with loss of SO_2.

$$(1) + SO_2Cl_2 \rightarrow (2) + \frac{1}{n}\ S_{5n} + SO_2$$

By this reaction we have now isolated pure cyclodecasulfur, S_{10} (n = 2). It crystallizes in characteristic, intensely yellow, rhombic platelets (from CS_2). Like S_6, S_{10} does not show a sharp melting point or decomposition point, but above ~60 °C polymerizes to a viscous state. Its sensitivity to light also parallels that of cyclohexasulfur. Even in the dark, it must

be stored at low temperature (~ −40 °C) if decomposition is to be avoided. As expected, the new sulfur modification is only slightly vaporizable without decomposition even under high vacuum, as is shown by the mass spectrum [8].

As a result of our experiments towards planned synthesis fo thermodynamically unstable element modifications the following defined cyclic sulfur molecules are now available for comparative observations: S_6, S_7, S_8, S_{10}, and S_{12}.

Experimental:

Synthesis of S_6 and S_{12}: Compound *(1)* (5 g, 14.8 mmoles) in CS_2 (250 ml) is treated in absence of light, at 0 °C, with stirring, with SCl_2 (1.52 g, 14.8 mmoles) in CS_2 (100 ml) (color change from violet to pale pink). The precipitated *(2)* is filtered off and S_6 is extracted with cold CS_2 (30 ml) from the orange-yellow solid residue obtained by evaporation of the filtrate. The undissolved residue is taken up in hot CS_2 (250 ml) from which it crystallizes on cooling. Yield of *(2)* 3.6 g (98 %), of S_7 2.48 g (87.3 %), and of S_{12} 0.32 g (11.3 %).

Synthesis of S_7: Compound *(1)* (1.35 g, 4 mmoles) in CS_2 (50 ml) with S_2Cl_2 (0.54 g, 4 mmoles) in CS_2 (10 ml); reaction as above. After 1 hour's stirring, the filtrate from *(2)* is evaporated in a vacuum. The orange-yellow oily residue is extracted 2–3 times with cold toluene (10 ml) and the extracts are cooled to −78 °C. 0.21 g (23.4 %) of S_7 crystallizes. Mol. wt. 218 (cryoscopic), 224 (osomometric) in benzene.

Synthesis of S_{10}: Compound *(1)* (0.68 g, 2 mmoles) in CS_2 (180 ml) is treated, dropwise at −78 °C with stirring and exclusion of light, with SO_2Cl_2 (0.27 g, 2 mmoles) in CS_2 (20 ml). After 3 h the precipitated *(2)* is filtered off in the cold, the solution is evaporated to 5 ml below −10 °C in a vacuum, and then treated with cold pentane (100 ml; −78 °C). A precipitate of S_{10} (0.11 g, 35 %) is formed, which is purified by dissolution in CS_2 and concentration of the solution. Mol. wt. 315 (osmometric) in benzene.

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[2] See, *e.g. L. Pauling*, Proc. nat. Acad. Sci. U.S.A. *35*, 495 (1949).

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Mass-Spectrometric Study of Cycloheptasulfur, S_7 and Cyclodecasulfur, S_{10}

By *U.-I. Záhorszky* [*]

The usual cyclooctasulfur, S_8, as well as cyclohexasulfur, S_6 [1] and cyclododecasulfur, S_{12} [2], have previously been prepared and studied by mass spectrometry.

The modifications cycloheptasulfur, S_7, and cyclodecasulfur, S_{10}, recently prepared for the first time [3], show the expected molecular weights in the mass spectrometer. When the usual electron energy (70 eV) is used the molecular ion peak (*m/e* 224) does not appear clearly in the spectrum of S_7, but if the energy is lowered this signal grows in relative intensity (Fig. 1, compare with Fig. 2). Because of the great volatility, the total ion flux could not be kept constant during the measurement [4].

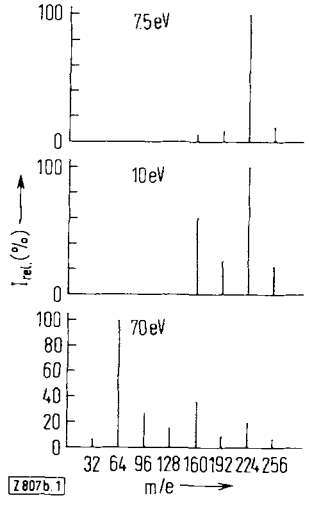

Figure 1. Mass spectrum [5] of S_7 at 70, 10, nd 7.5 eV.

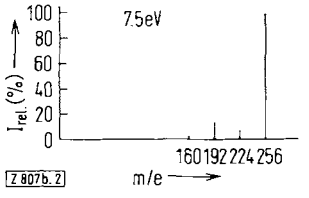

Figure 2. Mass spectrum [5] of S_8 at 7.5 eV.

In the spectrum of S_{10} the signal of highest mass number is the molecular ion peak (*m/e* 320). However, as in the case of S_{12}, the overall spectrum consists mainly of the spectrum of S_8 overlaid by the less intense spectrum of S_{10} (Table 1). It must therefore be assumed that the thermally labile modification passes mainly into S_8 during its residence in the mass spectrometer [4].

Table 1. Signal heights in the mass spectrum of S_{10}.

m/e	160	192	224	256	288	320
$I_{rel.}$	75	52	37	100	0.85	2.1

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[4] The sample was introduced directly into the ion source of the mass spectrometer (Atlas CH-4; temperature in the source *ca.* 70 °C).

[5] The ^{34}S isotopes are not included.

Tetrakis(cyclopentadienyl)neptunium(IV)

By *F. Baumgärtner, E. O. Fischer, B. Kanellakopulos,* and *P. Laubereau* [*]

Tetrakis(cyclopentadienyl)neptunium(IV) *(1)* is the first purely aromatic neptunium complex. It was obtained for the first time by treating $NpCl_4$ (3.8 g) with a five-fold molar amount (excess) of KC_5H_5 in benzene suspension under a protecting gas (argon).

$$NpCl_4 + 4\ KC_5H_5 \xrightarrow{\text{Benzene}} Np(C_5H_5)_4 + 4\ KCl$$

The mixture was heated under reflux for 160 h, then evaporated to dryness, and the residue was extracted for 50 h with benzene. This yielded the reddish-brown product (3.6 g, 72%) in analytically pure form.

The product *(1)* dissolves as monomer in benzene (osmometric mol. wt. in C_6H_6: 496). Its sensitivity to oxygen and water is considerably less than that of $Pu(C_5H_5)_3$ [1] and $Am(C_5H_5)_3$ [2]. It dissolves in benzene and tetrahydrofuran with different colors (benzene, greenish; tetrahydrofuran, yellowish-brown). The solubility is *ca.* 1.9 mg/ml in tetrahydrofuran and *ca.* 1.0 mg/ml in benzene.

The substance decomposes above 220 °C. Its IR spectrum, measured for polycrystalline samples in Nujol and Hostaflon, indicate the exclusive presence of symmetrical five-membered rings with characteristic bands at 780 and 810 (γ_{CH}), 1008 (δ_{CH}), 1447 (ω_{CC}), and 3077 cm^{-1} (ν_{CH}). The intensities and the positions of the bands correspond closely to those for $U(C_5H_5)_4$ [3], so that an analogous molecular structure is to be assumed.

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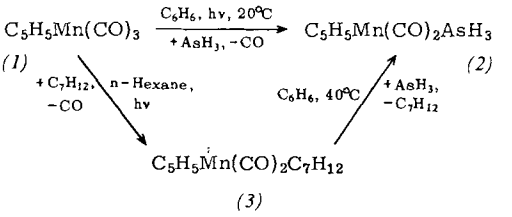
Arsinecyclopentadienyldicarbonylmanganese(I)

By *E. O. Fischer, W. Bathelt, M. Herberhold,* and *J. Müller* [*]

Following our recent publication [1] concerning the preparation of the first stable transition-metal derivatives of PH_3 [2] we now wish to report the first preparation of an analogous AsH_3 transition-metal complex.

The compound arsinedicarbonylcyclopentadienylmanganese(I) *(2)* has been prepared by the following two methods: firstly, by UV irradiation of a benzene solution of π-$C_5H_5Mn(CO)_3$ *(1)* under an atmosphere of AsH_3 and secondly, by the ligand exchange reaction which occurs when a benzene solution containing the π-cycloheptene complex $C_5H_5Mn(CO)_2C_7H_{12}$ *(3)* [3,4] is stirred at 40 °C under an atmosphere of AsH_3. The latter method of preparation is preferred to the former because in the former difficulties arise in the separation of the volatile product *(2)* from the more stable $C_5H_5Mn(CO)_3$ *(1)*.

On the basis of the method of preparation and analytical and spectroscopic data, the yellow, air- and light-sensitive,



sublimable arsine complex *(2)* is formulated as a substitution product of *(1)* of the well known type $C_5H_5Mn(CO)_2L$.

The infrared spectrum of *(2)* (KBr disc) shows a band of medium strength situated at 2150 cm^{-1}, which is attributed to the ν_{AsH} vibration. One of the two bands expected for the δ_{AsH} vibrations is observed at 911(s) cm^{-1} and the other is thought to be contained in the envelope of the strong band occurring at 1003 cm^{-1}, as is suggested by the intensity ratio. All three bands occur at similar frequencies to those found in the infrared spectrum of AsH_3 in the gaseous phase [5], *viz.* 2122, 1005, and 906 cm^{-1}, which would indicate a weak metal-arsine bond. This is in agreement with our view that the Mn–As d_π-d_π back-bonding plays the predominant role in the bonding of these arsine derivatives. Characteristic bands in the infrared spectrum of the symmetrical π-bonded C_5H_5 ring occur at 2919(w), 1422(w), 1112(w), 1003(s), and 839/823(m) cm^{-1}. The infrared spectrum of a benzene solution of the complex *(2)* in the metal-carbonyl stretching region shows two equally intense bands at 1937(vs) and 1874(vs) cm^{-1} corresponding to the two ν_{CO} stretching vibrations, which is consistent with the proposed C_{2v} disposition of the carbonyl groups in this molecule. The infrared spectrum of the complex $C_5H_5Mn(CO)_2As(C_6H_5)_3$ in benzene [6] is comparable and shows two bands at 1940 and 1869 cm^{-1}. The similarity of the spectra of the AsH_3 and $As(C_6H_5)_3$ derivatives in the carbonyl stretching region may indicate that the overall transfer of charge resulting from the σ-donating and π-accepting characteristics of these ligands is comparable.

The ^1H–NMR spectrum of *(2)* in $CDCl_3$ solution shows two singlets of relative intensity 5:3 occurring at τ = 5.46 and τ = 6.8 τ which have been assigned to the C_5H_5 and AsH_3 protons, respectively. Both signals are shifted downfield compared with the spectra of the starting materials, *viz.* $C_5H_5Mn(CO)_3$ ($\tau_{C_5H_5}$ = 5.16 in $CDCl_3$) and AsH_3 (τ_{AsH_3} = 8.45 in $CDCl_3$).

The mass spectrum of *(2)* shows a peak corresponding to the molecular ion at m/e = 254 (relative intensity I_{rel} = 26). Fragmentation of this ion occurs either stepwise with simultaneous elimination of the two CO ligands, accompanied by stepwise loss of the arsine hydrogen atoms [$C_5H_5Mn(CO)AsH_3^+$, I_{rel} = 0.2; $C_5H_5MnAsH_3^+$, I_{rel} = 20; $C_5H_5MnAsH_2^+$, I_{rel} = 7.9; $C_5H_5MnAsH^+$, I_{rel} = 1.7; $C_5H_5MnAs^+$, I_{rel} = 2.6], or by elimination of the arsine group and stepwise loss of the carbonyls [$C_5H_5Mn(CO)_2^+$, I_{rel} = 2.1; $C_5H_5MnCO^+$, I_{rel} = 6.8]. Both the arsine and carbonyl groups may be considered to be equally strongly bonded to the manganese atom. The base peak, corresponding to the ion $C_5H_5Mn^+$ (I_{rel} = 100), has been observed generally in the mass spectra of molecules of the type $C_5H_5Mn(CO)_2L$ [7]. Further fragmentation of this ion occurs as follows: $MnAsH_2^+$ (I_{rel} = 5.8); $MnAsH^+$ (7.7); $MnAs^+$ (5.9); $MnC_3H_2^+$ (2.6); MnC_2H^+ (2.4); MnH^+ (2.6); Mn^+ (60).

The mass spectroscopically measured ionization potential of *(2)* is 7.16 ± 0.1 eV. This value falls in the region observed for the ionization potentials of the analogous complexes $C_5H_5Mn(CO)_2L$ [where L = cyclic olefins, $C_6H_{11}NC$, or $(CH_3)_2SO$] (*ca.* 7.00 to 7.30 eV). [7]

Preparation of (2):

All operations must be carefully carried out under a protective gas in a good fume-cupboard. AsH_3 is an extremely poisonous gas and the product *(2)* is also appreciably volatile

at room-temperature, small concentrations in the air causing headache and nausea.

Compound *(3)* (1.2 g, 4.4 mmole) is dissolved in benzene (50 ml) in a 500 ml three-necked flask. The first neck is connected *via* a three-way tap to a manometer and a vacustat and another is connected to a trap containing condensed AsH_3 (cooled with liquid N_2). The reaction flask is then well cooled (−40 °C) and the system is evacuated with a water-pump and then closed. Cooling is then removed from the reaction flask and the trap containing the frozen AsH_3. When the benzene solution and the AsH_3 has attained a static equilibrium the internal pressure is allowed to increase to 10–30 torr. The reaction mixture is then stirred for 3 h at 40 °C during which time the original yellow-brown color of the solution becomes brown-red. The gases are displaced by N_2, the solvent removed *in vacuo*, and the product sublimed from the residue, under high vacuum at 30–40 °C, onto a cold-finger cooled with a methanol-dry ice mixture. The pure product was obtained as the first fraction of a further sublimation at 15 °C. The yellow crystalline product darkens at 39 °C and melts at 41 °C (yield *ca.* 1.5 %). Compound *(2)* is soluble in benzene and hexane giving yellow-red and yellow solutions, respectively; it is quantitatively decomposed within several minutes in hexane solution whereas in benzene solution it appears to be stabilized. In the solid state, *(2)* is light-sensitive and is stable for several hours only at room temperature, although it may be kept for several days at −40 °C without decomposition.

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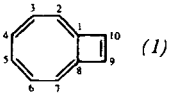
The Bicyclo[6.2.0]decapentaene System

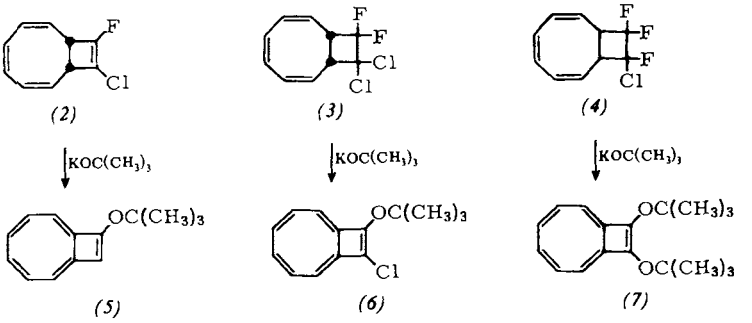
By *G. Schröder* and *H. Röttele* [*]

Bicyclo[6.2.0]deca-1,3,5,7,9-pentaene *(1)* [1] is isomeric with naphthalene and azulene. It contains ten π-electrons and, if it is assumed to be planar, then HMO calculations lead to a delocalization energy per π-electron that is somewhat less than comparable values for benzenoid aromatic compounds [2].

9-tert-Butoxy-10-chlorobicyclo[6.2.0]deca-1,3,5,7,9-pentaene (6): A solution of the cycloadduct *(3)* (1.5 g) [3] in pentane (*ca.* 30 ml) is poured slowly under nitrogen into an ice-cold suspension (excess) of pot. *tert*-butoxid in pentane/ether



(1)



(2) *(3)* *(4)*

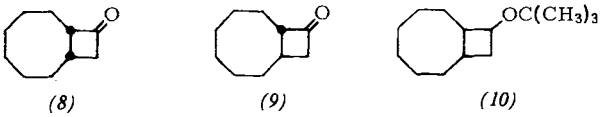
(5) *(6)* *(7)*

(30 ml). The solution becomes dirty red immediately addition is started. The mixture is then stirred for a further 2–3 h at 30–40 °C, treated with water, and extracted with ether. All these operations are effected with exclusion of oxygen. The solvent is susequently removed in a rotatory evaporator and the deep red residue is chromatographed at *ca.* −5 °C, first on basic Al_2O_3 (pentane/ether 9:1) and finally on silica gel (pentane). Pure *(6)* is thus obtained (50 % yield) as a compound that is crystalline up to *ca.* 25 °C, very sensitive to air, thermally stable up to 80 °C, and deep red [UV spectrum in ether: λ_{max} = 282 nm (52000), 376 nm (1100), and many shoulders indicated at 400–500 nm]. The mass spectrum proves the molecular formula [4]; the NMR spectrum shows a ratio of six olefinic (multiplet around τ = 3.9) to nine aliphatic protons (singlet at τ = 8.9).

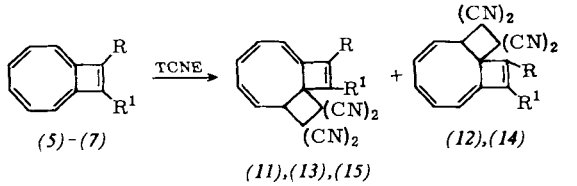
Compounds *(5)* and *(7)* were prepared analogously. 9-Chloro-10-fluorobicyclo[6.2.0]decatetraene *(2)* [3] gives *ca.* 10 % yield of 9-*tert*-butoxybicyclo[6.2.0]decapentaene *(5)*, which is red and very sensitive to air [UV spectrum in ether: λ_{max} = 277 nm (28000), 485 nm (350)]. In its NMR spectrum the six protons of the eight-membered ring appear as a multiplet around τ = 4.0, the cyclobutenyl proton as a singlet at τ = 3.1, and the nine *tert*-butyl protons as a singlet at τ = 8.6.

The cycloadduct *(4)* [5] is the starting material for the synthesis of the red, air-sensitive 9,10-di-*tert*-butoxybicyclo-[6.2.0]decapentaene *(7)* (*ca.* 30 % yield). The mass spectrum proves the molecular formula of this product [4]. The UV spectrum (ether solution) contains λ_{max} = 284 nm (43000) and 430 (2600). The resonance bands of the protons of the eight-membered ring appear in the NMR spectrum somewhat downfield in comparison with those for *(5)* and *(6)*, forming multiplets around τ = 3.5 and 3.8 (2:4); the eighteen *tert*-butyl protons absorb as a singlet at τ = 8.5.

Compounds *(5)*, *(6)*, and *(7)* can be catalytically hydrogenated with ease (Pd/C in C_2H_5OH). From *(5)* one obtains



(8) *(9)* *(10)*



(5)-(7) *(11),(13),(15)* *(12),(14)*

a mixture of *cis*- and *trans*-bicyclo[6.2.0]decan-9-one *(8)* and *(9)*, respectively, as well as a compound whose IR and NMR spectra suggest that it is 9-*tert*-butoxybicyclo[6.2.0]decane *(10)*. The two ketones —(8) is the preponderant product — were separated together from the small proportion of *(10)* by gas chromatography (Carbowax) and were identidifed by comparison of their IR spectra with those of authentic material [6].

Compounds *(5)*, *(6)*, and *(7)* react smoothly with tetracyanoethylene (TCNE), giving, respectively, the colorless crystalline 1,2-cycloadducts *(11)* + *(12)*, *(13)* + *(14)*, and *(15)*. UV and IR spectra support the formulas given [7]. The ratios in which the products *(11)*:*(12)* and *(13)*:*(14)* are formed vary markedly with the nature of the solvent. Tetracyanoethylene and *(5)* in benzene give two cycloadducts, but in acetonitrile give only one. The NMR spectrum of the single cycloadduct *(11)* or *(12)* shows six olefinic protons centered around $\tau = 4.1$, *i.e.* five protons of the eight-membered ring as a multiplet and one cyclobutenyl proton as a sharp singlet at $\tau = 4.5$, one tertiary proton as a multiplet at $\tau = 6.1$, and nine *tert*-butyl protons as a singlet at $\tau = 8.5$; the cyclobutenyl proton is at higher field than that of *(5)* itself ($\Delta = 1.4$ ppm).

Whether the π-electrons in the bicyclo[6.2.0]decapentaene system are delocalized cannot yet be decided.

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[7] All C,H-Analyses gave satisfactory values.

Proof of $N_\gamma N_\beta$-Elimination from Staudinger Adducts $R_3P{=}N_\gamma{-}N_\beta{=}N_\alpha{-}X$ by ^{15}N-Isotopic Labeling [**]

By *H. Bock* and *M. Schnöller* [*]

The second-order reaction [2, 3] between phosphine derivatives and organic azides

$$R_3P + N_3X \rightleftarrows [R_3PN_3X] \rightarrow R_3P{=}NX + N_2$$

was discovered by *Staudinger* and *Meyer* [1] in 1919. In the rate-determining step it involves the "Staudinger adduct" $[R_3PN_3X]$, which can be isolated, for instance, from the reaction of triphenylphosphine and *p*-toluenesulfonyl azide in diethyl ether at 0 °C quantitatively as a lemon-yellow compound that decomposes at 101 °C [4]. Syntheses on the micro-scale, starting from sodium [^{15}N]nitrite or [β-^{15}N]-azide (prepared from [^{15}N]ammonium chloride) [5] afforded 69 % of the [γ-^{15}N]-compound *(1)* and 52 % of the [β-^{15}N]-compound *(2)*, respectively.

$$Na^{15}NO_2 + H_2N{-}NHTs \xrightarrow{H_2O/CH_3COOH}$$

$$^{15}N_\gamma{=}N_\beta{=}N_\alpha{-}Ts \xrightarrow{R_3P/ether} R_3P{=}^{15}N_\gamma{-}N_\beta{=}N_\alpha{-}Ts \quad (1)$$

$$Na(N_\gamma{=}^{15}N_\beta{=}N_\alpha) + ClTs \xrightarrow{H_2O/acetone}$$

$$N_\gamma{=}^{15}N_\beta{=}N_\alpha{-}Ts \xrightarrow{R_3P/ether} R_3P{=}N_\gamma{-}^{15}N_\beta{=}N_\alpha{-}Ts \quad (2)$$

$R = C_6H_5$

$Ts = p{-}SO_2C_6H_4CH_3$

The linear structure of the Staudinger adducts *(1)* and *(2)* is supported by the IR spectra, in the 4000–400 cm^{-1} region of which distinct ^{15}N-isotope shifts are found only for the P=N stretching vibration ($\nu P{=}N = 1230\ cm^{-1}$, $\Delta^{15}N_\gamma = -17\ cm^{-1}$, $\Delta^{15}N_\beta = -18\ cm^{-1}$) and the N–N stretching vibration ($\nu_{N-N} = 980\ cm^{-1}$, $\Delta^{15}N_\gamma = -12\ cm^{-1}$, $\Delta^{15}N_\beta = -2\ cm^{-1}$) [6].

Thermal decomposition of the Staudinger adducts in benzene at 60 °C occurs with 91 % evolution of N_2. Decision between elimination of $N_\gamma N_\beta$, ($N_\gamma N_\alpha$), and $N_\beta N_\alpha$ can be taken by means of the isotope pattern (Table 1) determined by mass spectroscopy.

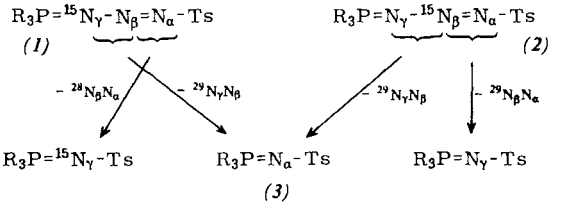
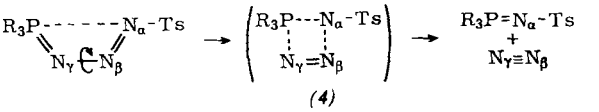


Table 1. Isotope pattern for $^{29}N_\gamma N_\beta$ elimination considering the natural ^{15}N content (0.37 %) and the ^{15}N enrichment in the starting materials $Na^{15}NO_2$ (96.7 %) and $^{15}NH_4Cl$ (95.4 %).

	$^{28}N_2$	$^{29}N_2$	$^{30}N_2$
(1) calc.	8.1	96.3	0.4
found [7]	3.3	91.6	0.3
(2) calc.	4.6	95.0	0.4
found [7]	5.4	94.2	0.4

The elimination of $^{29}N_\gamma N_\beta$ is further confirmed by the fact that the *P,P,P*-triphenylphosphine ^{14}N-toluenesulfonylimine *(3)* from both Staudinger adducts is always unlabeled ($\nu_{P=N} = 1230\ cm^{-1}$).

The elimination of $^{29}N_\gamma N_\beta$ on thermal decomposition of *(1)* and *(2)* in benzene at 60 °C supports the four-membered cyclic transition state *(4)* postulated by *Leffler* and *Temple* [3].



This could arise from a *trans*-Staudinger adduct by, *e.g.*, rotation around the $N_\gamma{-}N_\beta$ bond and subsequent conrotatory ring closure.

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[5] *K. Clusius* and *H. Schumacher*, Helv. chim. Acta *41*, 2255 (1958).

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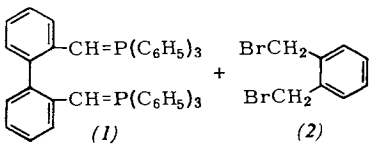
A New Synthesis of Benzocycloalkenes

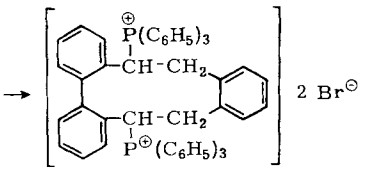
By *H. J. Bestmann* and *D. Ruppert* [*]

The treatment of bisalkylidenephosphoranes with bis(halogenomethyl) compounds opens new possibilities for the synthesis of cyclic compounds, and, in particular, of benzocycloalkenes.

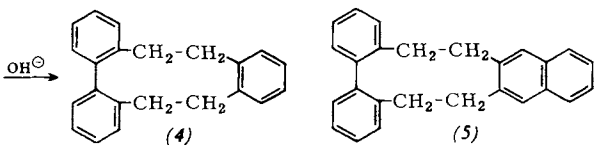
Reaction of the bisylide *(1)* [1] with *o*-xylene dibromide *(2)* gives a bisphosphonium salt *(3)*, which on alkaline hydrolysis gives, as well as triphenylphosphine oxide, a 44 % yield [calc. on *(1)*] of 9,10,15,16-tetrahydrotribenzo[*a,c,g*]cyclodecene *(4)*, m.p. 95 °C [2].



(1) *(2)*



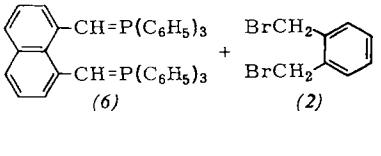
(3)



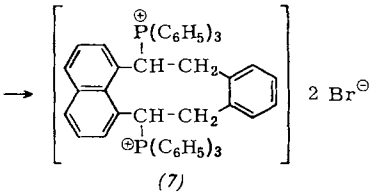
(4) *(5)*

A bisphosphonium salt is obtained analogously from *(1)* and 2,3-bis(bromomethyl)naphthalene and on alkaline hydrolysis affords 9,10,15-16-tetrahydrodibenzo[*a,c*]naphtho[2,3-*g*]-cyclodecene *(5)* [yield 36 %; m.p. 135 °C. NMR: aromatic protons 2.35–3.15 τ (m) (14H), $-CH_2-$ 7.18 τ (broad s) (8H). Mass spectrum: $M^+ = 334$. UV: λ_{max} (*n*-heptane) = 234, 265, 274, 284, 322 nm].

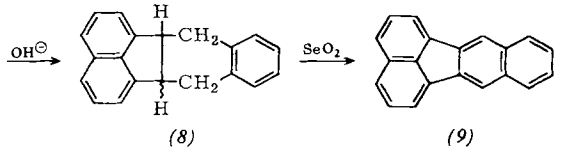
2,2'-Bis(bromomethyl)biphenyl and *(1)* afford a bisphosphonium salt whose hydrolysis gives 9,10,19,20-tetrahydrotetrabenzo[*a,c,g,i*]cyclododecene (50 % yield) which was obtained by *Wittig et al.* [3] by another route; it melts at 261 °C but, when heated, passes into the recorded form [3] having m.p. 266 °C.



(6) *(2)*



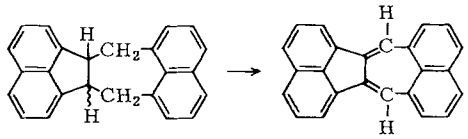
(7)



(8) *(9)*

Reaction of *(6)* [1] and *(2)* gives the bisphosphonium salt *(7)*, whose hydrolysis by alkali is accompanied by a transannular reaction. Triphenylphosphine and its oxide are liberated and 6b,7,12,12a-tetrahydrobenzo[*k*]fluoranthene *(8)*, m.p.158 °C [4], is formed in 44 % yield. Compound *(8)* can be dehydrogenated by SeO_2 to the known benzo[*k*]fluoranthene *(9)*, m.p. 218 °C [5].

The analogous reaction of *(6)* with 1,8-bis(bromomethyl)-naphthalene leads to a bisphosphonium salt whose alkaline hydrolysis also involves a transannular reaction and gives 6b,7,14,14a-tetrahydrodinaphtho[1,18a,8-*a,b*,1,8a,8-*f,g*]azu-6b,7,14,14a - tetrahydrodinaphtho[1,18a,8 - *a,b*,1,8a,8-*f,g*]-azulene *(10)* [yield 10 %, m.p. 276 °C]. NMR (accumulated spectrum): aromatic protons 2.4–3.1 τ (m); aliphatic protons 5.65–7.1 τ (m), 8.55 τ (m). UV: λ_{max} ($CHCl_3$) = 302, 307, 316, 321 nm. Mass spectrum: $M^+ = 306$].



(10) *(11)*

Dichlorodicyano-1,4-benzoquinone dehydrogenates *(10)* to the deep red dinaphthoazulene *(11)* [M.p. 295 °C. NMR (in C_6D_5Br): aromatic protons 2.0–3.3 τ (m), C=C–H 5.2 τ (s); UV: λ_{max}($CH\,Cl_3$) = 273, 281, 300 (shoulder), 394, 416, 442, 470, 516, 550 nm; mass spectrum: $M^+ = 302$].

Experimental:

Preparation of *(4)*: An equimolar amount of *(2)*, dissolved in benzene, is added to a suspension of *(1)* in benzene. After 10 h the precipitated salt *(3)* is filtered off and reprecipitated from chloroform with ethyl acetate. The salt is then boiled for 2 h in 10 % sodium hydroxide (100 ml) and extracted with benzene. The residue remaining after removal of the benzene is shaken thoroughly with petroleum ether (100 ml) and the undissolved triphenylphosphine oxide filtered off. The residue from the petroleum ether extract is chromatographed on aluminum oxide (neutral, activity grade II). On elution with benzene, *(4)* is obtained; this is recrystallized from ethanol and can be sublimed under vacuum. (Yield 44 %, m.p. = 95 °C).

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[2] All the spectroscopic data of the substance are identical with those of the material *(4)* recently described by *K. Grohmann* and *F. Sondheimer* [J. Amer. chem. Soc. *89*, 7119 (1967)].

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[4] All the spectroscopic data of the substance are identical with those of the compound *(8)* recently synthesized by a different route by *R. H. Mitchell* and *F. Sondheimer* (Tetrahedron Letters *1968*, 2873).

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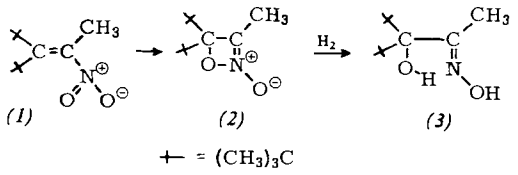
Sterically Induced Intramolecular Cyclization of an α,β-Unsaturated Nitro Compound

By *A. Berndt* [*]

3-*tert*-Butyl-4,4-dimethyl-2-nitro-2-pentene *(1)* [1] is the first α,β-unsaturated nitro compound for which intramolecular cyclization to a four-membered heterocycle has been observed.



(1) (2) (3)

+− = $(CH_3)_3C$

The product 4,4-di-*tert*-butyl-3-methyl-4*H*-1,2-oxazete 2-oxide *(2)* is the first derivative of the new system 4*H*-1,2-oxazete. It was isolated in quantitative yield when a solution of *(1)* in ethanol, after having been allowed to stand overnight, was evaporated down and the residue recrystallized from ethanol.

The structure of *(2)*, which melts at 85 °C and sublimes with spontaneous cyclization at 50 °C/10^{-3} torr, is proved by the following findings: C,H,N analysis; molecular weight (calc. 199; found 205, osmometrically); NMR spectrum (in $CDCl_3$, δ scale), 2 singlets at 1.2 and 2.1 ppm with relative areas 6:1; IR spectrum (in CCl_4), strong band at 1698 cm^{-1} in the stretching vibration region of C=N bonds in rings; UV spectrum, sharp band (half width 27 nm) at 222 nm, $\varepsilon = 7.4\times10^3$ (nitrones have similar UV spectra) [2]. On catalytic hydrogenation (room temperature; atmospheric pressure, Raney Ni, dioxane) the oxazete *(2)* slowly absorbs 1 molecular equivalent of hydrogen. The hydrogenation product *(3)* (m.p. 88 °C, sublimes at 60 °C/10^{-2} torr) is characterized by the following data: C,H,N analysis; NMR spectrum (in $CDCl_3$), four singlets at 1.1, 2.1, 5.0, 8.9 ppm with relative areas 18:3:1:1 (the signal at 8.9 ppm shows the characteristic broadening of oxime protons); IR spectrum in (CCl_4), two bands at 3594 and 3459 cm^{-1} in the O–H stretching region. Like other α-hydroxy oximes [3], compound *(3)* forms a Cu^{2+} complex. The hydrogenation occurs as for isoxazoline *N*-oxides [4].

The kinetics of the isomerization *(1)* → *(2)* was studied in several solvents by measuring the decrease in extinction of the UV band of *(1)* at 345 nm. In all cases, the reaction was clearly of the first order. The velocity increases with increasing polarity of the solvent; half-reaction times are 140 h in *n*-hexane, 70 h in diethyl ether, 2 h in ethanol. Solid *(1)* isomerizes to *(2)* within several weeks.

The unusual cyclization must be due to the strong steric hindrance by the four substituents around the C=C bond. In compound *(1)* this hindrance is avoided by rotation around the C=C bond; in *(2)* this angle of twist amounts formally to 90°. A similar strong rotation is observed also in the anion radical of *(1)* [1].

Compound *(2)* is stable to heat up to at least 100 °C and can be considered as a new example of stabilization of small rings by *tert*-butyl groups [5].

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Unit Cells and Absorption Spectra of the Cubic Squarates of Cobalt and Nickel [**]

By *A. Ludi* and *P. Schindler* [*]

On treatment of bivalent metal ions with potassium squarate (squarate anion = $C_4O_4^{2-}$, the anion of squaric acid, 3,4-dihydroxy-3-butene-1,2-dione), *West et al.* [1] obtained from the aqueous solution salts of the composition $MC_4O_4\cdot2\,H_2O$ (M = Ca, Mn, Fe, Co, Ni, Cu, or Zn). According to the temperature at which precipitation occurred and the excess of potassium squarate used we obtained three compounds that were readily distinguishable by X-rays. The pure cubic modification, of composition $MC_2O_4\cdot2\,H_2O$ is formed when a 0.5 M metal salt solution is precipitated at the boiling point by a three-fold excess of 0.5 M potassium squarate and the precipitate is heated under reflux in the mother liquor for a further three hours. When isolated and dried over KOH *in vacuo* the dihydrate shows remarkable thermal stability; loss of the two molecules of water is observed thermogravimetrically only between 200 and 260 °C.

Indexing of the Guinier photographs (internal standard: KCl) yields a simple cubic unit cell containing three formula units $MC_4O_4\cdot2\,H_2O$.

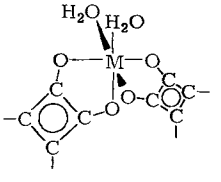
	a (Å)	d_4^{20} (g/cm³)	$d_{X\text{-ray}}$ (g/cm³)
$CoC_4O_4\cdot2\,H_2O$	8.16	1.87	1.90
$NiC_4O_4\cdot2\,H_2O$	8.06	1.93	1.97

The reflectance spectra of the powdered substances are typical of octahedral coordinated cobalt and nickel compounds, with absorption maxima (in cm^{-1}; sh = shoulder) at: $CoC_4O_4\cdot2\,H_2O$: 7800, 11400 sh, 16000 sh, 19600, 21500 sh $NiC_4O_4\cdot2\,H_2O$: 8600, 13300, 15200, 21500 sh, 25300.

The values of the ligand field parameters Dq and the Racah parameters B are collected in the annexed table, where the corresponding values for the hexaaquo complexes [2] are given (in parentheses) for comparison.

	Dq (cm^{-1})	B (cm^{-1})
$CoC_4O_4\cdot2\,H_2O$	890 (930)	860 (970)
$NiC_4O_4\cdot2\,H_2O$	860 (850)	850 (940)

The metal ion is bound to two water molecules and chelated to two squarate ions; it is assumed from the size and symmetry of the unit cell that the two water molecules are in *cis*-positions.



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[**] We thank the Schweizerischer Nationalfonds for financial support.

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Electrolytic Desulfurization of 2-Mercapto Carboxylic Acids and the Corresponding Disulfides

By *P. Rambacher* and *S. Mäke* [*]

Electrolytic reduction of cystine on tinned electrodes or on copper [1] leads to an almost quantitative yield of cysteine without detectable evolution of hydrogen sulfide. However, in attempts to reduce isocystine [2,2'-dithiodi-(3-amino-propionic acid)] to 3-amino-2-mercaptopropionic acid in the same way reduction was accompanied from the beginning by evolution of hydrogen sulfide, which ceased only when all

the sulfur had been removed. A similar evolution of hydrogen sulfide was also observed when isocysteine was used. The only further reduction product isolated was β-alanine in the form of its benzoyl derivative. This reductive exchange of sulfur for hydrogen occurs also with other 2-mercapto carboxylic acids and their derivatives. For instance, mercaptoacetic acid gives acetic acid, and 2-mercaptopropionic acid gives propionic acid. Desulfurizations of this kind were previously known only for reactions on Raney nickel [2].

Experimental:

Isocystine (12 g) was dissolved in a mixture of concentrated hydrochloric acid (12 ml) and water (200 ml) and reduced electrolytically at 2 A and 5 V at a copper cathode (current density 6 A/dm²). Graphite in hydrochloric acid served as anode, and was separated from the cathode chamber by a diaphragm. The transient SH reaction of the solution disappeared after 4 h, during which time hydrogen sulfide was continuously evolved. The solution was concentrated and 7.1 g of benzoyl-β-alanine (m.p. 133 °C) were isolated on benzoylation.

Isocysteine hydrochloride (4 g) was treated similarly. After 2.5 h at 1 A (current density 3 A/dm²) benzoylation afforded 3 g of benzoyl-β-alanine.

48 mmoles of hydrogen sulfide were evolved from 50 mmoles (4.6 g) of mercaptoacetic acid at a copper cathode (8 A/cm²) within 8 h; it was trapped in cadmium acetate solution and determined iodometrically. 2 g of acetic acid were determined by gas chromatography of the cathode liquid.

Analogous treatment of 50 mmoles (5.3 g) of 2-mercaptopropionic acid gave 47.8 mmoles of hydrogen sulfide and 2.3 g of propionic acid (determined by gas chromatography).

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[1] *P. Rambacher*, German Pat. 1024518 (Nov. 29, 1955), Aschaffenburger Zellstoffwerke; Chem. Zbl. *1958*, 11952.

[2] *R. Schröter* in *W. Foerst*: Neuere Methoden der Präparativen Organischen Chemie. 4th Edit., Verlag Chemie, Weinheim 1963, Vol. 1, p. 88.

σ,π-$C_8H_8Os(CO)_3$, an Unusual Cyclooctatetraene-Transition Metal Complex

By *M. I. Bruce, M. Cooke,* and *M. Green* [*]

Ultraviolet irradiation of dodecacarbonyltriosmium and cyclooctatetraene in benzene (room temperature, 72 h) affords a pale yellow crystalline complex *(1)*, m.p. 69 °C, of molecular formula $C_{11}H_8O_3Os$ (found: mol. wt. 380.00792; calc. for $C_{11}H_8O_3{}^{192}Os$: mol. wt. 380.00906). The parent ion shows stepwise loss of three carbonyl groups, and the infrared spectrum shows three bands at 2079.5 (s), 2008 (s), and 1995.5 (s) cm^{-1} (cyclohexane), characteristic of the ν_{CO} for an $M(CO)_3$ group. Other bands occur at 1640 (m), 1350 (m), 877 (m), 814 (m), 775 (s), and 708 (m) cm^{-1} (CS_2).

The ^1H–NMR spectrum at room temperature (100 and 220 MHz [1]) remains unchanged on cooling to −140 °C, and shows four absorptions (A, B, C, D; see Table).

Table 1. ^1H–NMR spectrum of *(1)* at 100 and 220 MHz.

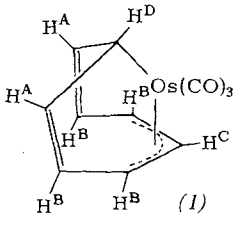
Resonance	τ (CCl_4)	Relative intensity	Multiplicity and coupling constants (Hz)
A	4.0	2	Double doublet; $J_{AB} = 6.5$, $J_{AD} = 4.5$
B	4.9	4	Assymetric complex multiplet
C	5.2	1	Broad triplet; $J_{BC} = 9.5$
D	7.45	1	Triplet; $J_{AD} = 4.5$

Double irradiation of A results in some simplification of B, and D collapses to a sharp singlet. Resonance A becomes a doublet when B is irradiated, and C changes to a broad singlet. The contour of B changes when C is irradiated, and irradiation of D causes A to collapse to a doublet, with some sharpening of resonance C.

Clearly, these NMR data do not correspond to those found with the familiar complexes π-$C_8H_8M(CO)_3$ (M = Fe, Ru), even in their fixed configuration [2]. In particular, the couplings between H_A and H_D, and between H_B and H_C, indicating one hydrogen coupling to two other identical hydrogen atoms in each case, severely restrict the possible structures of this complex.

We propose the novel structure *(1)* for this complex, in which the hydrocarbon is bonded to the $Os(CO)_3$ group by both a π-allyl system and by a metal-carbon σ bond, with the C_8H_8 assuming a boat configuration. The deshielding effect of the vinylic systems on the protons H_B of the π-allyl group causes H_C to be at higher field than H_B. The bands in the infrared spectrum at 1640 ($\nu_{C=C}$) and at 775 cm^{-1} (*cis*-C=C) lend support to this structure.

It is of interest that complex *(1)* isomerizes on gentle warming in solution to an orange-yellow complex *(2)*, m.p. 90.5 °C, which shows ν_{CO} at 2072 (s), 2001 (s), and 1989 (s) cm^{-1} (cyclohexane, and which shows a single resonance at 4.78 τ ($CDCl_3$). Complex *(2)* is evidently analogous to the now well-known iron [3] and ruthenium [2] cyclooctatetraene complexes, and the ease of isomerization is convincing evidence that the hydrocarbon ligand in complex *(1)* has a similar carbon skeleton to that in complex *(2)*.



(1)

As expected, the 1,2 motion of the $Os(CO)_3$ moiety around the ring is slower in complex *(2)* than that found in the iron and ruthenium complexes, as evidenced by the resolution of the ^1H–NMR spectrum at higher temperatures.

Complex *(1)* is not reformed from *(2)* either thermally or by ultraviolet irradiation. We suggest that the formation of *(1)* results from fragmentation of an initially formed complex between cyclooctatetraene and the Os_3 cluster, perhaps analogous to $(C_8H_8)_2Ru_3(CO)_4$ [4] or $C_8H_8Fe_2(CO)_5$ [5], both of which have been shown to contain π-allyl systems.

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[1] We thank Dr. *J. Becconsall* for the 220 MHz ^1H–NMR spectra.

[2] *F. A. L. Anet, H. D. Kaesz, A. Maasbol,* and *S. Winstein*, J. Amer. chem. Soc. *89*, 2489 (1967); *M. I. Bruce, M. Cooke,* and *M. Green*, J. organometallic Chem. *13*, 227 (1968); *W. K. Bratton, F. A. Cotton, A. Davison, A. Musco,* and *J. W. Faller*, Proc. nat. Acad. Sci. USA *58*, 1324 (1967).

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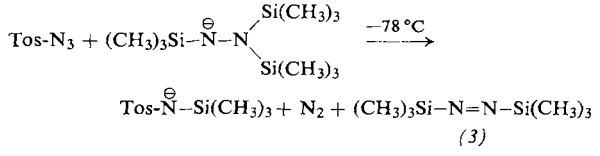
Bis(trimethylsilyl)diimine and Tetrakis(trimethylsilyl)hydrazine[1]

By *N. Wiberg, W.-Ch. Joo,* and *W. Uhlenbrock* [*]

Whereas bisalkyldiimines (azoalkanes) which contain the characteristic atomic grouping *(1)* have long been known, attempts to synthesize bissilyldiimines (azosilanes)[2,3], which contain the atomic grouping *(2)* have hitherto remained unsuccessful[4].

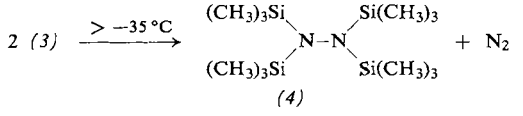
(1) *(2)*

In reaction of *p*-toluenesulfonyl azide[5] with tris(trimethylsilyl)hydrazide we have obtained access to the class of bissilyldiimines:



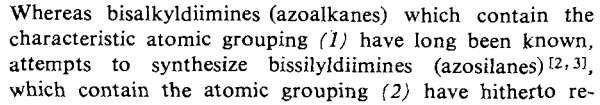
(3)

The product is light blue [λ_{max} = 786 nm (ether)], volatile in a high vacuum at −40 °C, and sensitive to hydrolysis. That it is bis(trimethylsilyl)diimine (hexamethylazosilane) follows from elemental analysis, the mass spectrum (base peak for the molecular ion at m/e = 174), the ^{1}H–NMR spectrum (one signal at δ = −12.5 Hz referred to TMS as internal standard; determined in ether at −40 °C), and thermolysis. The azo compound *(3)* decomposes quantitatively above about −35 °C according to the scheme:



(4)

This affords molecular nitrogen and the sterically hindered tetrakis(trimethylsilyl)hydrazine *(4)* which was previously unknown. The structure of *(4)*, m.p. 271 °C, was proved by analyses, mass spectrum, ^{1}H–NMR spectrum (only one proton signal, namely, at δ = −13.0 Hz referred to TMS as internal standard, recorded in benzene), and by independent synthesis as follows:



Experimental:

Preparation of *(3)*: Suspensions of *p*-toluenesulfonyl azide (12.0 mmoles) and lithium tris(trimethylsilyl)hydrazide (12.0 mmoles) each in ether (25 ml) were mixed at −78 °C with exclusion of moisture and oxygen. After reaction for 2 h at −78 °C, during which 12.2 mmoles of nitrogen was evolved, first the ether was condensed off from the reaction mixture in a high vacuum at −55 °C, and then pure *(3)* at −5 °C (yield 50 to 60%). *N*-Lithio-*N*-(trimethylsilyl)-*p*-toluenesulfonamide, containing *(4)* as an impurity, remained as a solid residue.

Preparation of *(4)*: Equimolar amounts of *N*-lithium tris(trimethylsilyl)hydrazide and trimethylchlorosilane in benzene are heated in a Carius tube at 120 °C for 48 h. After separating off the lithium chloride which has been formed, the benzene is distilled from the reaction solution and the residue *(4)* remaining is purified by several sublimations in high vacuum at 65 °C.

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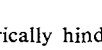
[1] Part 7 of "Silicon Compounds". – Part 6: *N. Wiberg, F. Raschig,* and *K. H. Schmid,* J. organometallic Chem. *10*, 29 (1967).

[2] *H. Bock,* Z. Naturforsch. *17b*, 423 (1962).

[3] *U. Wannagat* and *C. Krüger,* Z. anorg. allg. Chem. *326*, 288 (1964).

[4] Azo compounds containing the grouping  are known [3].

[5] Or *p*-toluenesulfonyl chloride.

CONFERENCE REPORTS

International Symposium on the Chemistry of Small Rings

The *Société Chimique de Belgique* held a symposium on the chemistry of small rings at Louvain (Belgium) from September 12 to 15, 1967.

From the lectures:

Syntheses of Cyclopropanes and Azirines by Means of Alkylidenephosphoranes

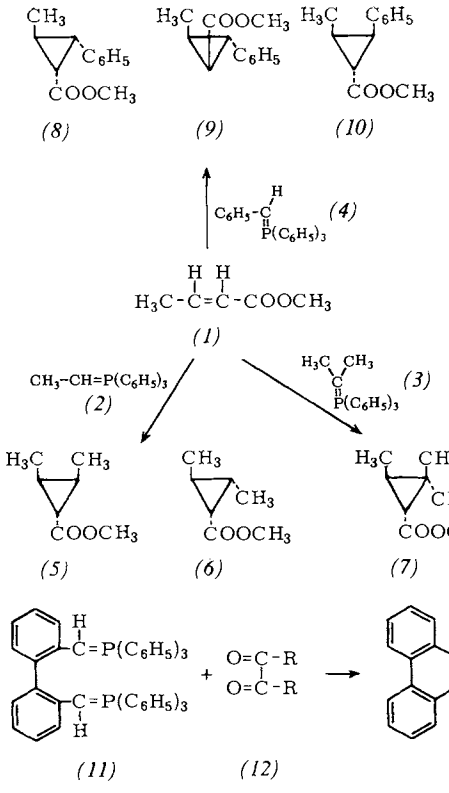
By *H. J. Bestmann* [*]

In the reaction of alkylidenephosphoranes with compounds containing "electron-deficient" double bonds, cyclopropane derivatives and triphenylphosphine are formed[1] by way of an intermediate betaine that is formed in a reversible reaction. The stereochemistry of this cyclopropane formation has been studied in detail. The ylide *(2)* and methyl 2-butenoate *(1)* afford the cyclopropane derivatives *(5)* and *(6)*. 93% of *(5)* and 7% of *(6)* are obtained independently of whether one starts from the *cis*- or the *trans*-ester.

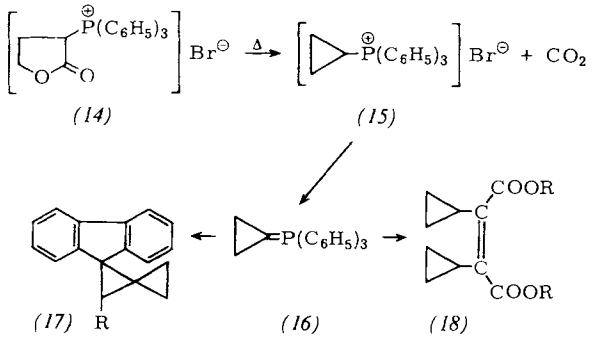
cis- or *trans*-*(1)* and the alkylidenephosphorane *(3)* give the sterically homogeneous cyclopropane derivative *(7)*. The benzylidenephosphorane *(4)* and the ester *(1)* afford the derivatives *(8)* (11%), *(9)* (33%), and *(10)* (56%).

Reaction of the diylide *(11)* with 1,2-diketones *(12)* gives sterically homogeneous dibenzonorcaradiene derivatives *(13)*[2], whose structure was determined by nuclear resonance and in particular the solvent-dependence of the chemical shift[3] of the cyclopropane protons.

When heated above the melting point, the phosphonium salt *(14)* loses CO_2 and gives cyclopropyltriphenylphosphonium bromide *(15)*[4], which can be converted into cyclopropylidenetriphenylphosphorane *(16)* by phenyllithium. This product *(16)* reacts as nucleophile with many compounds,



yielding cyclopropane derivatives[5], *e.g.* with alkylidenefluorenes it gives the spiro compounds *(17)* and with fumaric or maleic ester gives the di(cyclopropyl)maleic ester *(18)*.



On reaction of nitrile oxides with alkylidenephosphoranes loss of triphenylphosphine oxide may be accompanied by formation either of a ketene imine with concomitant rearrangement or of an azirine[6]. The mechanism of these reactions was discussed, as was its dependence upon the substituents present on the alkylidenephosphorane and on the nitrile oxide.

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[1] *H. J. Bestmann* and *F. Seng*, Angew. Chem. *74*, 154 (1962); Angew. Chem. internat. Edit. *1*, 116 (1962).

[2] *H. J. Bestmann* and *H. Morper*, Angew. Chem. *79*, 578 (1967); Angew. Chem. internat. Edit. *6*, 561 (1967).

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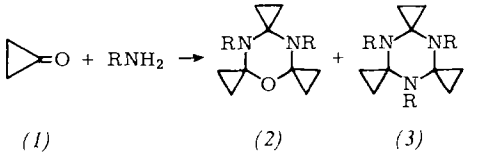
[6] *H. J. Bestmann* and *R. Kunstmann*, Angew. Chem. *78*, 1059 (1966); Angew. Chem. internat. Edit. *5*, 1039 (1966); *R. Huisgen* and *J. Wulff*, Tetrahedron Letters *1967*, 917.

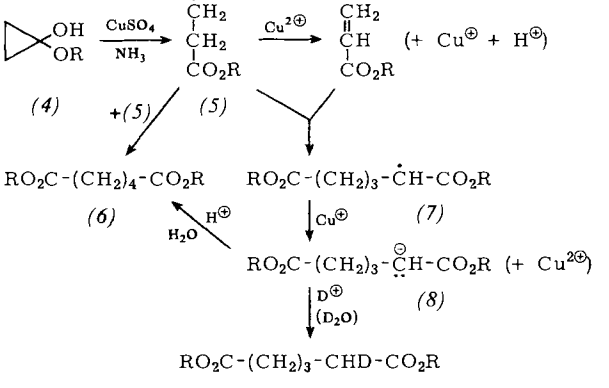
Reactivity of Cyclopropanone and Some of its Adducts

Von *Th. J. de Boer*[*]

Reaction of diazomethane with an excess of ketene in liquid propane at −78 °C yields cyclopropanone *(1)*, which is obtainable as a practically pure liquid after removal of ketene and propane. Cyclopropanone can be stored for a few days at the temperature of liquid nitrogen. At higher temperatures and with traces of water it polymerizes – without ring fission – like formaldehyde. All common nucleophiles, *e.g.* water, alcohols, thiols, acetic acid, hydrocyanic acid, and amines, react with cyclopropanone to form 1:1 adducts. The adducts *(2)* and *(3)* can easily be obtained from *(1)* and amines.



Metal ions oxidize simple adducts like cyclopropanone-hydrate or -hemiacetal *(4)* to adipic acid or its esters *(6)* (R = CH_3).



The intermediary radical *(5)* was detected by ESR spectroscopy. Dimerization of *(5)* yields the ester *(6)*, but only to the extent of 20%; the rest of *(6)* is formed from *(5)* and methyl acrylate *via* the intermediates *(7)* and *(8)*, as was shown when the reaction was carried out in D_2O.

(7) can also be added to other olefinic compounds such as methyl vinyl ketone, cyclopentenone, butadiene, or furan. In the case of methyl- and *gem*-dimethyl-substituted cyclopropanones the ring opening (and thus the product distribution) depends strongly on the nature of the oxidizing metal ions.

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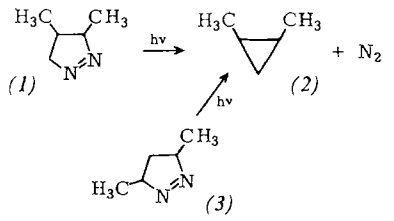
Triplet Trimethylene Species

By *R. J. Crawford* and *R. Moore*[*]

The benzophenone photosensitized decomposition of both *cis*- and *trans*-3,4-dimethyl-1-pyrazoline *(1)* gives rise to a 70:30 mixture of *trans*- and *cis*-1,2-dimethylcyclopropane *(2)*. No 3-methyl-1-butene is produced. It is believed that the triplet pyrazoline decomposes to nitrogen and triplet trimethylene. The latter species is the same as that produced when triplet methylene is added to *cis*- or *trans*-2-butene. Stereochemistry is lost by rotation and both isomers give



rise to the same product ratio. This supports the contention of *Doering* and *Skell* that triplet methylene forms an intermediate that is able to undergo rotation prior to ring closure.

Using *cis*- or *trans*-3,5-dimethyl-1-pyrazoline *(3)* a ratio of 40:60 *cis*- to *trans*-dimethylcyclopropane was produced. This ratio implies that the triplet formed from *(1)* is not readily interconverted to the triplet species produced from *(3)*. The absence of olefins here suggests that in the reactions of triplet methylene with the butenes the olefins are not being formed *via* a 1,4-hydrogen-atom shift.

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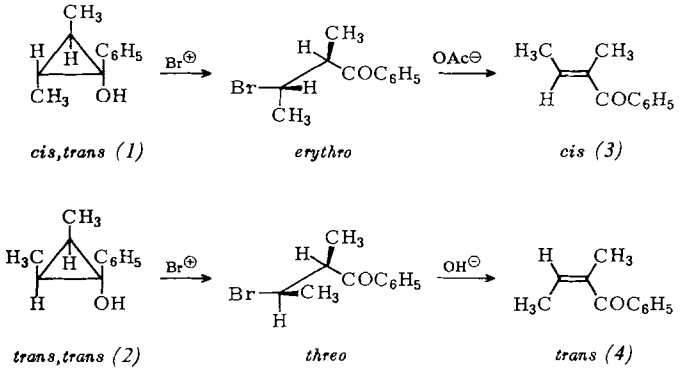
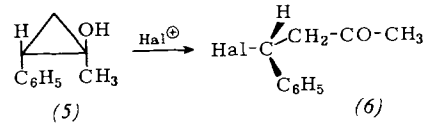
Electrophilic Cleavage of Cyclopropanols by Halogenating Agents

By *C. H. DePuy, W. C. Arney jr.*, and *D. H. Gibson*[*]

Electrophilic ring-opening of cyclopropanols by protons in acid solution has been shown previously to occur with retention of configuration at the carbon to which the hydrogen becomes attached. Many cyclopropanols react readily with sources of positive halogen (*tert*-butylhypohalite, halogen, *N*-halosuccinimide) in a variety of solvents (*tert*-butyl alcohol, CCl_4, acetic acid). *cis,trans*- and *trans,trans*-2,3-dimethyl-1-phenylcyclopropanol (*(1)* and *(2)*, resp.) and their corresponding acetates react stereospecifically with brominating



agents exclusively with inversion to give *erythro*- and *threo*-β-bromo-ketones respectively. These compounds are stereospecifically converted into *(3)* and *(4)* on treatment with weak bases.



Optically active *trans*-2-phenyl-1-methylcyclopropanol *(5)* reacts with chlorinating agents and brominating agents to give 4-halo-4-phenyl-2-butanone *(6)* as the sole product. This reaction also occurs with inversion of configuration. Assignment of configuration of *(6)* was based upon close analogies.

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Induced Paramagnetic Ring-current in the Four-membered Ring of Biphenylene and Related Hydrocarbons

By *H. P. Figeys*[*]

Several authors have noted that the signals of the biphenylene protons appear in the NMR-spectrum at a higher field than those of the benzene protons[1,2]. We have found that the same is true for certain protons of the benzobiphenylenes. This behavior can have two different causes: either the occurrence of very low deshielding ring-currents in the various rings, or the presence of an induced paramagnetic shielding ring-current in the four-membered ring of this series of compounds. Such "reversed" ring-currents have indeed been observed in the monocyclic annulenes and dehydroannulenes having $4n$ π-electrons[3].

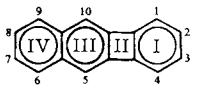
We have obtained experimental evidence for this second hypothesis by analyzing the NMR-spectrum (solvent $CDCl_3$; standard TMS, internal) of benzo[*b*]biphenylene *(1)*; the spectrum contains a broad singlet at 6.90 ppm which is attributed, by comparison with several substituted derivatives[2], to protons 1 to 5 and 10. Protons 6 to 9 give an A_2B_2 multiplet centered at about 7.30 ppm. However, in the hypothesis of deshielding ring-currents, δH^1 should appear at a lower field than δH^2, whatever the relative values of the individual ring-currents, owing to the closer proximity of rings II, III, and IV. The only way to explain the experimental observations is to postulate a shielding ring-current in the four-membered ring, whose difference in shielding effect on protons 1 and 2 is almost completely compensated by the difference in deshielding effect of rings III and IV.

Calculation of the ring-currents in biphenylene and in benzobiphenylenes by *McWeeny*'s method[4] showed that an induced paramagnetic ring-current occurs in the four-membered ring of each of these compounds. Condensation of a benzene ring onto biphenylene *(2)* along the long axis of the molecule results in a diminution of the shielding ring-current, while condensation in a non-linear way has the opposite influence. Another interesting feature is the very low ring-current in the benzene rings adjacent to the four-membered ring. These two effects are thus responsible for the position of the high-field multiplet in the spectrum of these molecules.

The occurrence of a shielding ring-current in the four-membered ring in biphenylene raised another interesting problem, namely the attributions of the individual resonance frequencies of protons 1 and 2 in *(2)*. The contributions $\delta_{R.C.}$ of the different rings to the calculated chemical shifts are given in the Table.

The calculated chemical shifts are in good agreement with experimental values: 6.598 and 6.702 ppm in $CDCl_3$[6], 6.47 and 6.60 ppm in CCl_4 solution[1]. Theoretical considerations indicate that proton 2 is more deshielded than proton 1. These assignments were confirmed by the analysis of the NMR spectra of [1-D]- and [2-D]biphenylene prepared by unambiguous syntheses[**]. The spectra of the deuterated compounds were in excellent agreement with the calculated 7 H spectra obtained by *S. Castellano* and *A. A. Bothner-By*'s LAOCOON computer program[7].

Finally, in the series of molecules investigated, it appeared that the shielding ring-current decreases when the structure of the four-membered ring changes progressively from the "cyclobutadiene-like" to the "tetramethylenecyclobutane-like" structure.



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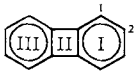

(2)

Table. Contributions of the different rings to the calculated chemica shifts of protons 1 and 2 in biphenylene *(2)*.

(2), Proton	$\delta_{R.C.}$ (ppm) [a] Ring I	Ring II	Ring III	Calculated chemical shift (ppm)
1	+ 0.648	− 0.165	+ 0.050	6.662
2	+ 0.648	− 0.040	+ 0.019	6.756

[a] Obtained by assuming $\delta_{R.C.}$ = 1.15 ppm for the benzene molecule [5].

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[**] This work was carried out in collaboration with Prof. *J. F. W. McOmie*, Bristol University.

[1] *A. R. Katritzky* and *R. E. Reavill*, Recueil Trav. chim. Pays-Bas *83*, 1230 (1964).

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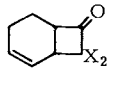
[7] *S. Castellano* and *A. A. Bothner-By*, J. chem. Physics *41*, 3863 (1964).

Cycloadditions of Dichloroketene

By *L. Ghosez, R. Montaigne, H. Vanlierde*, and *F. Dumay*[*]

Dichloroketene, generated *in situ* from dichloroacetyl chloride and triethylamine in refluxing pentane, reacts readily with cyclopentadiene and cyclopentene[1] according to the cycloaddition scheme 2 + 2 = 4.

The reaction can be extended to other olefins; for example the 1,2-cycloadducts *(1)* to *(4)*, X = Cl, have been obtained in satisfactory yields (40–75%) from cyclohexadiene, cyclohexene, dihydropyran, and indene.



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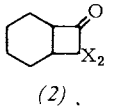

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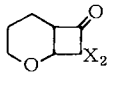

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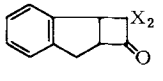

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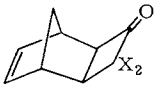

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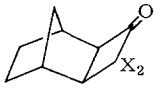

(6)

The *exo*-adducts *(5)* and *(6)*, X = Cl, have been obtained in 25% and 10% yield respectively from the reaction of dichloroketene with norbornadiene and norbornene. All adducts could be dehalogenated in high yield to the parent cyclobutanones *(1)* to *(6)*, X = H, by refluxing in cyclohexane containing two equivalents of tributyltin hydride.

Our present findings can be summarized as follows:

1. Substituting chlorine for hydrogen on a system of cumulative double bonds appears to increase considerably its reactivity (*e.g.* dichloroketene *vs.* ketene; tetrachloroallene *vs.* allene).

2. The orientation of the cycloaddition is uniform and compatible with a nucleophilic attack of the olefin on the central carbon atom of the ketene molecule.

3. No 1,4 cycloadducts are formed even with cisoid dienes such as cyclopentadiene or cyclohexadiene. Furthermore, in contrast to 1,1-dichloro-2,2-difluoroethylene[2] or tetracyanoethylene[3], dichloroketene does not add across the homodiene system of norbornadiene.

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Naamsestraat 96
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[1] *H. C. Stevens, D. A. Reich, D. R. Brandt, K. R. Fountain*, and *E. J. Caughan*, J. Amer. chem. Soc. *87*, 5257 (1965); *L. Ghosez, R. Montaigne*, and *P. Mollet*, Tetrahedron Letters *1966*, 135.

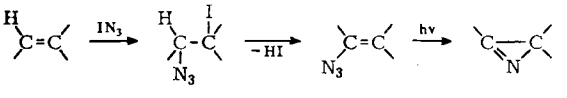
[2] *P. D. Bartlett, G. E. H. Wallbillich*, and *L. K. Montgomery*, J. org. Chemistry *32*, 1290 (1967).

[3] *A. T. Blomquist* and *Y. C. Meinwald*, J. Amer. chem. Soc. *81*, 667 (1959).

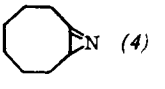
Synthesis and Chemistry of 1-Azirines

By *A. Hassner*[*]

Azirines (azacyclopropenes) *(3)* represent a difficulty accessible ring system. We now describe a general synthesis of azirines from olefins. The sequence involves stereospecific addition of IN_3 to olefins followed by elimination of HI to give vinyl azides *(2)*. The latter are photolyzed to 1-azirines *(3)*. In this manner highly strained azirines such as *(4)* are also accessible as components of bicyclic ring systems.

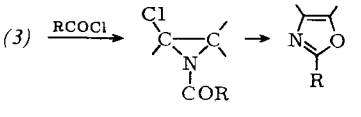


(1) (2) (3)



(4)

Azirines are only weakly basic compounds, insoluble in cold dilute acid, and do not react with alkyl halides. On the other hand, reaction occurs readily with acid chlorides to yield oxazoles *(6)*, *N*-acyl-2-chloroaziridines *(5)* being formed as intermediates.



(5) (6)

Reduction of 2,3-substituted azirines with $LiAlH_4$ occurs stereospecifically from the less hindered side to give *cis*-aziridines. In this way, *cis*-aziridines can be synthesized from either *cis* or *trans* olefins or a mixture of both. The IN_3 adduct of bromophenylacetylene pyrolyzes under mild conditions to diphenyldicyanoethylene, presumably *via* an azirinium ion or radical.

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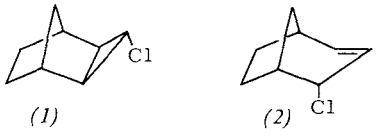
The *exo*-Tricyclo[3.2.1.$0^{2,4}$]octane System

By *C. W. Jefford*[*]

The addition reactions of monochlorocarbenoid to bicyclo[2.2.2]oct-2-ene, to norbornene, and to 1-methyl- and 2-methylnorbornene have been studied. In the case of the last three compounds the *exo* addition took place exclusively. Quite strikingly, for all four olefins the addition occurred with pronounced *anti* stereoselectivity, the *syn-anti* ratios being 1:5, 1:6, 1:1.5, and 1:9.8 respectively. A typical *syn-anti* ratio for a *mono*cyclic olefin is 3:1. It should be pointed out that these ratios apply to the generation of the carbene from equimolar quantities of CH_2Cl_2 and CH_3Li (from CH_3Cl) in the presence of a 25% excess of olefin. The *syn-anti* ratios have been rationalized in terms of dispersion forces.

All the *anti* products, *e.g. anti*-3-chlorotricyclo[3.2.1.$0^{2,4}$]-octane *(1)*, were quite stable to heat and to Ag^+ in aqueous solution. Clearly, ionization of the cyclopropyl chloride portion is prevented by the geometric restriction of the appropriate disrotatory mode.



(1) *(2)*

In the case of the norbornene derivatives, the *syn*-adducts were not observed, only their rearrangement products, the *exo*-4-chlorobicyclo[3.2.1]oct-2-enes, *e.g. (2)*. Although the *syn* adduct from bicyclo[2.2.2]oct-2-ene could be observed below 60 °C, it rearranged readily on warming to 4-chlorobicyclo[3.2.2]non-2-ene. The geometry of the *syn* adducts permits ionization to the allylic system.

The addition of chlorocarbenoid to 2-methylnorbornene gave the stable *exo-anti* adduct and 2-methylenebicyclo-[3.2.1]oct-3-ene which is derived from the *exo-syn* adduct. It can be seen, therefore, that the elimination of hydrogen chloride from the *exo-syn* adduct depends upon prior rearrangement or ionization to the allylic system.

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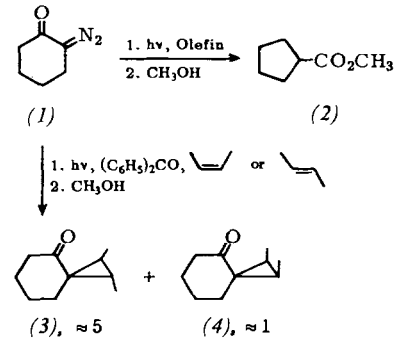
The Photosensitized Decomposition of Diazoketones

By *M. Jones jr.* and *W. Ando*[*]

Whereas diazoketone *(1)* undergoes the photochemical Wolff rearrangement to *(2)*, even in the presence of carbene acceptors, spiroketones are produced in 20–50% yield when the decomposition is photosensitized with benzophenone. The same mixture of the adducts *(3)* and *(4)* is formed from both *cis-* and *trans*-2-butene. Presumably the triplet carbene is produced on photosensitization but does not rearrange to the triplet ketene, adding instead to the acceptor olefin to give the spiroketones observed.



(1) *(2)*

(3), ≈ 5 *(4)*, ≈ 1

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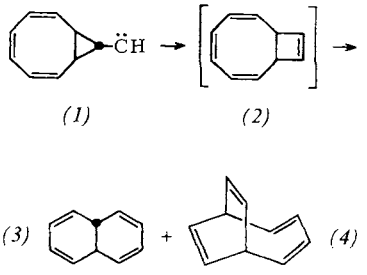
Rearrangements of Highly Unsaturated Cyclopropyl Carbenes

By *M. Jones jr., S. D. Reich, L. T. Scott,* and *L. E. Sullivan*[*]

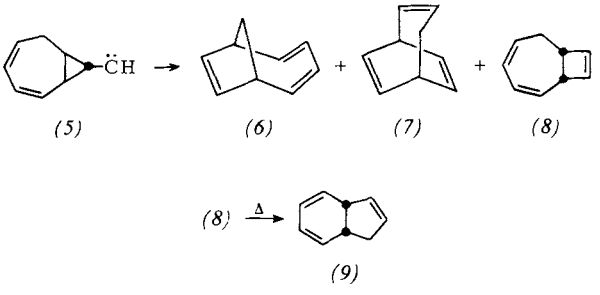
Generation of unsaturated cyclopropyl carbenes of the type *(1)*, *(5)*, or *(12)* yields besides the normal ring-expanded product, other rearrangement compounds[1,2]. Thus *(1)* gives *trans*-9,10-dihydronaphthalene *(3)*, a product derived[3] from the cyclobutene *(2)* and bicyclo[4.2.2.]deca-2,4,7,9-tetraene *(4)*. *A priori (4)* could result from rearrangement of



(1) *(2)*

(3) + *(4)*

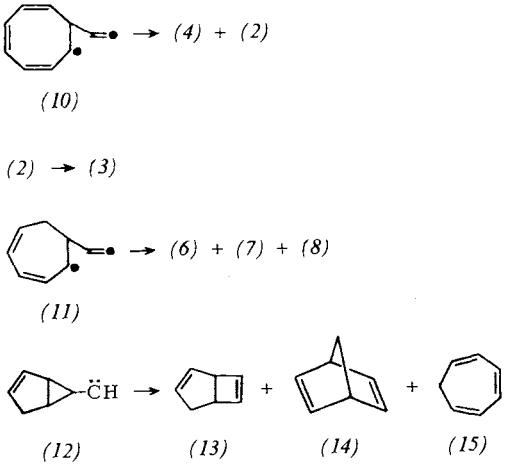
either *(1)* or *(2)*. Rearrangement of *(5)* leads to *(6)* and *(7)*, which are both possible rearrangement products of *(8)*, and *(8)* itself. Compound *(8)*, however, rearranges to *(9)* and not



(5) *(6)* *(7)* *(8)*

(9)

to either *(6)* or *(7)*. It seems likely, therefore, that the carbenes *(1)* and *(5)* are involved in the production of the rearranged products. A mechanism involving the opened species



(12) *(13)* *(14)* *(15)*

(10) and *(11)* is proposed. Similar rearrangements take place in smaller systems. For example *(12)* yields *(13)*, *(14)*, and *(15)*.

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[1] *M. Jones jr.* and *L. T. Scott*, J. Amer. chem. Soc. *89*, 150 (1967).

[2] *M. Jones jr.* and *S. D. Reich*, J. Amer. chem. Soc. *89*, 3935 (1967).

[3] *S. Masamune, C. G. Chin, K. Hojo*, and *R. T. Seidner*, J. Amer. chem. Soc. *89*, 4804 (1967).

The Synthesis and Chemistry of Bicyclo[x.2.0] Systems

By *A. P. Krapcho* and *J. H. Lesser* [*]

The 1,2-cycloaddition of dimethylketene to cycloolefins has been shown to be a general method for the preparation of fused bicyclo[x.2.0]alkanones where $x = 6$ or 7. Product structures were determined by infrared, ultraviolet, and NMR spectroscopy in conjunction with deuterium exchange experiments and elemental analysis.

Several of the bicyclo[x.2.0]alkanones were subjected to isomerization conditions. In these experiments, particular attention was focused on the stability of the *cis*-ring fusion. The NMR spectra of the isomerization products, especially the geminal dimethyl region, facilitated product identification. It was found that the *trans*-bicyclo[6.2.0]decane and -[7.2.0]-undecane ring systems were more stable than their *cis*-analogs for the compounds studied.

Using a model system, the preliminary steps of a synthesis of the sesquiterpene isocaryophyllene were investigated.

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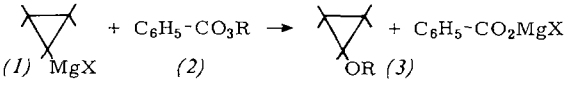
The Direct Conversion of Cyclopropyl Bromides into Cyclopropyloxy Derivatives

By *D. T. Longone* [*]

Cyclopropyl alcohols and esters are key intermediates in a variety of current mechanistic investigations. Detailed studies of these compounds have been limited only by their synthetic availability. Cyclopropyl halides, despite their ease of preparation *via* halocarbene reactions, have not been useful as precursors of cyclopropyloxy compounds (esters, ethers, and alcohols). The halides are virtually inert in S_N2 displacements and react *via* the S_N1 path only with assisted ring-opening.

We wish to report the first synthetically useful conversion of cyclopropyl halides into the corresponding cyclopropyloxy derivatives. The method developed utilizes cyclopropyl carbanions as agents for nucleophilic attack on the oxygen atom of an appropriate substrate. For example, the reaction of a cyclopropyl Grignard reagent *(1)* with benzoyl peroxide *(2a)* or *tert*-butyl perbenzoate *(2b)* affords a cyclopropyl benzoate *(3a)* or a *tert*-butyl cyclopropyl ether *(3b)* in good yield.



(1) *(2)* *(3)*

(a), R = $-\overset{\overset{O}{\|}}{C}-C_6H_5$ *(b)*, R = $C(CH_3)_3$

Compounds of type *(3b)* are particularly useful because they can be converted into acetates in virtually quantitative yield by the reagent acetic anhydride/BF_3-ether. Cyclopropyl esters *(3a)* are reductively cleaved to cyclopropanols by methyllithium or $LiAlH_4$; thus, the conversion of halide to alcohol is possible.

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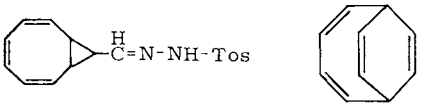
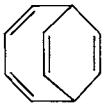
Bicyclo[6.2.0]deca-2,4,6,9-tetraene [**]

By *S. Masamune* [*]

A solution of bicyclo[6.1.0]nona-2,4,6-triene-*trans*-9-carboxaldehyde tosylhydrazone *(1)* in dry tetrahydrofuran containing an equivalent amount of sodium methoxide was irradiated at −30 °C with a Hanovia mercury lamp (Pyrex



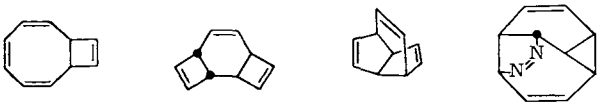
(1)



(2)

filter). Workup, at temperatures below 0 °C, of the reaction products yielded two new compounds, A (45% yield) and B (21%), in addition to bicyclo[4.2.2]deca-2,4,7,9-tetraene *(2)* (7%) and cyclooctatetraene (27%).

NMR-, UV-, and mass-spectrometric data and chemical evidence proved that compound A was bicyclo[6.2.0]deca-2,4,6,9-tetraene *(3)*. The two structures *(4)* and *(5)* were suggested for compound B.



(3) *(4)* *(5)* *(6)*

Compound *(3)* readily and quantitatively isomerizes to *trans*-9,10-dihydronaphthalene. The isomerization is first order and is characterized by the following kinetic data.

$k_{46.8°C} = (6.9 \pm 0.2) \times 10^{-5}\ sec^{-1}$
$k_{74.8°C} = (1.72 \pm 0.05) \times 10^{-3}\ sec^{-1}$
$\Delta H^{\ddagger} = 24.9$ kcal/mole,
$\Delta S^{\ddagger} = -0.4$ cal·deg^{-1}·mole^{-1}

Upon irradiation with a low pressure mercury lamp at −80 °C for one minute, *(3)* isomerized to *trans*-9,10-dihydronaphthalene (20–30% yield), *cis*-9,10-dihydronaphthalene (10 to 15%), *(2)* (50%), and bullvalene (3–10%).

The sodium salt of *cis*-*(1)* provided the pyrazoline *(6)* in excellent yield. Thermolysis of *(6)* at 110–115 °C afforded an approximately 1:1 mixture of bullvalene and *(2)*. Examination of an NMR spectrum (−100 °C) of the photolyzate of VI (photolysis was performed at 77 °K) revealed that the product mixture consisted of *(2)* (65% yield), bullvalene (27%), and compound B (8%). These reactions were compared with the formation of tetracyclo[4.4.0.0^{5,7}.0^{2,10}]deca-3,8-diene.

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[**] Investigation carried out in collaboration with *C. G. Chin, H. Zenda, K. Hojo*, and *R. T. Seidner*.

Preparation of Small Rings by Cycloaddition of Polar Compounds

By *G. Opitz* [*]

Methanesulfonyl chloride and triethylamine in acetonitrile at −40 °C afford mesylsulfene, $SO_2=CH-SO_2-CH_3$. In the presence of vinyl ethers 3-alkoxy-2-mesylthietane 1,1-dioxides are formed in good yields by 2+2 cycloadditions.

Cycloaddition to *cis*- and *trans*-butenyl butyl ether is stereospecific with respect to olefin configuration. The *cis*-olefin gives 86% of *cis,trans*-2-ethyl-3-propoxy-4-mesylthietane 1,1-dioxide, the *trans*-olefin gives an 80% yield of a liquid mixture of 91 parts of *trans,trans*- and 9 parts of the *trans,cis*-isomer.

However, cycloaddition of sulfene (from methanesulfonyl chloride and triethylamine) to 4-(*cis*-propenyl)morpholine is not stereospecific. The *cis*-enamine in ether at −10 °C affords 60–70% yields of a mixture of 51 parts of *cis*-2-methyl-3-morpholinothietane 1,1-dioxide and 49 parts of the *trans*-isomer. As expected, only the *trans*-product was obtained from the *trans*-enamine.

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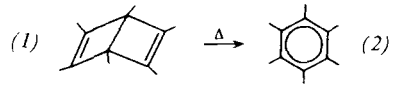
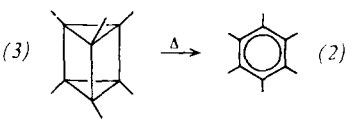
The Kinetics and Thermochemistry of the Thermal Rearrangement of Hexamethyl(Dewar benzene) and of Hexamethylprismane

By *J. F. M. Oth* [*]

Hexamethylbicyclo[2.2.0]hexa-2,5-diene [hexamethyl(Dewar benzene)] *(1)* rearranges thermally into hexamethylbenzene *(2)* above 80 °C.

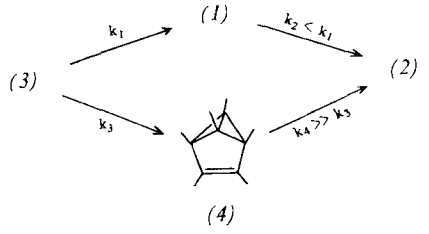


This exothermal reaction was followed in a temperature-programmed calorimeter. From the curve recorded, the kinetic parameters and the heat of the reaction could be deduced (see Table 1).



The curve recorded with the calorimeter, together with kinetic experiments carried out at different temperatures and followed by NMR spectroscopy, showed that this rearrangement *(3)* → *(2)* proceeds *via* two parallel kinetic paths: In one hexamethyl(Dewar benzene) *(1)* is formed as intermediate and accumulates appreciably in the course of the reaction; in the second, the rearrangement proceeds *via* the hexamethyltricyclo[2.1.1.$0^{5,6}$]hex-2-ene (hexamethylbenzvalene) *(4)*, the stationary concentration of which remains always very small [NMR signals at $\tau = 8.375$ (2 olefinic CH_3), $\tau = 9.05$ (2 aliphatic CH_3) and $\tau = 9.17$ (2 aliphatic CH_3)].

The scheme of the thermal rearrangement of *(3)* is thus the following:



with the implications that $k_1 > k_2$ and $k_4 \gg k_3$.

The kinetic parameters for the steps characterized by the rates k_1, k_2, and k_3 are given in Table 1.

The overall heat of isomerization for the reaction *(3)* → *(2)* was found to be:

$$\Delta H_{\text{isom}}\ (3)\rightarrow(2) = H_{(2)} - H_{(3)} = -91.2 \text{ kcal/mole}$$

From this value, the heat of combustion of *(2)*, and thermochemical data we calculated the strain energy in *(3)* to be 116 kcal/mole. This quantity is essentially the strain energy of the prismane skeleton but comprises also the non-bonding interactions between the methyl groups.

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Table 1. Kinetic data. All reactions being of first order.

Reaction	$k_{150\,°C}$ (sec^{-1})	E_a (kcal·mole^{-1})	$\log_{10}A$	$\Delta G^{\ddagger}$ (kcal·mole^{-1})	$\Delta S^{\ddagger}$ (kcal·mole^{-1})	$\Delta H^{\ddagger}$ (cal mole^{-1} deg^{-1})	$\Delta H_{\text{isom.}}$ (kcal·mole^{-1})
(1)→*(2)*	$k_2 = 6.57 \times 10^{-5}$	37.2	15.03	33.2	36.4	7.5	−59.5
(3)→*(1)*	$k_1 = 1.06 \times 10^{-3}$	33.8	14.50	30.8	33.0	5.1	−31.7 [a]
(1)→*(2)*	$k_2 = 5.67 \times 10^{-5}$	37.7	15.22	33.3	36.8	8.4	−59.5
(3)→*(4)*	$k_3 = 6.32 \times 10^{-4}$	33.2	13.94	31.3	32.3	2.5	?
(4)→*(2)*	$k_4 \gg 6.32 \times 10^{-4}$	?	?	?	?	?	?
(3)→*(2)*	$k_1 + k_3 = 1.69 \times 10^{-3}$						−91.2

[a] Value obtained by difference (91.2−59.5).

From the heat of isomerization *(1)* → *(2)* ($\Delta H_{\text{isom. } (1)\rightarrow(2)} = -59.5$ kcal/mole), the heat of combustion of *(2)*, and thermochemical data, we have computed the strain energy in *(1)* to be 44.5 kcal/mole. This quantity is essentially the strain energy as accumulated in the bicyclic system, but it also includes the non-bonding interactions between the methyl groups.

Hexamethyltetracyclo[2.2.0.$0^{2,6}$.$0^{3,5}$]hexane (hexamethylprismane) *(3)* rearranges thermally into hexamethylbenzene *(2)* above 60 °C.

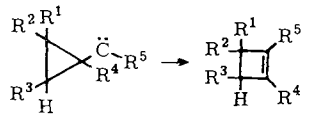
Reactions of Cyclopropyl Carbenes

By *I. D. R. Stevens, H. M. Frey,* and *C. L. Bird* [*]

The reaction of cyclopropyl carbene to give cyclobutene and of cyclopropyl methyl carbene to give 1-methylcyclobutene, discovered by *Friedman* and *Shechter* [1], has been shown to be a general reaction of cyclopropyl-substituted carbenes (see Table 1).

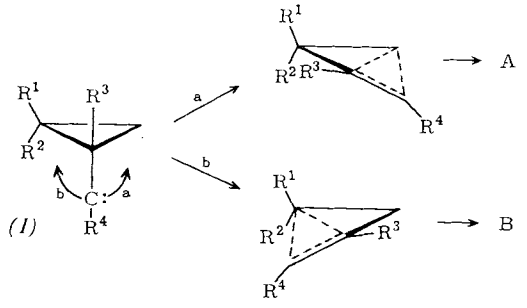
The reaction has great synthetic utility for the preparation of cyclobutanes and gives yields in the range of 50–70% (based

Table 1. Rearrangement of symmetrically substituted cyclopropyl carbenes.



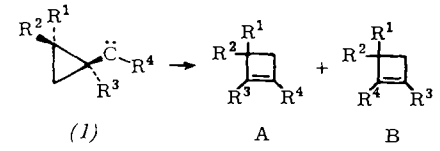
R^1	R^2	R^3	R^4	R^5	Ref.
H	H	H	H	H	[1]
H	H	H	H	CH_3	[1]
H	$-(CH_2)_3-$		H	H	[2]
H	$-(CH_2)_4-$		H	H	[2]
H	$-(CH_2)_5-$		H	H	[2]
CH_3	CH_3	H	H	H	[3]
C_2H_5	C_2H_5	H	H	H	[4]
CH_3	C_2H_5	H	H	H	[4]
CH_3	H	H	CH_3	CH_3	[3]
H	H	H	H	Cyclopropyl	[3]
H	H	H	H	Cl	[5]

on starting aldehyde or ketone). For those cases in which the cyclopropane ring is not symmetrically substituted (Table 2), a rationalization of the major product is proposed in terms of the steric effects dominant in the intermediate carbene *(1)*.



Conversion to cyclobutene necessarily involves rotation of the "carbene" carbon into the plane of the ring and route (a) or route (b) is followed depending on whether the interaction between R^1, R^2, and the "carbene" carbon is respectively larger or smaller than the interaction between R_1, R_2, and R_3. Thus in *(1a)–(1c)* (Table 2) this leads to preferential migration by route (a) *viz*: the less substituted bond migrates and in *(1d)* these are nearly equal leading to reaction by both routes in equal amounts.

Table 2. Rearrangement of unsymmetrically substituted cyclopropyl carbenes *(1)*.



(1) A B

	R^1	R^2	R^3	R^4	A (%)	B (%)	Ref.
a	CH_3	CH_3	H	CH_3	97.5	2.5	[6]
b	H	CH_3	H	CH_3	95.6	4.4	[6]
c	CH_3	H	H	CH_3	72.1	27.9	[6]
d	CH_3	H	CH_3	H	49.3	50.7	[7]

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[1] *L. Friedman* and *H. Shechter*, J. Amer. chem. Soc. *82*, 1002 (1960).

[2] *W. Kirmse* and *K.-H.* Pook, Chem. Ber. *98*, 4022 (1965).

[3] *H. M. Frey* and *I. D. R. Stevens*, unpublished.

[4] *H. M. Frey* and *R. M. Solly*, personal communication.

[5] *G. F. Bradley* and *I. D. R. Stevens*, unpublished.

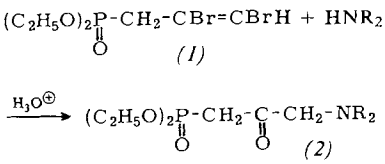
[6] *C. L. Bird*, *H. M. Frey*, and *I. D. R. Stevens*, Chem. Commun. *1967*, 707.

[7] *C. L. Bird* and *I. D. R. Stevens*, unpublished.

Aminomethyl Cyclopropyl Ketones from 3-Amino-2-oxoalkylphosphonates

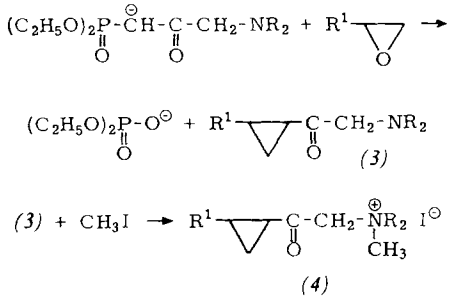
By *G. Sturtz* [*]

Molecules containing cyclopropyl or amino-ketonic groups have interesting pharmacological properties. We therefore tried to include both such groups in one molecule. Diethyl 2,3-dibromoallylphosphonate *(1)* and an amine afford readily the *N,N*-disubstituted 3-aminoacetonylphosphonate *(2)* [1], which serves as our intermediate.



(a), R = CH_3
(b), R = C_2H_5
(c), R_2 = $-(CH_2)_2-O-(CH_2)_2-$
(d), R_2 = $-(CH_2)_5-$

We have shown previously [2] that carbanions from 2-oxoalkylphosphonates react with epoxides to yield alkyl cyclopropyl ketones. The carbanion from *(2)* yields the desired aminomethyl cyclopropyl ketones *(3)* in one step.



For interpretation of the results of the reaction of *(2)* with epoxides (see Table 1) the yields of *(3)* were compared with the differences in the mobility of the protons on each side of the carbonyl group. To a first approximation the difference in mobility can be determined from the chemical shift $\Delta\delta = \delta_{H(P)} - \delta_{H(N)}$ [cf. *(3c)* and *(3d)*]. The substitution on nitrogen appears also to play a part [cf. *(3b)* and *(3c)*]. From gas chromatography it can be seen that preponderatingly (95%) one of the two stereoisomers of *(3)* is formed. The change in the chemical shift by a factor of 2 on going from benzene to $CDCl_3$ indicates a *trans*-configuration [3].

Table 1. $\Delta\delta = \delta_{H(P)} - \delta_{H(N)}$ of *(2)* and yields of *(3)*.

	(a)	(b)	(c)	(d)
$\Delta\delta \cdot 10^{-6}$ of *(2)*	−0.01	−0.12	−0.07	+0.07
Yield (%) of *(3)*	47	54	35	65

Compounds *(3)* react with methyl iodide, yielding salts *(4)* in which R^1 = H, R = R^2 = CH_3; R = R^1 = R^2 = CH_3; R^1 =

$R^2 = CH_3$, $R_2 = -(CH_2)_2-O-(CH_2)_2-$; $R^1 = R^2 = CH_3$, $R_2 = -(CH_2)_5-$. These products have a laming action similar to that of decamethonium[4].

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[1] Bull. Soc. chim. France *1967*, 1345.

[2] *G. Sturtz*, Bull. Soc. chim. France *1964*, 2349.

[3] *J. Seyden, P. Arnaud, J. L. Pierre*, and *M. Plat*, Tetrahedron Letters *1967*, 3719.

[4] We are grateful to the Institute Pasteur, Paris, where the pharmacological tests were carried out.

Formation of Small Rings by Intramolecular Nucleophilic Substitution

By *C. J. M. Stirling*[*]

Comparative kinetic information on the ease of ring closure by intramolecular nucleophilic substitution is scarce. Data available[1] show that rates of ring formation are in the following order of ring size: $5 > 6 > 4$. Rates of closure of three-membered rings are always greater than for four-membered rings and sometimes even faster than for five- and six-membered rings (see Table). These variations are to be considered in terms of the balance between the enthalpy and entropy of activation for ring closure; the former is unfavorable and latter is favorable for three-membered rings and *vice versa* for five- and six-membered rings.

In recent work[2] on the formation of aryl cycloalkyl sulfones from aryl ω-bromoalkyl sulfones under basic conditions (Table 1, reaction 5), closure of a three-membered ring occurred much more rapidly than that of a five-membered ring. Measurement of isotope effects showed[3] that the cyclopropyl sulfone was formed in a stepwise process. We postulate that, in a transition state which leads to the formation of a three-membered ring, attachment of a conjugative substituent in such a way as to allow resonant interaction between the ring being formed and the substituent reduces the unfavorable enthalpy term for this process. Such interactions are well known for both ground and excited states of cyclopropanes[4].

The data collected in Table 1, which contains the results of some of our own investigations, support our postulate for systems in which (cf. reactions 1–6 *versus* 10–13) carbocyclic rings are produced. Formation of a five-membered ring, however, is preferred when the nucleophilic atom is that of a first row element other than carbon even when a conjugative substituent is attached to it (cf. reactions 8 and 9).

This behavior is in accord with other experimental evidence on poor conjugation *via* a heteroatom in a three-membered ring[5] and is supported by theoretical considerations[6]. Systems in which the heteroatom is a second-row element appear to obey the generalization (cf. reactions 7 and 13).

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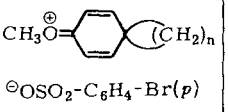
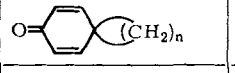
[1] *B. Capon*, Quart. Rev. (chem. Soc., London) *18*, 45 (1964).

[2] *A. C. Knipe* and *J. C. M. Stirling*, J. chem. Soc. (London) *B 1967*, 808.

Table 1. Relative rates (k_{rel}) of ring closure *versus* number of ring members.

Nr.	Starting material	Product	Solvent	Temp. (°C)	k_{rel} $n=3$	$n=4$	$n=5$	$n=6$
1	p-$CH_3O-C_6H_4-(CH_2)_n-O-SO_2-C_6H_4-Br(p)$		CH_3COOH	75	1	—	6×10^{-3}	—
2	$^{\ominus}O-C_6H_4-(CH_2)_nBr(p)$		CH_3OH	25	1	—	9.1×10^{-4}	—
3	$C_6H_5-CH_2-SO_2-(CH_2)_3Cl$	$C_6H_5-CH_2-SO_2-$ cyclopropane [a]	$NaNH_2$/Diglyme	60	1	—	0.25 [b]	—
4	$CH_3-CO-(CH_2)_3Cl$	CH_3-CO- cyclopropane [a]	12 N NaOH	100	1	—	0.25 [b]	—
5	Tosyl-$(CH_2)_nBr$	Tosyl-CH $(CH_2)_{n-1}$	[c]	55	1	1×10^{-4} [b]	0.01 [b]	1×10^{-4} [b]
6	$(C_2H_5OCO)_2CH-(CH_2)_nCl$	$(C_2H_5OCO)_2C$ $(CH_2)_n$	[c]	25	1	1.5×10^{-6}	0.01	8×10^{-6}
7	$C_6H_5S-(CH_2)_nCl$	$C_6H_5\overset{\oplus}{S}$ $(CH_2)_nCl^{\ominus}$	Dioxane/H_2O	100	1	5×10^{-3} [b]	0.2	—
8	Tosyl-NH-$(CH_2)_nCl$	Tosyl-N $(CH_2)_n$	C_2H_5ONa/C_2H_5OH	25	1	6×10^{-5}	10 [d]	6×10^{-3}
9	$C_6H_5-NH-(CH_2)_nBr$	C_6H_5N $(CH_2)_n$	$NaHCO_3/H_2O$	25	1	—	10 [d]	—
10	$NH_2-(CH_2)_nBr$	HN $(CH_2)_n$	H_2O	25	1	0.017	850	15
11	$^{\ominus}OCO-(CH_2)_n-CHBr-CH_3$	H_3C-HC—O / $(H_2C)_n-CO$	H_2O	25	1	0.8	1.2×10^{-4}	—
12	$^{\ominus}OCH_2-(CH_2)_nCl$	O $(CH_2)_{n+1}$	H_2O	18	1	—	5	5×10^{-3}
13	$C_2H_5S-(CH_2)_nCl$	$C_2H_5\overset{\oplus}{S}$ $(CH_2)_nCl^{\ominus}$	H_2O	18	1	4×10^{-4}	10 [d]	—

[a] Sole product. [b] Max. value [c] K *tert*-butoxide in *tert*-butanol. [d] Min. value.

[3] *R. Bird* and *J. C. M. Stirling*, J. chem. Soc. (London) *B 1968*, 111.

[4] *R. Hoffmann*, Tetrahedron Letters *1965*, 3819.

[5] *A. T. Bottini* and *C. P. Nash*, J. Amer. chem. Soc. *84*, 734 (1962).

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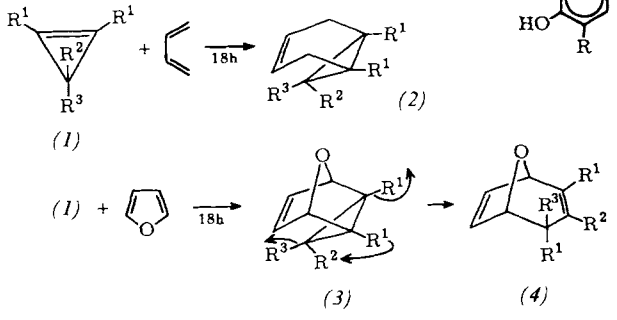
Diels-Alder Reactions of Tetrahalocyclopropenes

By *S. W. Tobey* and *D. C. F. Law*[*]

All tetrahalocyclopropenes of type *(1)*[1] undergo 1,4 addition to butadiene at 80 °C in CCl_4 to give stable Diels-Alder adducts of type *(2)* in high yield. These same cyclopropenes react with furan to provide structures *(3)* and/or *(4)* (see Table 1). Cyclopentadiene reacts with compounds of type *(1)* to provide analogous products.



(1) *(2)* *(3)* *(4)*

Table 1. Relative reaction rate (k_{rel}) of *(1)* with furan at 79 °C in CCl_4.

	(1)			k_{rel}	Product
	R^1	R^2	R^3		
(a)	Br	Br	Br	1.42 ± 0.05	*(4)*
(b)	Cl	Cl	Cl	1.00	*(4)*
(c)	Cl	Cl	F	0.48	*(3)*
(d)	Cl	F	Cl	0.31	*(4)*
(e)	Br	F	F	0.45	*(3)*
(f)	Cl	F	F	0.29	*(3)*

In accord with the predictions of the Woodward-Hoffmann rules, ring opening of *(3)* to *(4)* occurs only *via* ionization of the halide situated *syn* to the double bond. When R^3 = F [as in *(1c)*, *(1e)*, and *(1f)*], the original adduct *(3)* is stable; if R^3 = Cl or Br, ring opening to *(4)* occurs so readily that *(3)* is not isolated.

The observed order of dienophilic character of cyclopropene *(1)* towards furan suggests that in 3,3-difluorinated cyclopropenes [*(1e)* and *(1f)*] ring bonding is stabilized and the energy of the ground state is lowered, thus increasing the activation energy for Diels-Alder adduct formation. The high thermal stabilities of *(2a)* and *(2b)* relative to *(3a)* and *(3b)* reflect the strain built into structures of type *(3)* by the oxygen and methylene bridges. These bridges distort the Diels-Alder adducts in precisely the direction required to initiate disrotatory cyclopropane-ring opening[2].

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[1] *S. W. Tobey* and *R. West*, J. Amer. chem. Soc. *88*, 2481 (1966). For a complete account of this work, see *D. C. F. Law* and *S. W. Tobey*, J. Amer. chem. Soc. *90*, 2376 (1968).

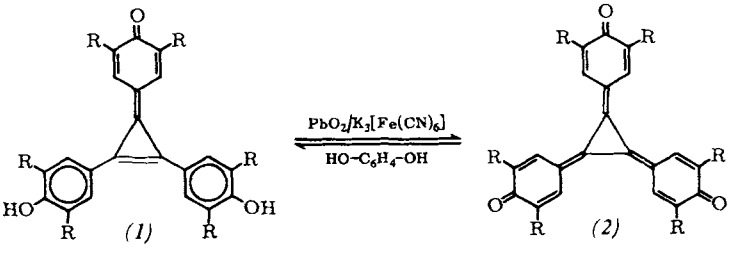
Derivatives of the Trichlorocyclopropenylium Ion

By *R. West*[*]

Trichlorocyclopropenylium tetrachloraluminate, $C_3Cl_3^{\oplus}AlCl_4^{\ominus}$, reacts with aromatic hydrocarbons with replacement of one, two, or three chlorines by aromatic groups. When one of the aromatic rings bears a hydroxyl group, proton elimination takes place and quinocyclopropene is formed readily.

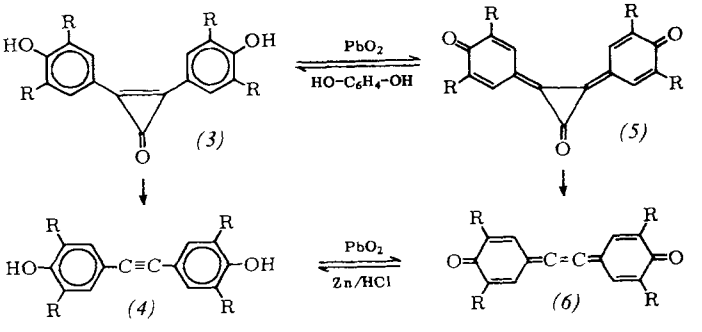
When $C_3Cl_3^{\oplus}$ is allowed to react with three equivalents of a 2,6-dialkyl-substituted phenol, the initially formed triarylcyclopropenylium is converted into a bis(hydroxyaryl)-quinocyclopropane *(1)*. Oxidation of *(1)* leads to the formation of a triquinocyclopropane *(2)*.

All six compounds of type *(2)* that have been prepared so far are dark violet solids which exhibit a strong absorption band at 770 nm. Compounds *(2)* can be regarded as unusually stable derivatives of [3]-radialene; when R = *tert*-butyl these compounds can be heated to 280 °C without decomposition.



(1) *(2)*

The reaction *(1)*→*(2)* proceeds *via* intermediary monoradicals. The ESR spectra of the radical anions of *(2)* show that the unpaired electron is fully delocalized over the three six-membered rings.



(3) *(5)* *(4)* *(6)*

Reaction of 2,6-disubstituted phenols with $C_3Cl_3^{\oplus}$ at 0 °C leads to bis(hydroxyaryl)cyclopropenones *(3)*, which on irradiation lose carbon monoxide and are converted into diarylacetylenes *(4)*. Compounds *(3)* undergo reversible oxidation to compounds *(5)*, which lose carbon monoxide spontaneously to yield diquinoethylenes *(6)*. Compounds *(6)* are also obtained from *(4)* by oxidation.

[VB 159 IE]
German version: Angew. Chem. *80*, 628 (1968)

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Structure of Glutamate Dehydrogenase from Ox Liver

By *H. Sund*[*]

Measurement of light scattering as a function of protein concentration (in the concentration range 25 µg/ml–8 mg/ml) afforded results, which, on comparison with the calculated interdependence of apparent molecular weight and protein concentration, indicate that the association-dissociation

equilibrium between the subunits of the glutamate dehydrogenase (molecular weight 270000) and the octamer proceeds in a stepwise manner[1]. From the dependence of the X-ray small-angle scattering on the protein concentration (1–33 mg/ml) it follows that the radius of gyration (R_q = 30.3 Å), the mass per 1 Å length (M/1 Å = 2340), and the shape of the cross-section of glutamate dehydrogenase are independent of protein concentration. From the comparison of the experimental scattering curves with theoretical cross-section curves for elliptical cylinders it is concluded that the cross-section is either circular (diameter 86 Å) or elliptical with an axial ratio of 0.8:1 (long axis 95 Å, short axis 76 Å). The length of the associated molecule was found to be 800–900 Å. On the basis of these results, the shape of the molecule can best be described as cylindrical; furthermore, the results confirm the earlier conclusion that the dissociation of the prolate molecule into subunits involves a transfer cleavage. The mass per unit length measurements and the pronounced side maxima of the scattering curve suggest that glutamate dehydrogenase is very loosely built and posseses voids[2].

Lecture at Giessen on December 19, 1967 and at the Max-Plank-Institut für Experimentelle Medizin, Göttingen, February 2, 1968 [VB 157 IE]
German version: Angew. Chem. *80*, 669 (1968)

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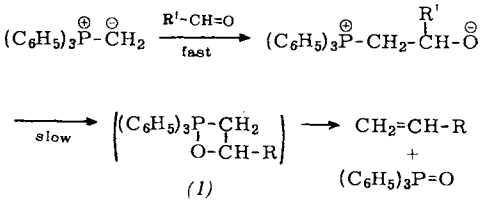
[1] Experiments with *W. Burchard.*

[2] Experiments with *M. Herbst* and *I. Pilz.*

Mechanism and Stereochemistry of Wittig-Olefin Syntheses

By *M. Schlosser*[*]

The velocity of, and the yield obtained in, carbonyl olefination by triphenylphosphonium ylids is strongly influenced by the reaction conditions. Kinetic studies showed that the slowest step is usually the decomposition of the zwitterionic adduct, the betaine, to olefin and triphenylphosphine oxide by way of the oxaphosphetane *(1)*.



(1)

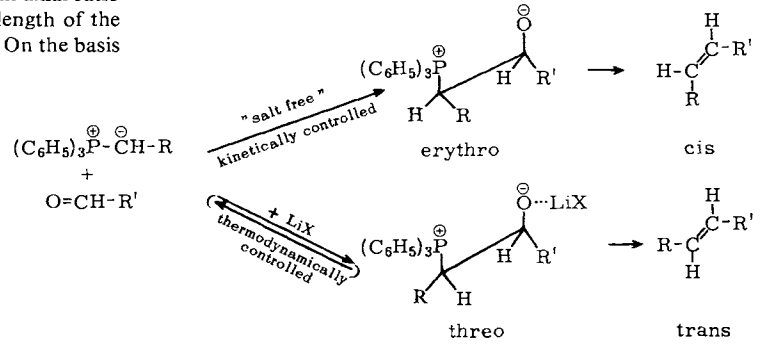
This decomposition is particularly strongly hindered by lithium salts, which give betaine-LiX adducts. In sum the following order of increase in reaction rate is observed: apolar solvent + presence of lithium salts < polar solvent < salt-free apolar solvent.

On the basis of this mechanistic knowledge procedures have been developed that direct the carbonyl olefination according to choice towards *cis*- or *trans*-olefins. For this purpose two stereochemical principles are used:

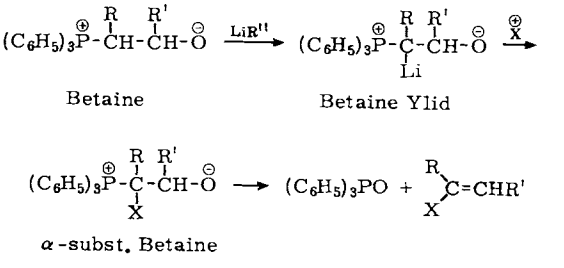
1. Under kinetic control salt-free phosphorus ylids link to give preferentially the thermodynamically unstable *erythro*-betaines.

2. In the presence of lithium salts the equilibrium between the two diastereoisomeric betaines is shifted far towards the *threo*-epimer.

The equilibrium between the diastereoisomeric betaines can be reliably and rapidly established by way of the betaine ylids. This new type of compound also offers further prepar-



ative possibilities: addition of an electrophile $X^{\oplus}$ (X = *e.g.*, D, CH_3, F, Cl, Br) leads to an α-substituted betaine (*erythro*/*threo* mixture or pure *threo*-form) and thence the corresponding unsaturated compound.



Lecture at Giessen (Germany) on July 9, 1968 [VB 158 IE]
German version: Angew. Chem. *80*, 637 (1968)

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The Biochemistry of Fructose Metabolism

By *W. Lamprecht*[*]

Metabolism of fructose in animal tissues differs markedly from the normal degradation of glucose with respect to organ specificty and the sequence of the metabolic pathway. In mammals, fructose can be degraded only in liver, kidney, and mucosa of the small intestine; only these organs contain the appropriate enzyme pattern. Ketohexokinase catalyzes phosphorylation of fructose to its 1-phosphate; in liver this particular enzyme is about twice as active with fructose than with glucose. Fructose 1-phosphate is further degraded to dihydroxyacetone phosphate and D-glyceraldehyde by liver-aldolase which differs in its specificity from that of muscle. Dihydroxyacetone phosphate enters the normal glycolytic pathway. However, D-glyceraldehyde may function as a substrate in four enzymatic reactions competing with each other:

1. D-glyceraldehyde can be phosphorylated to its 3-phosphate by means of ATP and triokinase.

2. and 3. D-glyceraldehyde can also be reduced to glycerol, either by a NADH- or a NADPH-dependent alcohol-dehydrogenase. Glycerol is phosphorylated to L-glycerol-3-phosphate (an intermediate of normal glycolysis) by means of glycerokinase. The reduction, however, seams rather unlikely in liver, due to the high K_M of the NADH-specific

alcohol dehydrogenase and the low activity of the NADPH-specific enzyme. This is confirmed by isotope experiments. 4. D-glyceraldehyde can be oxidized to D-glyceric acid in a NAD^+-dependent reaction by means of aldehyde-dehydrogenase. By this enzymatic step one "half of the fructose molecule" may bypass the insulin-dependent regulation of triosephosphate-dehydrogenation.

D-glyceric acid either enters the normal glycolytic pathway by phosphorylation to 2-glycerophosphoric acid, or is oxidized to hydroxypyruvic acid, which by transaminations may be converted to the amino acid serine, an important metabolic intermediate.

D-glycerate-dehydrogenase is pyridine-nucleotide-dependent and strongly stereo-specific. Together with lactate-dehydrogenase, which reacts with L-glycerate as well as with L-lactate, the enzyme D-glycerate-dehydrogenase can catalyze a configurational change from L- to D-glycerate, or vice versa.

Since both, NAD^+ and $NADP^+$, are coenzymes for D-glycerate-dehydrogenase, this enzyme may also simulate the function of a transhydrogenase $NADH \rightleftharpoons NADPH$.

Lecture at Hannover (Germany) on May 16, 1968 [VB 160 IE]
German version: Angew. Chem. *80*, 669 (1968)

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Structures of Compounds of Elements in Valence States with $4s^2$ and $5s^2$ Electron Configurations

By *S. E. Rasmussen*[*]

In agreement with the single electron approximation a number of elements exist in a valence state in which the outer electrons have the $4s^2$ or $5s^2$ configuration

[Ar] $3d^{10}4s^2$: Zn^0, Ga^I, Ge^{II}, As^{III}, Se^{IV}, Br^V, Kr^{VI}

[Kr] $4d^{10}5s^2$: Cd^0, In^I, Sn^{II}, Sb^{III}, Te^{IV}, I^V, Xe^{VI}

Since the four sp^3 hybridized orbitals can be occupied by eight electrons it can be assumed that these elements are able to coordinate three ligands provided that each ligand carries a free electron pair. The coordination number 3 should be dominant for these elements in the valence states noted.

Compounds of this type can, however, be described also in other ways.

For halides and oxides the electrostatic description has proved very useful, as has *V. M. Goldschmidt*'s principle of the close packing of spheres for many simple structures.

If there is only a small energy difference between two possible structures for one compound, directed valences playing a dominant role in one structure and geometrical and electrostatic considerations in the other, then it can be expected that a low-temperature modification and a high-temperature-modification will both be possible.

In this connection the structures of Zn^0Sb^0, Cd^0Sb^0, InCl, $HGeCl_3$, GeF_2, $CsGeCl_3$, $Ge^{II}Te$, pilocarpinium trichlorogermanate(II), $CsSnCl_3$, $AsCl_3$, 3CsCl, $2AsCl_3$, $SbCl_3$, H_2SeO_3, $KHSeO_3$, $KBrO_3$, HIO_3, and some other compounds have been investigated. The expected coordination number (3) was confirmed in all cases, and for several compounds a low-temperature as well as a high-temperature modification was found (*e.g.* $CsGeCl_3$ and $CsSnCl_3$).

Lecture at Giessen (Germany), on June 4, 1968 [VB 162 IE]
German version: Angew. Chem. *80*, 669 (1968)

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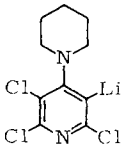
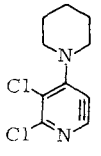
SELECTED ABSTRACTS

The adduct of a 2,3-didehydropyridine with furan has been described by *J. D. Cook* and *B. J. Wakefield*. Reaction of *n*-butyllithium with 2,3,5,6-tetrachloro-4-piperidylpyridine in ether at −75 °C yields 2,5,6-trichloro-4-piperidyl-3-pyridyllithium *(1)*. When the solution is kept at room temperature in


(1)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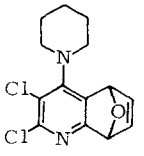
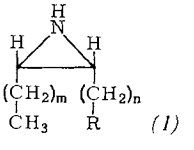
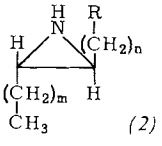

(3)

the presence of furan there results a 45 % yield of the adduct *(3)* of furan and 5,6-dichloro-2,3-didehydro-4-piperidylpyridine *(2)*, which reacts as a dienophile. / Chem. Commun. *1968*, 297 / −Ma. [Rd 853 IE]

Synthesis of long-chain *cis*- and *trans*-epiminoalkanes *(1a)* and *(2a)* and the corresponding epiminoalkan-1-ols *(1b)* and *(2b)* has been described by *J. F. McGhie* and *B. T. Warren*. The addition products formed by iodoisocyanate with *cis*-and *trans*-alkenes or *cis*- and *trans*-alkenols react with methanol to give iodocarbamates, which on treatment with alkali afford *cis*- and *trans*-epiminoalkanes and *cis*- and *trans*-epiminoalkan-1-ols in yields of 30–65 %. The aziridine ring of *(2a)* and *(2b)* is stable to NaN_3 and $LiAlH_4$ in alkaline solution. In acid solution, on the other hand, the ring is cleaved. With acetic acid for example, *(2a)* and *(2b)* give


(1)

(a), R = CH_3
(b), R = CH_2OH


(2)

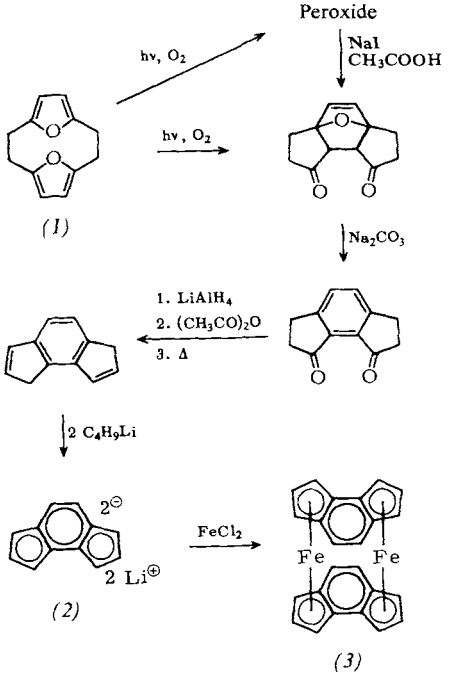
threo- and *erythro*-aminodiol, respectively. Treatment with HN_3 – a new reagent for cleaving the aziridine ring – leads to *threo*- and *erythro*-diamino alkan-1-ols. / Chem. and Ind. *1968*, 253 / −Ma. [Rd 858 IE]

The direct observation of twisting vibration of C_2H_6, CH_3CD_3, and C_2D_6 in the IR spectrum has been achieved by *S. Weiss* and *G. E. Leroi* by the use of large path length (10 m) and high gas pressures (3–7 atm). Under these conditions, the vibration, which is in itself forbidden, becomes IR-active on account of Coriolis interactions with other vibrations. The fundamental twisting frequencies for C_2H_6, CH_3CD_3, and

C_2D_6 are 289, 253, and 208 cm^{-1}, respectively. The first overtone of CH_3CD_3 is at 482 cm^{-1}. This is not found in the other two compounds, since they are symmetrical, and Coriolis interactions cannot activate this overtone. The measured frequencies give what is probably the most reliable value at present for the height of the potential barrier of the twisting in the ethane molecule, namely 2928 ± 25 cal/mole. / J. chem. Physics *48*, 962 (1968) / –Hz. [Rd 861 IE]

Surface tension of liquids can be measured automatically by two devices designed by *T. Smith* and *H. Schlein*. Both measure the pressure differences of bubbles introduced into the liquid from two tubes of different radii (*e.g.* 0.14 and 0.015 cm). In the simpler variant, the fluctuations caused by the non-simultaneous exit of the bubbles (1/sec or slower) from the tubes of different diameters are averaged by an electronic attenuator and relayed to a recorder. This gives an accuracy of 2 % in the measurement of the surface tension. In the more complicated variant, the pressure peaks, converted into electric voltage signals, are compared when the bubbles are expelled from the two tubes. The attending error of measurement is 0.3 %. These devices can be used even without calibration. The accuracy of measurement is then determined by the uncertainty of the radii of the tubes and the pressure difference. / Rev. sci. Instruments *39*, 302 (1968) / –Hz. [Rd 862 IE]

Synthesis of bis(*as*-indacenyliron) *(3)* has been accomplished by *T. J. Katz, V. Balogh,* and *J. Schulman* by treating $FeCl_2$ with dilithium-*as*-indacenide *(2)*, whose preparation from *(1)* is shown below. *(3)* is the first compound in which two metal atoms are sandwiched in between two aromatic ring systems. The reddish brown compound *(3)* belongs to the



space group P $2_1/c$ and can be heated to 350 °C without melting (slow sublimation at 150 °C and 10^{-6} torr). / J. Amer. chem. Soc. *90*, 734 (1968) / –Kr. [Rd 866 IE]

Formulas for the calculation of the detonation properties of explosives containing only C, H, N, and O have been given by *M. J. Kamlet* and *S. J. Jacobs*. When the initial density ρ_0 exceeds 1 g/cm^3, the detonation pressure P (in kbars) is

$$P = K \rho_0 {}^2\varphi$$

and the detonation velocity D (in mm/μsec) is

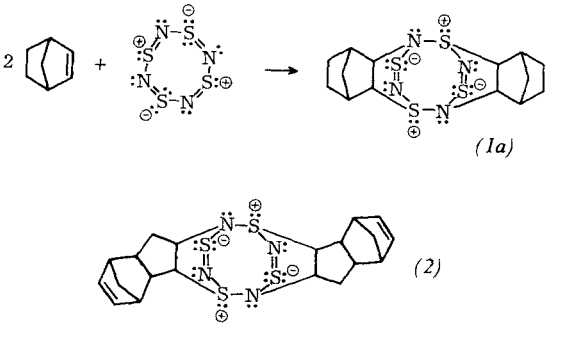
$$D = A \varphi^{1/2} (1 + B\rho_0)$$

where the constants have the following values: $K = 15.58$, $A = 1.01$, and $B = 1.30$, and

$$\varphi = N M^{1/2} Q^{1/2}$$

N is the amount of gaseous products (in moles) per gram of explosive, M is the average molecular weight of the product gases (in g·$mole^{-1}$), and Q is the heat of reaction (in cal/g). The values of N, M, and Q can be calculated with the aid of a rule, according to which N_2, H_2O, and CO_2 are the main products, while practically no CO is formed, and first H and then C are fully oxidized whenever there is an oxygen deficiency. Thus, the only data needed are those of elemental analysis, heat of formation, and the density of the explosive. The detonation pressures calculated with this simple equation do not differ by more than 10 % (generally by considerably less) from the values obtained by a computer with a RUBY program based on a very accurate equation of state, and using exact equilibrium data and heat of reaction values. / J. chem. Physics *48*, 23 (1968) / –Hz. [Rd 863 IE]

Tetrasulfur tetranitride reacts as an inorganic diene, as has been found by *M. Becke-Goehring* and *D. Schläfer*, who obtained the heptacyclic *(1a)* (decomp. 130 °C) with norbornene and the analogous product *(1b)* (decomp. 170 °C) with norbornadiene. Cyclopentadiene forms the 1:4-adduct *(2)* (m.p. 135–136 °C, decomp.). The colorless compounds *(1a)*, *(1b)*,



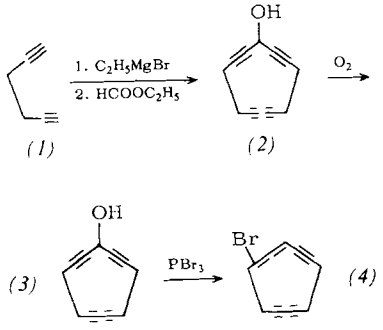
and *(2)* are not sensitive to water. Their solutions in CH_2Cl_2 or $CHCl_3$ turn blood-red after a few minutes; after a longer time, they fade again. Clearly, charge-transfer complexes are formed. / Z. anorg. allg. Chem. *356*, 234 (1968) / –Kr. [Rd 867 IE]

Pentacoordinated metal(0)-trifluorophosphine derivatives of iron, ruthenium, and osmium have been prepared by *Th. Kruck* and *A. Prasch* by the reaction:

$$MX_n + n\,Cu + 5\,PF_3 \xrightarrow[150-250\,^\circ C]{> 400\ atm} M(PF_3)_5 + n\,CuX$$

M = Fe, X = I, $n = 2$, pale yellow crystals with m.p. 45 °C, decomp. 270 °C; M = Ru, X = Cl, $n = 3$, white crystals with m.p. 30 °C. The compound $Os(PF_3)_5$, which is formed only in the absence of hydrogen-containing impurities, is also composed of volatile white crystals. The compounds are entirely non-polar and have a trigonal bipyramidal structure. / Z. anorg. allg. Chem. *356*, 118 (1968) / –Kr. [Rd 868 IE]

1-Bromocyclotrideca-1,2-diene-4,8,10-triine *(4)*, a highly unsaturated cyclic allene, has been synthesized by *C. C. Leznoff* and *F. Sondheimer* from 1,5-hexadiine *(1)* *via* the intermediates *(2)* and *(3)*. The ring closure is effected in a solution highly concentrated for such reactions, the yield

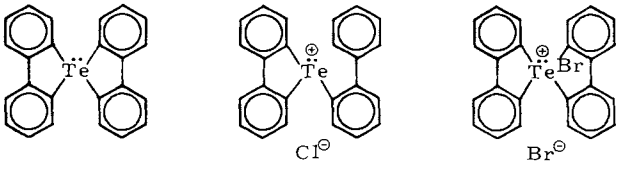


being 80%. Compound *(3)* reacts with PBr_3 in tetrahydrofuran to give the crystalline substance *(4)*, which explodes at about 65 °C and slowly decomposes even at 0 °C in the dark. / J. Amer. chem. Soc. *90*, 731 (1968) / –Kr. [Rd 869 IE]

The perbromate ion has been detected in different ways by *E. H. Appelman*. Thus, on β-decay, $^{83}SeO_4^{2-}$ gives $^{83}BrO_4^-$, which is precipitated by Rb salts in the presence of ClO_4^- and BrO_3^-. The electrolytic oxidation of $^{82}BrO_3^-$ in a divided cell (cold) similarly gives BrO_4^- on being cooled; 2% of the 36-hour ^{82}Br activity can be coprecipitated with $RbClO_4$, but not with $Ba(BrO_3)_2$. The chemical oxidation of $NaBrO_3$ by XeF_2 in aqueous solution also leads to perbromate. The mass spectrum of perbromic acid was investigated by *M. H. Studier*. Alkali metal perbromate solutions were acidified with dilute H_2SO_4, evaporated to dryness at room temperature, and examined in a modified time-of-flight mass spectrometer. As expected, the following ions were observed: $HBrO_4^+$, $HBrO_3^+$, BrO_3^+, $HBrO_2^+$, and BrO_2^+. / J. Amer. chem. Soc. *90*, 1900, 1901 (1968) / –Kr. [Rd 870 IE]

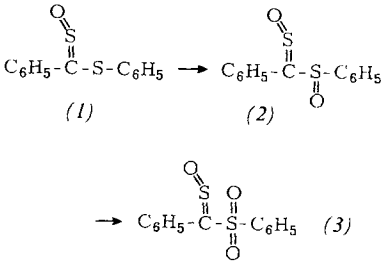
Explosive mixtures of periodic acid and dimethyl sulfoxide have been found by *J. J. M. Rowe, K. B. Gibney, M. T. Yang*, and *G. G. S. Dutton*. 70 ml of DMSO was added to 34 g of periodic acid in a flask covered with aluminum foil, and the mixture was shaken for a short time. An explosion occurred in 5–10 min. Mixtures in unwrapped flasks also exploded, but a batch containing a tenth of the original amount of reagents in a small conical flask did not. / J. Amer. chem. Soc. *90*, 1924 (1968) / –Kr. [Rd 872 IE]

Synthesis of bis(2,2'-biphenylylene)tellurium *(1)*, a tellurium spirane, has been accomplished by *D. Hellwinkel* and *G. Fahrbach* in several ways, *e.g.* by treating $TeCl_4$ with 2,2'-dilithiumbiphenyl (yield 44%), treating 2,2'-biphenylylenetellurium with chloramine T in DMF *via* a 2,2'-biphenylylenetelluridetosylimine (44%), as well as from $Te(OCH_3)_4$ (49%) and $Te(OCH_3)_6$ (48%). Compound *(1)* is a stable substance; it melts between 205 and 214 °C, depending on the rate of heating, and it gives yellow solutions with *e.g.*



THF, benzene, and acetone, these solutions being stable in dry air. With ethanolic HCl, *(1)* gives telluronium salt *(2)*, while with bromine in CCl_4, it gives the salt *(3)*. At temperatures down to –55 °C, the NMR spectrum of bis(4,4'-dimethyl-2,2'-biphenylylene)tellurium contains only one methyl proton signal. This agrees with the assumed rapid interconversion between a trigonal bipyramidal and a tetragonal pyramidal configuration. / Liebigs Ann. Chem. *712*, 1 (1968) –Kr. [Rd 873 IE]

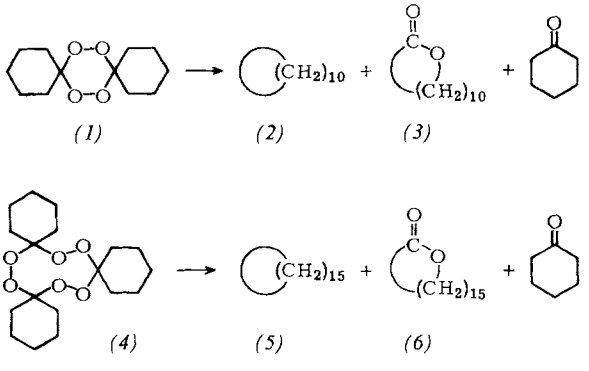
A sulfinylsulfine and a sulfonylsulfine have been described by *B. Zwanenburg, L. Thijs*, and *J. Strating*. The oxidation of the sulfine *(1)* with 0.75 equivalents of monoperoxyphthalic acid at 0 °C affords *trans*-benzenesulfinylphenylsulfine *(2)* (m.p. 131–136 °C, yield 51%). Further oxidation with 1 equivalent



of monoperoxyphthalic acid gives *trans*-benzenesulfonylphenylsulfine *(3)* (m.p. 150–154 °C, yield 59%). Unlike methane sulfonylmethylsulfone, both these compounds are stable. / Tetrahedron Letters *1968*, 2871 / –Kr. [Rd 874 IE]

Synthesis of alkyl iodides has been achieved by *D. D. Tanner* and *G. C. Gidley* in a new way. *tert*-Butylhypochlorite and HgI_2 in CCl_4 gave a purple solution, which can be regarded formally as *tert*-butylhypoiodite. On irradiation (200-w incandescent light bulb), freshly prepared and aged solutions gave with hydrocarbons preparatively useful yields of alkyl iodides. For example: neopentane → neopentane iodide (28%); cyclohexane → cyclohexane iodide (71%); toluene → benzyl iodide (34%). Tertiary hydrogens are not replaced by iodine. The reaction is thought to proceed *via* the radical $(CH_3)_3CO\dot{O}C(CH_3)_3$. / J. Amer. chem. Soc. *90*, 808 (1968) / –Kr. [Rd 875 IE]

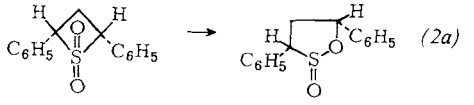
A new general synthesis of macrocyclic compounds has been described by *P. R. Story, D. D. Denson, C. E. Bishop, B. C. Clark jr.*, and *J.-C. Farine*. For example, photolysis of *(1)*,



gave *(2)* (14%), *(3)* (10%), and cyclohexanone (*ca.* 20%). Its thermolysis gave *(2)* (44%), *(3)* (23%), and cyclohexanone (21%). The starting material can be obtained from cyclo-

hexanone and H_2O_2. On photolysis, the trimeric cyclohexanone peroxide *(4)* forms *(5)*, *(6)*, and cyclohexanone in yields of 15, 25, and 20% respectively, the corresponding thermolytic yields being 16, < 1, and 15%. Further examples are as follows: dimeric cycloheptanone peroxide → cyclododecane, 13-tridecalactone, and cycloheptanone; dimeric cyclododecanone peroxide → cyclodocosane, 23-tricosalactone, and cyclododecane. The risk of explosion must be remembered while carrying out thermolysis. / J. Amer. chem. Soc. *90*, 817 (1968) / –Kr. [Rd 876 IE]

***cis*- and *trans*-2,4-Diphenylthietane *S,S*-dioxides** *(1a)* and *(1b)* undergo stereospecific rearrangements into *cis*- and *trans*-3,5-diphenyl-1,2-oxathiolan *S*-oxide *(2a)* and *(2b)*, as has been

(1a)  *(2a)*

found by *R. M. Dodson, P. D. Hammen,* and *R. A. Davis* on treating the compounds with *tert.*-butanol and C_2H_5MgBr (1:1) in ether. NMR spectra confirm the structure of *(2a)* (m.p. 121.5–122.5 °C, yield 70%) and *(2b)* (m.p. 73–74.5 °C). *(2a)* has also been synthesized from 3-mercapto-1,3-diphenyl-1-propanol. / Chem. Commun. *1968*, 9 / –Kr. [Rd 877 IE]

The dipole moment of *o*-dimethoxybenzene increases with rising temperature; *L. M. DiBello, H. M. McDevitt,* and *D. M. Roberti* found values of 1.24 to 1.64 D for the pure liquid and for solutions in benzene, decalin, and liquid paraffin between –20 and +165 °C. For solutions in decalin and liquid paraffin, constant values of 1.64 and 1.58 D respectively are reached at about 90 °C; the calculated value based on the assumption of completely free rotation of the methoxy groups is 1.93 D. The difference is explained by the failure of conformers with particularly pronounced steric hindrance to make their full contribution to the dipole moment, even at high temperatures. The dipole moments of *m*- and *p*-dimethoxybenzene are constant in decalin from 20 to 130 °C. / J. physic. Chem. *72*, 1405 (1968) / –Hz. [Rd 887 IE]

The wetting and adhesion behavior of liquid indium on solid aluminum has been studied by *R. G. Aldrich* and *D. V. Keller jr.* A polycrystalline Al surface was produced by vapor deposition, and a drop of liquid indium was forced out of a reservoir onto this surface. The interfacial tension of indium on aluminum at 160 °C and 10^{-10} torr is 658 (± 10%) dyn/cm; the relatively large error may simply be due to the difference in the interfacial tensions at different crystallographic faces. The effects of H_2, N_2, and O_2 at pressures up to 1 torr were also studied. The interfacial tension remained unchanged under H_2 or N_2, but decreased considerably in the presence of O_2, and the drop spread out. The strength of the metal-metal interface after the solidification of the drop of indium was always greater than the tensile strength of indium itself, except when H_2 or N_2 was present before the application of the drop. / J. physic. Chem. *72*, 1092 (1968) / –Hz. [Rd 890 IE]

The arrangement of the atoms in vitreous selenium has been studied by *R. Kaplow, T. A. Rowe,* and *B. L. Averbach* by X-ray diffraction. Comparison with the positions of the atoms in hexagonal and monoclinic selenium was used to find which of the two lattices would give the interatomic distances found in vitreous selenium with the least possible disturbance of the atomic positions. It was found that vitreous selenium must consist predominantly of slightly deformed Se_8 rings (which give monoclinic selenium in an undisturbed arrangement), interspersed with a few rings that are so open that they form a zone with a chain structure related to that of hexagonal selenium. / Physic. Rev. [2] *168*, 1068 (1968) / –Hz. [Rd 891 IE]

Tungsten hexahydride 3(dimethylphenylphosphine) a colorless crystalline compound that is stable in air, was obtained by *J. R. Moss* and *B. L. Shaw* on reduction of *trans*-$WCl_4[P(CH_3)_2C_6H_5]_2$ (from *cis*-$W(CO)_4[P(CH_3)_2C_6H_5]_2$ and Cl_2) with $NaBH_4$ in CH_3OH. The complex melts at 110 to 112 °C with decomposition and dissolves readily in organic solvents. The chemical shift of the WH_6-hydrogen is τ = 11.94 (quartet with $J(^1H^{31}P) = 36.9$ and $J(^1H^{183}W) = 27.8$ Hz); WH stretching frequencies are observed at 1731–1834 cm^{-1}. $WH_6 \cdot 3\,PR_3$ probably corresponds in its structure to the analogous Re compounds ReH_9^{2-} and $ReH_7 \cdot 2\,PR_3$. / Chem. Commun. *1968*, 632 / –HB. [Rd 892 IE]

BOOK REVIEWS

1,4-Cycloaddition Reactions. By *I. Hamer.* Vol. 8 of the series "Organic Chemistry". Edited by *A. T. Blomquist.* Academic Press, New York-London 1967. 1st Edit., xii, 500 pp., numerous figures and tables, $ 22.00.

1,4-Cycloaddition reactions leading to heterocyclic five- and six-membered rings are described in 13 chapters by 17 authors. Applicability and limitations of the reactions, the effect of substituents, and mechanisms are discussed, in addition to further reactions and side reactions. Reaction conditions, yields, and physical properties of the cyclic adducts are compiled in numerous tables. Detailed working instructions are given in some instances.

Generous space is provided for numerous clear and instructive formulas and reaction schemes. Each chapter is self-contained. All the relevant literature to 1964 and some from 1965 has been listed at the end of each chapter. In all, about 1150 references are given. The book's aim of providing an instructive survey of thermal and photochemical 1,4-cycloadditions leading to the formation of five- and six-membered rings has been fully achieved.

I. Hamer introduces the book in the opening 11-page chapter. The make-up of the work is explained and systems that are not dealt with later are briefly mentioned.

S. D. Turk and *R. L. Cobb* are the authors of Chapter 2 (44 pages) on the five-membered cyclic sulfones. Examples are given with SCl_2 and SeO_2 as the dienophiles, as well as for SO_2.

Chapter 3 (50 pages) by *L. D. Quin* describes the reactions of dihalogenophosphines, phosphorus trihalides, and dihalogenated phosphoric esters with dienes and α-dicarbonyl compounds. The ionic formulation of the adducts is preferred. In Chapter 4, *G. J. Janz* reports on the synthesis of pyridine derivatives with cyanogen and nitriles as the dienophiles (30 pages); the literature is only covered up to 1959. Chapter 5 (15 pages) lists the 1,4-cycloadditions with imino compounds and is compiled by *M. Lora-Tamayo* and *R. Madranero.*

B. T. Gillis is the author of Chapter 6 (34 pages), dealing with the reactions of azo compounds with acyclic, cyclic, and aromatic systems to give pyridazines. Tables listing more

than 170 syntheses, reaction conditions, yields, and literature references are given.

In Chapter 7 (25 pages) *N. Lora-Tamayo* and *J. L. Soto* discuss open-chain and cyclic conjugated systems with 2 nitrogen atoms used as dienes. Chapter 8 (16 pages) by *I. Hamer* and *J. A. Turner*, deals with the little-investigated use of carbonyl and thiocarbonyl compounds as dienophiles. *J. Colonge* and *G. Descotes* describe the dimerization of α,β-unsaturated carbonyl compounds and their application as dienes (*C*-vinyl, *O*-vinyl and *N*-vinyl enamines, carbamates, and urea derivatives) in Chapter 9 (38 pages).

K. Gollnick and *G. O. Schenk* wrote Chapter 10 (90 pages) on oxygen as a dienophile. After a brief introduction to theoretical and preparative aspects, the photo-initiated cycloaddition of O_2 to conjugated dienes, the photochemical cycloaddition to aromatic compounds and aryl-substituted carbocyclic and heterocyclic pentadienes is discussed. About 150 transannular peroxides are tabulated (350 references).

In Chapter 11 (74 pages) *G. Pfundt* and *G. O. Schenk* report on cycloadditions to *o*-quinones, 1,2-diketones, and some of their derivatives – 1,4-dioxines, 1,3,2-dioxathioles, 1,3,2-dioxaphospholes, 1,3-dioxoles, and oxazoles representing the possible products. The 1,5-addition of ketenes to *o*-quinone diazides and the thermolysis of the adducts to 1,3-dioxoles or indazoles is reported in detail. In Chapter 12 (33 pages), *I. Hamer* and *M. Ahmad* list the Diels-Alder reactions of nitroso compounds for synthesizing oxazine derivates. In the final Chapter 13 (19 pages) *G. Kresze* reports on the dienophilic reactions of *N*-sulfinyl compounds.

The carefully compiled author index is worth noting; all the co-authors are listed. The printing quality is excellent – only a single misprint was found.

The chemist working in the field of heterocyclic chemistry and Diels-Alder reactions will gladly add the book to his library. The work can be strongly recommended to students on account of its lucid presentation. *W. Ried* [NB 717a IE]

Cyclobutadiene and Related Compounds. By *M. P. Cava* and *M. J. Mitchell*. Vol. 10 of "Organic Chemistry". Edited by *A. T. Blomquist*. Academic Press, New York-London 1967. 1st Edit., xiii, 503 pp., $ 22.00.

As on previous occasions in this series, the editor has succeeded in finding two specialists in the field who have themselves made decisive contributions to the chemistry of cyclobutadiene and benzocyclobutadiene.

The contents can be gleaned from the twelve chapter headings: Cyclobutadiene, Cyclobutadiene-metal-complexes, Cyclobutadiene divalent ions, Cyclobutadienequinone, Methylene analogs of cyclobutadienequinone, Benzocyclobutadiene, Benzocyclobutadienequinone, Methylene analogs of 1,2-benzocyclobutadienequinone, Higher aromatic analogs of benzocyclobutadiene, Biphenylene, The benzobiphenylenes, and Theoretical aspects of the cyclobutadiene problem (the last by *H. E. Simmons* and *A. G. Anastassion*).

A good monograph should be comprehensive, up-to-date, lucid, and critical. All of these epithets may be applied to the present work. The authors have not relied solely on periodicals for source material; extensive reference is made to dissertations, theses, and personal communications collected from enquiries among colleagues in the field. The literature has been abstracted to 1964; an appendix lists work published in 1965 and 1966. A sensible classification marks the individual chapters which are so written that each can be read on its own without having to refer to a previous chapter.

Extravagant use of structural formulas is manifest. The historical introduction and sections describing unsuccessful synthesis of the compounds discussed are outstanding features.

The chemistry of cyclobutadiene is a small but fascinating part of organic chemistry. All chemists, not only those working concerned with the chemistry of small carbon ring systems, can derive much stimulation from this unusually thorough book. All libraries at least should possess a copy.

R. Criegee [NB 717b IE]

Toxikologie-Fibel für Ärzte, Apotheker, Naturwissenschaftler, Juristen, und Studierende (Toxicology Primer for Physicians, Pharmacists, Scientists, Lawyers, and Students). By *W. Wirth, G. Hecht*, and *Chr. Gloxhuber*. Georg Thieme Verlag, Stuttgart (1967). 1st ed., xiv, 394 pp., 17 figures, DM 36.–.

This book is no "primer" but an expansion of Fühner's "Medizinische Toxikologie" (Medical Toxikology), which last appeared 16 years ago under the names of *Wirth* and *Hecht*. The chapter on "General Toxicology" (pp. 1–46), as before, deals with the concept and detection of poisons and general treatment in cases of poisoning. A new feature is the table of MAC values valid in 1966. In "Special Toxicology", substances are again discussed according to their chemical constitution. The topics discussed under "Inorganic Compounds ("pp. 47–129) are cases of poisoning by nonmetals, metals, and radioactive substances, while "Organic Compounds" (pp. 130–246) covers CO, CO_2, aliphatic halogenohydrocarbons, alcohols, acids, *etc.*, up to aromatic or heterocyclic compounds. The next section, on "Poisonous Plants and Plant Poisons" (pp. 247–323), also deals with the toxicity of the alkaloids, ethereal oils, and vitamins; hormones and biogenic amines are discussed under "Animal Poisons and Poisonous Animals" (pp. 324–342).

The topics dealt with under each substance include chemical properties, structural formula, uses, possibilities of acute and chronic poisoning, and symptoms of poisoning. Any possible specific treatments are indicated at the end. References to the original literature are included throughout.

The original literature cited should be consulted frequently, particularly since one then sometimes makes a different assessment of the toxicities from the authors. It was unnecessary, in the reviewer's opinion, to discuss plants so unimportant as *Catha ed.* (p. 258) *Cycas circ.* (p. 290), *Eupatorium urticaefolium* (p. 308) and *Blighia sapida* (p. 309), or water lilies (p. 341) and sea cucumbers (p. 342). The reviewer feels that in any new edition, the subject index at least should contain general headings such as stain removers (astonishingly, only the obsolete stain remover "Puran" is mentioned), paint thinners, and delining agents, since these are the headings under which the practical worker searches to find what the agents generally contain. Owing to the frequency of poisoning with solvents and cleaning agents of unknown composition, any new edition should mention the possibilities of detecting poisons of this type in the exhaled air with Dräger tubes, and the various Dräger tubes should be listed together with MAC and MIC values, as is now universal practice.

It is not wrong to include MAC tables in a textbook on poisons, but the "preamble" to the MAC list should be reproduced in full to enable the values to be used correctly. It seems unnecessary to the reviewer to include MIC values (for short-term and long-term exposure!). Neither the practical physician nor the chemist can know how uncertain is the basis of these MIC values, and that more than just these values has to be taken into account in the case of substances such as nitrobenzene and aniline. Since the book is also intended for scientists and lawyers, there is a danger that not only the MAC values, but also the MIC values will quickly fall into disrepute.

The authors are very cautious in their judgement of tabacco smoke. The sentence (p. 268) "The increase in lung cancer is partly explained by the inhalation of cigarette smoke" no longer reflects the latest knowledge, nor does the advice: "The principal dangers of tobacco smoke can be avoided if low-nicotine tobacco is smoked as slowly as possible, with-

out inhaling, the last third of cigars and cigarettes being rejected. Filtration of the smoke through impregnated wadding also makes smoking more hygienic." The reviewer would have preferred a sterner warning, even in a "primer".

On the whole, however, the book is a welcome addition to the German literature on toxicology. It can be recommended, not only to physicians and hospital doctors, but also to chemists and works managers as a source of ready information on the dangers involved in handling chemicals. Intelligent use of the MAC tables is also important for chemists.

H. Oettel [NB 726]

An Introduction to the Alkaloids. By *G. A. Swan*. Blackwell Scientific Publications. Oxford-Edinburgh 1967. 1st Edit., viii, 326 pp., 63 s.

Because of the tendency to use increasingly smaller molecules for descriptions of chemical and physical methods, many organic chemistry textbooks have become more or less removed from the field of natural products, where many of these methods were in fact developed. However, natural products not only constitute the original and literal object of study in "organic" chemistry, but also a good medium for training students. Their structure and biological function offers an abundance of problems full of methodological and theoretical aspects. Alkaloids represent a particularly good example and in this introduction by *Swan* have been given an excellent presentation very suitable for use in colleges.

A good, competent selection of chemical, biogenetic, and pharmacological information is used to illustrate why the alkaloids have been, and still are, a fascinating object of study. Among others, the stereochemistry of yohimbine and morphine, *Woodward*'s strychnine synthesis, mass spectrometry of the indole alkaloids, the biosynthesis of tropane, opium, and indole alkaloids and the medicinal utilization of quinine and reserpine, all illustrated by excellent formulas, make exciting reading. A further stimulating feature of this book is the occasional interposition of amusing bits of information in the otherwise concentrated scientific text. The reader is told how the Spanish Jesuits calculated the cost of cinchona bark in the 17th century and that spiders spin more regular webs after being given LSD. The contents are divided into 21 chapters on the basis of the heterocyclic structures. The wide margin left on each page to enable supplementary notes to be added is useful. Almost 900 references extending to 1966 are given and few misprints are evident.

The book deserves every recommendation as a modern introduction to the alkaloids for advanced students and others possessing some basic knowledge of heterocyclic compounds. The low price will encourage its wide distribution.

B. Franck [NB 718 IE]

Drugs Affecting the Peripheral Nervous System. By *A. Burger*. Medical Research Series, Vol. 1. Marcel Dekker, Inc., New York 1967. 1st Edit., xxiii, 620 pages, $ 27.50.

In the introductory chapter *S. Ehrenpreis* reports on the transfer of cholinergic stimulation in terms of molecular biology. He finds that it has not so far been possible to isolate the receptor, and that all postulates are thus purely hypothetical. *H. L. Friedman* describes postganglionic parasympathetic stimulants and the variability of the acetylcholine molecule in connection with the muxcarine-like effect. *J. C. Cannon* and *J. P. Long* discuss cholinolytic atropine-like drugs and the relationships between biological action and stereochemical configuration. *L. Gyermek* reports in a remarkably concise and clear manner about drugs stimulating or blocking the peripheral ganglion. Substances which influence the nervous transfer to the skeletal muscle, above all muscle relaxants, are discussed by *J. J. Lewis* and *T. C. Muir* in terms of their mode of action. *J. P. Long* and *C. J. Evans* discuss reversibly acting cholinesterase inhibitors from the aspect of model postulates, whereas the kinetics of the irreversible phosphorus-containing cholinesterase inhibitors are dealt with in a short article by *I. B. Wilson* with reference to the extensive literature. Two other chapters deal with sympathomimetic agents (*A. M. Lands* and *T. G. Brown jr.*) and sympatholytic agents (*N. B. Chapman* and *J. D. B. Graham*). In conclusion, *C. M. Smith* reports on the medicinal influencing of the afferent nervous system, with particular attention to pain, and pressor and chemoreceptors. Despite the certain amount of overlapping inevitable in a collective work, the book seems to be self-contained. The theoretical introduction to each chapter does much to help the reader who is not so familiar with the field, thus making the contents more useful to a wider audience.

G. Quadbeck [NB 712 IE]

Molecular Biophysics. By *D. Chapman* and *R. B. Leslie*. Contemporary Science Paperbacks, Vol. 4. Oliver and Boyd, Edinburgh-London 1967. 1st Edit., vi, 151 pages, several figures and tables, paperback 7s. 6d.

This little book attempts to describe what is meant by molecular biophysics. In doing so it renders a service neither to molecular biophysics nor to the reader, if it is in fact possible to establish for whom this book is intended. For example, the term codon is explained at length, but the term relaxation effect is assumed to be understood by itself. Is one expected to know what this term means and yet to have to be told what nuclear resonance denotes?

The meaning that the authors attach to the term molecular biophysics is likewise obscure. In an initial descriptive part the extended formula of lecithin occupies a special page. It seems that molecular biophysics does not presuppose even an elementary acquaintance with the chemistry of natural products. Then a morphological discussion is used to define molecular biophysics and finally we wander into the theory of evolution. The respiratory chain is once more described on the basis of the redox potentials of the isolated constituents, the nonheme iron and copper are suppressed "for the sake of clarity". The entire Krebs cycle, which can hardly be regarded as forming a part of molecular biophysics, is given; so are the inevitable photographs of the Perutz hemoglobin model. Much is made of electron spin resonance and free radicals without defining the term radical. By contrast, the triplet oxygen molecule, a phenomenon unique to molecular biophysics, is not mentioned.

Finally, Chapter 6 discusses some "selected problems in biophysics". The chapter is a pleasure to read and obviously this is where the interest of the authors lies. In some instances concluding chapters can justify a book; this is not one of them.

P. Hemmerich [NB 724 IE]

L'Analyse Cinétique de la Transformation Chimique (Kinetic Analysis of Chemical Reactions), Vol. 1. By *J. C. Jungers* and *L. Sajus*, with the collaboration of *I. de Aguirre* and *D. Decroq*. Edition Technip, Paris 1967. 1st Edit., 604 pages, 224 figures, 163 tables, bound, F 145.—.

The title of the book defines the scope: kinetics is not discussed for its own sake.

In the preface it is stressed that first gas reactions were treated, then reactions in extremely dilute solutions, while in laboratory and industry one works with solutions as concentrated as possible. It is rightly pointed out that even the choice of reaction systems already involved simplifications.

The present book deals with the analysis and control of complex reactions in concentrated systems of the type usually encountered in practice. Its value lies in the treatment of a large number of experimentally investigated reactions, many of which were carried out in the authors' own laboratory. In this way detailed data are made available to an extent unobtainable in any other work; flow sheets and photographs of operational plants are given in some cases.

A more theoretical background might be desirable, at least with regard to the influence of deviations from ideal behavior. However, the second part of the book, with chapters entitled Study of the medium, Scheme and mechanism, Correlation between reactivity and structure, is still to be published, and it would be unfair to level criticism at this stage.

Despite the empirical orientation this book is the only work known to the reviewer in which empirical data for the fundamentally interesting multicomponent first-order systems[1] have been compiled. The book will be of value to all interested in the field concerned. *W. Jost* [NB 697 IE]

[1] For a theoretical treatment, see *W. Jost*, Z. Naturforsch. *2a*, 159 (1947); *J. Wei* and *C. D. Prater*, "The Structure and Analysis of Complex Reaction Systems" in: Advances in Catalysis. Academic Press, New York 1962, Vol. 13, pp. 203–392; A. I. Ch. E. Journal *9*, 79 (1963).

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Observations on the Crystal Structures of Electron Donor-Acceptor Complexes

C. K. PROUT AND J. D. WRIGHT[*]

The theoretical interpretation of electron donor-acceptor complex formation in terms of charge transfer interactions has stimulated many structure determinations for these complexes. These fall into three classes, depending on the type of orbitals involved in charge transfer. In σ-σ complexes, intermolecular bonds become shorter and intramolecular bonds become longer as charge transfer increases. Relative orientations correspond to overlap of donor and acceptor molecules in directions of "preferred polarizability". Intermolecular bond lengths in σ-π complexes show similar trends, and the axial orientation in the benzene-halogen complexes is probably the result of the best compromise between orbital overlap and energy factors. π-π Complexes contain stacks of alternate plane-to-plane donor and acceptor molecules, arranged in three characteristic ways. There is little correlation between interplanar spacing in these stacks and charge transfer properties. The relative orientations of donor and acceptor molecules within the stacks are determined by a combination of charge transfer interactions (maximized when aromatic rings of donor and acceptor molecules are displaced by half a ring diameter) and dipole-induced dipole interactions (maximized, for example, when a polar bond of one molecule overlaps a polarizable region of another). Crystal packing requirements and dispersion forces modify these effects, and no satisfactory theoretical treatment of this complex combination of interactions is yet available.

1. Introduction

Molecular complex formation is an association of definite stoichiometry between two molecules of closed shell electronic structures, and is stronger than an ordinary van der Waals interaction. Molecular complexes are frequently formed when molecules of low ionization potential interact with molecules of high electron affinity. These complexes are recognized by the almost invariable appearance of new intense broad spectral bands in the visible or ultraviolet spectrum, generally accompanied by perturbations of the spectral bands arising from electronic transitions of the component molecules and by indications of compound formation in phase diagrams. All complexes have small heats of formation and definite formation constants which may be measured by spectrophotometry and other methods. Dipole moments and semiconductivities are different from those of the component molecules, and marked anisotropies in light absorption, semiconductivity, compressibility and other physical properties are frequently observed. The experimental observations were given a theoretical basis in 1952 by *Mulliken*[1], who interpreted molecular complex formation as the interaction of electron donor and electron acceptor molecules.

Mulliken's theory stated that the electronic ground state wave functions of the complex was a combination of a "no-bond" wave function ψ_0 and one or more "dative bond" functions ψ_1, ψ_2 *etc.* The no-bond function includes the electronic energy of the component molecules, plus terms representing the effect of dipole interactions, dispersion forces, hydrogen bonding, and other intermolecular forces. The dative bond functions represent states where an electron has been transferred from the donor molecule to the acceptor, introducing electrostatic interactions and forming a weak covalent link

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[1] *R. S. Mulliken*, J. Amer. chem. Soc. *74*, 811 (1952).

between the resulting radical ions. The new ground state wave function ψ_N, which may be written

$$\psi_N = a\psi_0 + b\psi_1 + c\psi_2 + \cdots \quad (1)$$

(where a, b, and c are coefficients with $a > b > c$) corresponds to a more stable state than that represented by any of the component wave functions. Excited states, with a dative structure as the main contributor, have the same form, with the coefficients varied to give predominance to the dative bond contribution.

This treatment immediately provided the theoretical basis for interpretation of spectroscopic and formation constant data, and initiated research on semiconductivity and magnetic properties of molecular complexes. By predicting the preferred relative orientations of donor and acceptor molecules for maximization of charge transfer interactions, it stimulated structural work on donor-acceptor complexes. For maximum charge transfer interaction, the relative orientations of the two molecules must provide maximum overlap of the filled donor orbital and the vacant acceptor orbital. This is known as *Mulliken*'s "Overlap and Orientation" principle[2]. The overlap and orientation principle is neither proved nor disproved by individual crystal structure determinations. It is a theoretical principle applying to idealized systems involving no intermolecular forces other than charge transfer forces. The questions which can be answered by experimental structure determinations are:

(a) What factors affect the relative orientations of molecules in crystalline donor-acceptor complexes?

(b) Which of these factors exert the greatest orientational effects in particular complexes? and

(c) Is there structural evidence for the correlation of the magnitude and importance of charge transfer forces in the crystal and the donor and acceptor strengths of the component molecules?

Finally, *Mulliken*'s treatment provided a simple classification of molecular complexes according to the type of orbitals involved in charge transfer[3]. In this review, the classification is simplified to three general types, $\sigma-\sigma$, $\sigma-\pi$, and $\pi-\pi$, referring to complexes where the orbitals involved in charge transfer are both σ orbitals, one σ and one π, or both π orbitals, respectively. Examples are: –

σ donors: aliphatic amines, dioxane, dithiane, acetone, *etc.*

σ acceptors: halogens, oxalyl halides, BF_3, *etc.*

π donors: aromatic hydrocarbons, metal complexes with aromatic ligands such 8-hydroxyquinolinates and porphyrins.

π acceptors: aromatic or ethylenic hydrocarbons with electron-withdrawing substituents (*e.g.* 1,2,4,5-tetracyanobenzene, 1,3,5-trinitrobenzene, quinones).

(Some compounds have both σ and π donor orbitals *e.g.* heterocyclic aromatics such as pyridine and quinoline.)

[2] *R. S. Mulliken*, Recueil Trav. chim. Pays-Bas *75*, 845 (1956).

[3] *R. S. Mulliken*, J. Chim. physique Physico-Chim. biol. *61*, 20 (1964).

2. σ-σ-Complexes

$\sigma-\sigma$-Complexes have been reviewed on previous occasions by *Hassel*[4–6]. The simplest $\sigma-\sigma$-complexes whose structures have been determined are complexes of boron trifluoride[7]. The results are summarized in Table 1.

Table 1. Structural data for some $\sigma-\sigma$ complexes of BF_3.

	BF_3	$CH_3CN{\cdot}BF_3$	$H_3N{\cdot}BF_3$	$(CH_3)_3N{\cdot}BF_3$
N–B distance (Å)	–	1.63	1.60	1.58
B–F distance (Å)	1.30	1.33	1.38	1.39
F–B–F angle (°)	120	114	111	107

In all these complexes the N–B bond length is longer than would be expected for a single covalent bond. As the donor strength increases, charge transfer stabilization of the complex increases and the intermolecular nitrogen-boron distance decreases. As this bond becomes shorter and presumably stronger, the BF_3 molecule distorts from its original trigonal planar form towards a tetrahedral configuration. The lengthening of the B–F bond may indicate that the acceptor orbital is delocalized over the B–F bonds, or it may be the result of a reduced tendency towards intramolecular dative bonding between boron and fluorine as the configuration is changed.

The other $\sigma-\sigma$ complexes that have been investigated show relatively small changes in geometry and interatomic distances of the donor and acceptor molecules. The available structural results are summarized in Table 2. Increasing donor or acceptor strength results in increased charge transfer stabilization, which shortens the donor-acceptor contact and lengthens the intramolecular bond(s) in the acceptor molecule, since the acceptor orbital has antibonding character. The order of donor strength Se > S > O and the order of acceptor strength $I_2 > ICl > Br_2 > Cl_2$ may both be deduced from the variations in bond lengths given in Table 2. In the extreme case of pyridine with iodine, the weakening of the iodine bond by charge transfer is so great that the bond is broken and the final product is $[C_5H_5N.I.NC_5H_5]^+I^-$, with two equal nitrogen-iodine distances of 2.16 Å in the

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Table 2. Structural data of σ—σ complexes investigated. A: Intermolecular contact (Å). B: van der Waals radius sum (Å). C: Covalent radius sum (Å). D: Acceptor intramolecular bond length (Å). E: Intramolecular bond length in free acceptor (Å).

Complex	A		B	C	D		E	Stoichiometry	Configuration	Ref.
4-Picoline·I_2	N—I	2.31	3.65	2.03	I—I	2.83	2.67	1:1	γC···N···I—I linear	[8]
Pyridine·ICN	N—I	2.57	3.65	2.03	I—C		1.99	1:1	γC···N···I—CN linear	[9]
Pyridine·IBr	N—I	2.26	3.65	2.03	I—Br	2.66	2.47	1:1	N···I—Br linear	[9]
Pyridine·ICl	N—I	2.26	3.65	2.03	I—Cl	2.51	2.32	1:1	N···I—Cl linear	[10]
$(CH_3)_3N·I_2$	N—I	2.27	3.65	2.03	I—I	2.83	2.67	1:1	N···I—I linear	[11]
$(CH_3)_3N·ICl$	N—I	2.30	3.65	2.03	I—Cl	2.52	2.32	1:1	N···I—Cl ≈ linear (within 3 °)	[12]
3 Quinoline·CHI_3	N—I	2.99	3.65	2.03	C—I	2.12	2.12	3:1	CHI_3 on trigonal axis N···I—C linear	[13]
Hexamethylenetetramine·2 Br_2	N—Br	2.16	3.45	1.84	Br—Br	2.43	2.28	1:2	N tetrahedral; N···Br—Br linear	[14]
1,4-Dioxane·Oxalyl chloride	O—Cl	3.18	3.20	1.65	C—Cl	1.70	1.72	n:n	Chains (alternating); equatorial bonding O···Cl—C linear	[15]
1,4-Dioxane·Cl_2	O—Cl	2.67	3.20	1.65	Cl—Cl	2.02	1.99	n:n	Chains with equatorial dioxane-Cl bonding	[16]
Oxalyl bromide	O—Br	3.27	3.35	1.80				n:n	Nonplanar sheets; each molecule linked to 4 others; ∢ CO···Br = 169 °	[17]
p-Bromophenylsydnone	O—Br	3.16	3.35	1.80	C—Br	1.89				[18]
1,4-Dioxane·Oxalyl bromide	O—Br	3.21	3.35	1.80	C—Br	1.96	1.85	n:n	As in 1,4-dioxane·oxalyl chloride	[15]
1,4-Dioxane·Br_2	O—Br	2.71	3.35	1.80	Br—Br	2.31	2.28	n:n	As in 1,4-dioxane·Cl_2	[19]
Acetone·Br_2	O—Br	2.82	3.35	1.80	Br—Br	2.28	2.28	n:n	Chains (alternating) planar, ∢ Br—O—Br = 110 °	[20]
2 Methanol·Br_2	O—Br	2.80	3.35	1.80	Br—Br	2.28	2.28	2 n:n	$CH_3OH—Br_2—CH_3OH$-units; linked into H-bonded structure	[21]
1,4-Dioxane·2 ICl	O—I	2.57	3.55	1.99	I—Cl	2.33	2.32	1:2	Cl—I—dioxane—I—Cl-units; O···I—Cl linear	[22]
Diethylether·I_2				1.99			2.67			[23]
1,4-Cyclohexanedione·$HgCl_2$	O—Hg	2.79		2.03	Hg—Cl	2.34	2.28	n:n	Chains (alternating) ∢ O—Hg—O = 86 °, ∢ O—Hg—Cl = 96 °	[24]
Dibenzyl sulfide·I_2	S—I	2.78	4.00	2.37	I—I	2.82	2.67	1:1		[25]
Dithiane·2 I_2	S—I	2.87	4.00	2.37	I—I	2.79	2.67	1:2	I_2-molecule, equatorial	[26, 27]
Dithiane·CHI_3	S—I	3.29	4.00	2.37	C—I	2.20	2.12		Equatorial chains; only 2 iodine atoms of CHI_3 involved; ∢ C—I—S = 175 °	[6]
3 Cyclooctasulfur·CHI_3	S—I	3.44	4.00	2.37			2.12	3:1	CHI_3 bound equatorially to S_8 rings S···I—C linear	[6]
Dithiane·2 SbI_3	S—Sb	3.27 3.34	4.00		Sb—I	2.76 2.78	2.72	n:2 n	Chains of dithiane bridged by two SbI_3 molecules with unsymmetrical bridging (axial and equatorial links)	[28]
Diselenacyclohexane·2 I_2	Se—I	2.83	4.15	2.50	I—I	2.87	2.67	1:2	Chair form, with axial I_2	[27, 29]
Selenacyclopentane·I_2	Se—I	2.76 3.64	4.15	2.50	I—I	2.91	2.67	1:1	Axial I_2 molecule, interacting more weakly with a second selenium atom also axial.	[30]
Diselenacyclohexane·CHI_3	Se—I	3.47	4.15	2.50			2.12	n:2 n	Sheets, with each Se linked to two CHI_3 and CH_3I linked to two Se atoms. Chair form diselenane, linked axially and equatorially	[31]
3 Cyclooctasulfur·SbI_3	S—I	3.60	4.00	2.37			2.72	3:1	∢ Sb—I—Se = 169 ° equatorial structure allows short Sb—I and additional short S—I interactions.	[32]
Thiaselenane·I_2									Disordered structure.	[33]

cation [34]. In complexes formed from donor and acceptor molecules each containing two or more σ donor or acceptor sites, the crystal frequently contains chains of alternating donor and acceptor molecules with the lengths of the charge transfer bonds to both neighbors of any given molecule in the chain usually, but not always, equal. Their structures in solution or in the gas phase, where the formation of chains is much

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[34] *O. Hassel* and *H. Hope*, Acta chem. scand. *15*, 407 (1961).

less likely, may be very different from those observed in single crystals. In a crystal, a particular orientation of donor and acceptor may be favored over others because it allows the formation of a chain structure, while the most stable orientation for a 1:1 gas phase complex may be quite different. The charge transfer bonds in chain complexes are likely to be weaker than those in 1:1 complexes, since the increase in the negative charge on an acceptor molecule involved in two charge transfer bonds reduces the tendency to attract negative charge.

Despite the difficulties in interpreting the structures of complexes which form infinite chains or sheets in the solid state, several of the main features of the relative orientations of the molecules show the influence of charge transfer interactions. The linear arrangements N···X–Y observed in the pyridine and amine complexes maximize the overlap between the lone pair of electrons on the donor atom and vacant orbitals of the electron acceptors, and in the acetone/bromine complex (Fig. 1) the chain structure provides similar good

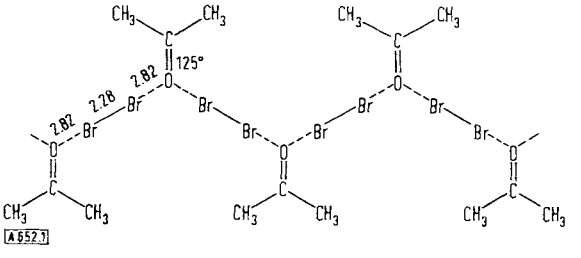


Fig. 1. Schematic diagram of the acetone/bromine complex with interatomic distance in Å.

overlap if the oxygen pair electrons are considered to be in sp^2 hybrid orbitals. This formalism of idealized hybrid orbitals, however, may be misleading, because it could be argued that the most energetically favorable orientation in this complex would involve charge transfer interactions with a pair of electrons in a pure p orbital of acetone, which would have a lower ionization potential. The arrangement about the oxygen atom evidently depends on the best combination of overlap of orbitals and the ionization potentials of electrons in those orbitals. A better qualitative picture is obtained if the donor is considered as having several directions of "preferred polarizability", limited by the number and type of electrons and by their ionization potentials, the actual directions involved in charge transfer being determined by the nature of the electron acceptor and by packing considerations. This has been discussed in a similar way in connection with the role of molecular complexes as reaction intermediates by *Mulliken*[1], and is equivalent to a concept of directional softness and hardness. In complexes of dioxane[16,19], dithiane[26,27], and diselenacyclohexane[27,29] (Fig. 2) the directions of the charge transfer bonds correspond roughly to the axial and equatorial directions of bonding in related carbon compounds, suggesting that the donor atom lone pairs have their preferred polarizability directions coinciding with the 3-fold axes of a tetrahedron. There is evidence that the strongest bonds are formed when the direction of the bond between the donor and acceptor atoms is closest to an ideal axial or equatorial position.

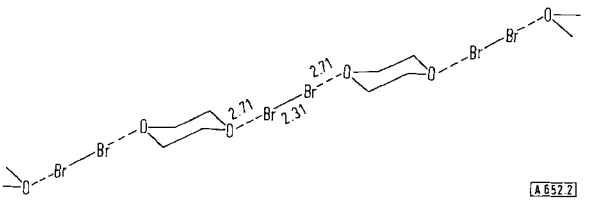


Fig. 2. Schematic diagram of the 1,4-dioxane/bromine complex with interatomic distances in Å.

Table 3 shows that in the SbI_3/1,4-dithiane complex the antimony-sulfur charge transfer bond in the equatorial position is shorter and is closer to the "ideal" direction than is the case with the corresponding axial bonding.

Table 3. Structural data for 1,4-dithiane-antimony triiodide.

	Equatorial	Axial
S–S–Sb angle (°)	147.3	124.6
Ideal equatorial and axial angles (°)	146	105
Bond length (sulfur-antimony) (Å)	3.274	3.336

The equatorial position in dithiane is quite close to the perpendicular to the C–S–C plane, and an acceptor in this position may also benefit from the preferred polarizability perpendicular to the C–S–C plane, corresponding to the formal structure with a lone pair of electrons in a 2 p orbital. In the dithiane/iodine complex, where there is only one charge transfer bond at each end of the dithiane molecule[26], the iodine occupies an approximately equatorial position, 16° from the perpendicular to the C–S–C plane, and in the dibenzyl sulfide/iodine complex[25], where no chains are involved, the S···I–I direction makes an angle of 15° with the normal to the C–S–C plane. The directions of preferred polarizability for diselenacyclohexane are not the same as for dithiane, possibly due to the availability of d orbitals, and the diselenacyclohexane/iodine complex[29] has approximately axial charge transfer bonding.

3. σ-π-Complexes[*]

The crystal structures of the chlorine[35] and bromine[36] complexes of benzene have been determined by two-dimensional methods, assuming the centrosymmetric space group C_{2h}^3. The structure consists of infinite chains of alternate benzene and halogen molecules, with the halogen placed perpendicular to the plane of the benzene ring along the 6-fold axis of the ring and equidistant from the two benzene molecules. The benzene-halogen distances are slightly shorter than the van der Waals distances, but the halogen-halogen distances are the same as in the free halogen molecules (Table 4).

A recent infrared study[37] of single crystals of the benzene/bromine complex shows that the benzene and

[35] *O. Hassel* and *K. O. Strømme*, Acta chem. scand. *13*, 1781 (1959).

[*] Note added in proof: The 1:1 complex benzotrifurazan-triethylphosphate is a further example of a σ-π-complex (*T. S. Cameron* and *C. K. Prout*, Chem. Commun. *1968*, 684).

[36] *O. Hassel* and *K. O. Strømme*, Acta chem. scand. *12*, 1146 (1958).

[37] *W. B. Person*, *C. F. Cook*, and *H. B. Friedrich*, J. chem. Physics *46*, 2521 (1967).

Table 4. Bond lengths in $C_6H_6 \cdot Hal_2$ complexes.

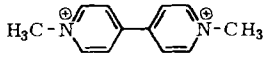
	C_6H_5—Hal distance (Å)	von der Waals radius sum (Å)	Hal—Hal distance (Å)	Hal—Hal distance (Å) (free halogen)
C_6H_5/I_2	3.36	3.65	2.28	2.28
C_6H_5/Cl_2	3.28	3.50	1.99	1.99

bromine molecules are not at centers of symmetry as required by the space group C_{2h}^3, and suggests a structure with alternating long and short benzene-bromine distances. It is possible that this apparent contradiction is a result of disorder in the crystals, even though the anisotropic temperature factors found in the structure determination which are larger in the direction perpendicular to the chain than parallel to it, do not suggest this.

The axial position of the halogen was not predicted originally by *Mulliken*[1], as the theory initially considered only the interaction between the highest energy filled orbital of benzene and the lowest energy vacant orbital of the halogen. The ionization potential for an electron in the highest energy orbital of benzene with the D_{6h} symmetry that is required for charge transfer interaction in the axial model is higher (11.5 eV) than that for the highest energy filled orbital of benzene (9.24 eV). However, the orbital overlap for charge transfer is very probably greater in the axial model with the orbital with 6-fold symmetry than in other possible configurations using the highest energy filled orbital. Therefore the stabilization of the complex by charge transfer may well be greater with the axial model using the lower energy donor orbital than with other arrangements. The balance of overlap and energy factors may give a different arrangement in solution.

Closely related to the benzene/bromine complex is the complex of *p*-xylene with carbon tetrabromide[38], the crystals of which are built up from $(C_8H_{10} \cdot CBr_4)_n$ chains. Two bromine atoms of a CBr_4 molecule are above the centers of two benzene rings 3.34 Å distant. Each *p*-xylene is equidistant from two bromine atoms which lie on the 6-fold axis of the benzene ring, as do the carbon atoms attached to the bromine atoms. There is no cross-linking between the chains.

Some salts of the paraquat ion pq^{2+} *(1)* with metal halides ($CuCl_4^{2-}$, $CuCl_3^{2-}$, $CuCl_2^{2-}$, $CoCl_4^-$ and $FeCl_4^-$) have intense "charge-transfer" spectral bands, and the



(1)

crystal structures show specific interactions which may be associated with charge transfer bonding of the $\sigma-\pi$ type. The compounds $pqFeCl_4$, $pqCoCl_4$, $pqMnCl_4$, and $pqZnCl_4$ are isomorphous[39], $pqCuCl_4$[40] is similar but with a distorted tetrahedral $CuCl_4^{2-}$ ion, and $pq(CuCl_3)_2$[39] and $pq(CuCl_2)_2$[39] have polymeric anions. All the compounds have charge transfer bands in their spectra which are associated with electron transfer from the anion to the pq^{2+} ion.

[38] *F. J. Strieter* and *D. H. Templeton*, J. chem. Physics *37*, 161 (1962).

[39] *C. K. Prout* and *P. Murray-Rust*, unpublished.

[40] *S. C. Wallwork*, personal communication.

In all crystals the pq^{2+} ion is planar, and in crystals of each compound there are chlorine to nitrogen contacts along the perpendiculars to the plane of the pq^{2+} at the nitrogen atoms (Fig. 3). These contacts shorten as the charge transfer spectral bands move to lower energy: $pqCoCl_4$, pale green crystals, d(N–Cl) 3.75 Å; $pq(CuCl_3)_2$, dark red crystals, d(N–Cl) 3.47 Å; $pq(CuCl_2)_2$, black crystals, d(N–Cl) 3.23 and 3.27 Å. In $pqPdCl_4$[39] there are no nitrogen-chlorine contacts as short as these, or of the same orientation, the pq^{2+} ion is not planar, and there is no charge transfer band.

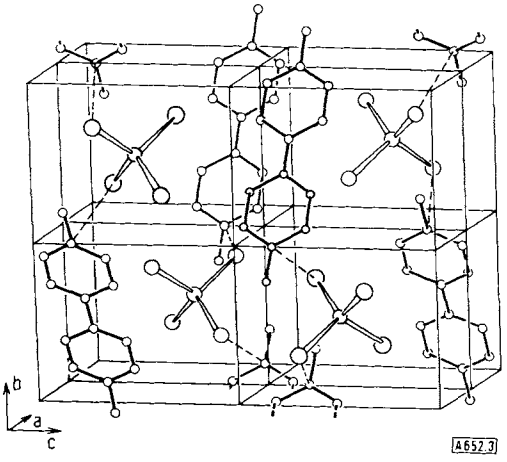


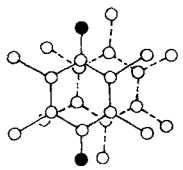
Fig. 3. The crystal structure of "paraquat" tetrachlorocobaltate. The short N—Cl contacts are shown by broken lines.

4. π-π-Complexes

All crystals of $\pi-\pi$ type molecular complexes (*e.g.* 1,3,5-trinitrobenzene/anthracene) are formed from stacks of alternate donor and acceptor molecules. The *Mulliken* treatment[1] suggests that these stacks are to be expected. However, there is little guidance to the relative orientations of molecules within the stacks.

Mulliken considered the hypothetical case of the complex between a polymethyl benzene Me_nBz and a polynitrobenzene $Bz(NO_2)_{n'}$, with n and n' decreasing to zero. If the two molecules were stacked with their symmetry axes coincident and their planes parallel, the symmetry would be D_{6h}. Then ψ_1 and ψ_2 of equation 1, ground state Bz^+ and Bz^-, would be of types $^2E_1$ and $^2E_2$. Although a proper combination of these states gives many states of Bz.Bz, not one is of the species ^1A_1g required for resonance with ψ_0. Hence a different stacking of the two Bz molecules is indicated. To *Mulliken* it seemed likely that an arrangement obtained by sliding one Bz about half a ring diameter over the other would give maximum resonance. Unfortunately, in assessing the relative orientations of two molecules in the plane-to-plane stack it is not possible to separate directly the influence of charge transfer and that of dispersion forces. The latter tend to be largest in orientations bringing maximum polarizabilities into play, and contrast with the former governed by considerations of quantum mechanical symmetry.

The majority of the known crystal structures of $\pi-\pi$ complexes are summarized in Table 5. In this Table, the relative orientations of donor and acceptor molecules are demonstrated by the projection of the donor and acceptor molecules onto the least squares best plane through the atoms of the donor molecules. The diagrams are sketches, and in the case of the less



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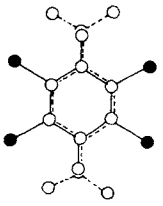

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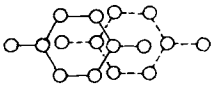

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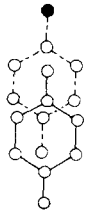

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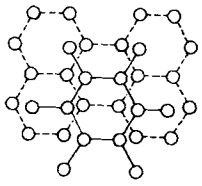

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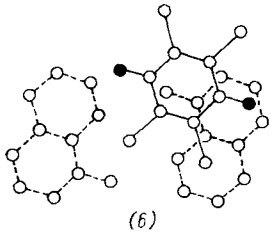

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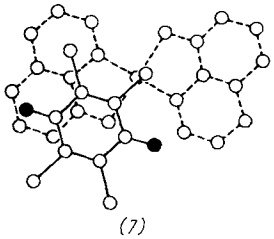

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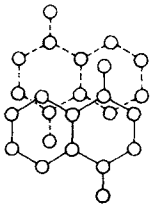

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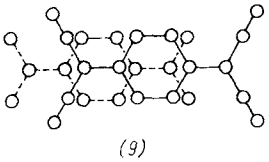

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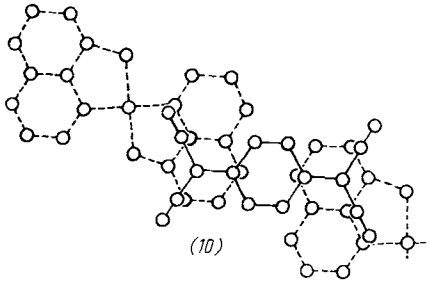

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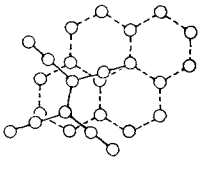

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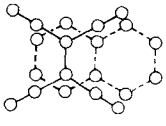

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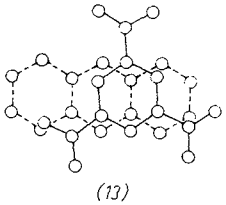

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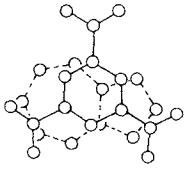

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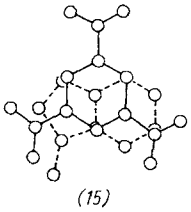

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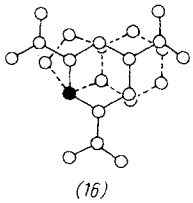

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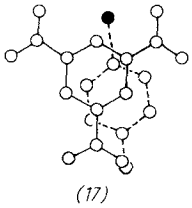

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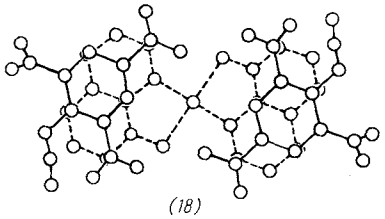

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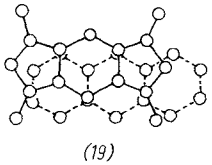

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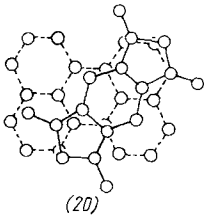

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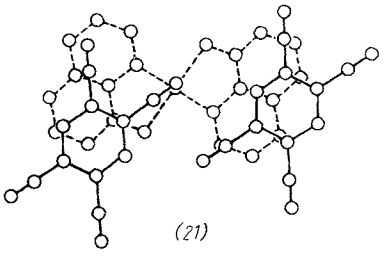

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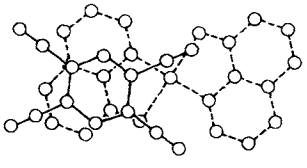

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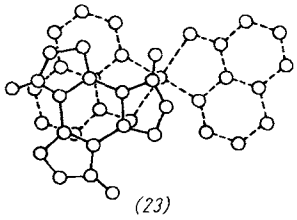

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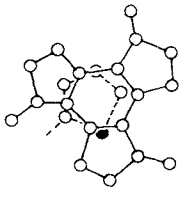

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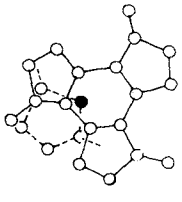

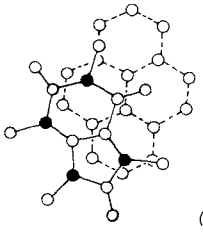

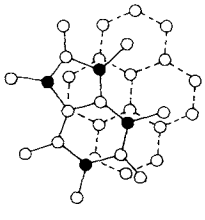

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Table 5. Structure data of π—π complexes. A: Relative orientation of donor and acceptor corresponding to the figures on page 664. B: Space group (Schönfliess space-group symbols; C_{2h}^5, C_i^1, C_{2h}^3, C_{2h}^6, C_s^2 are denoted by the numbers 14, 2, 12, 15, and 7 in Ref. [69]. C: Interplanar perpendicular spacing (in Å). D: Shortest interplanar contacts (in Å). E: Angle of inclination of planes in degrees (? parallel indicates that there is no comment in the original paper on any deviation from parallel arrangement. F: Ionization potential of donor (eV). G: Electron affinity of acceptor (eV). [a] The data in this column is incomplete because (i) in some cases the charge transfer bands are obscured by bands of the component molecules and (ii) crystallographic papers tend not to contain a record of charge transfer band positions even when they are known. [b] The donor molecule in this complex contains two thiophene ring systems which lie in different orientations with respect to benzotrifuroxane molecules; the two orientations are shown. [c] In the pyrene/tetramethyl uracil complex, tetramethyl uracil molecules overlap opposite sides of the pyrene molecule in different orientations.

Complex	A	B	C	D	E	F	G	Charge-transfer bands [a] (nm)	(10³·cm⁻¹)	Ref.
Hexamethylbenzene·Chloranil	*(1)* • = O	C_{2h}^5	3.50	—	2.1	8.0	2.59	505	19.8	[41]
N,N,N'N'-Tetramethyl-*p*-phenylene-diamine·Chloranil	*(2)* • = Cl	—	3.26	—	—	6.6	2.59	Bands of radical ions observed		[42]
Quinhydrone mon. modification	*(3)*	C_{2h}^5	3.16	C—O 3.17, 3.42 C—C 3.21	? parallel	—	—	550	18.2	[43]
tric. modification	*(3)*	C_i^1	3.19	C—O 3.17, 3.37 C—C 3.20	? parallel	—	—	—	—	[44]
p-Chlorophenol·Quinone	*(4)* • = Cl	C_{2h}^5	3.27	C—O 3.24, 3.36, 3.37 C—C 3.31, 3.31, 3.36, 3.36	3.0	8.6	—	—	—	[45]
2 *p*-Chlorophenol·Quinone	*(4)*	C_{2h}^5	3.20	C—O 3.11, 3.29, 3.33 C—C 3.25, 3.28, 3.29	6.0	8.6	—	—	—	[46]
Perylene·Fluoranil	*(5)*	C_{2h}^5	3.23	C—O 3.29 C—C 3.34 C—F 3.36	? parallel	—	—	—	—	[47]
2 8-Hydroxyquinoline·Chloranil	*(6)* • = O	C_i^1	—	C—O 2.96, 3.09, 3.21 C—C 3.18, 3.22, 3.35, 3.36	9.5	7.6	2.59	510	19.6	[48]
Bis(8-hydroxyquinolinato)-palladium(II)·Chloranil	*(7)* • = O	C_i^1	—	Pd—Cl 3.44 C—O 3.09, 3.37 C—C 3.12, 3.34	15.5	7.1	2.59	675	14.8	[49]
1,4-Naphthoquinone	*(8)*	C_{2h}^5	3.49	—	—	—	—	No charge transfer		[50]
N,N,N',N'-Tetramethyl-*p*-phenylene diamine·Tetracyanoquinodimethane	*(9)*	C_{2h}^3	3.30	—	? parallel	6.6	—	—	—	[51]
Bis(8-hydroxyquinolinato)copper(II)·Tetracyanoquinodimethane	*(10)*	C_i^1	3,25	C—C 3.24, 3.27, 3.31 N—N 3.30	—	7.3	—	—		[52]
Pyrene·Tetracyanoethylene	*(11)*	C_{2h}^5	3.32	C—C 3.33	? parallel	—	2.85	724	13.8	[53]
Naphthalene·Tetracyanoethylene	*(12)*	C_{2h}^3	3.30	C—C 3.37	—	8.12	2.85	550	18.2	[54]
Anthracene·*s*-Trinitrobenzene	*(13)*	C_{2h}^6	—	C—C 3.30, 3.32, 3.35, 3.38 C—N 3.35 C—O 3.28	? parallel	7.4	1.86	460	21.7	[55]
Azulene·*s*-Trinitrobenzene	*(14)*	C_{2h}^5	3.33	C—N 3.30 3.30	? parallel	—	1.86	459	21.8	[56]
Skatole·*s*-Trinitrobenzene	*(15)*	C_{2h}^5	3.30	—	? parallel	—	1.86	—	—	[57]
Indole·*s*-Trinitrobenzene	*(16)* • = N	C_{2h}^5	—	—	? parallel	—	1.86	—	—	[57]
p-Iodoaniline·*s*-Trinitrobenzene	*(17)* • = I	C_{2h}^5	3.42	C—C 3.5 C—O 3.4	? parallel	—	1.86	—	—	[58]
Bis(8-hydroxyquinolinato)copper(II)·2 Picryl azide	*(18)*	C_{2h}^6	3.45	C—C 3.45, 3.50 C—O 3.19, 3.20, 3.34, 3.39	2.0	7.3	2.2	510	19.6	[59]
Anthracene·Pyromellitic anhydride	*(19)*	C_i^1	3.23	—	? parallel	7.4		—	—	[60]
Perylene·Pyromellitic anhydride	*(20)*	C_{2h}^5	3.33	C—C 3.31, 3.34	? parallel	—	—	—	—	[61]
Bis(8-hydroxyquinolinato)copper(II)·1,2,4,5-Tetracyanobenzene (1:2)	*(21)*	C_i^1	—	Cu—N 2.96 C—C 3 20, 3.26, 3.34, 3.46	—	7.3	2.30	558	17.9	[62]
Bis(8-hydroxyquinolinato)palladium(II)·1,2,4,5-Tetracyanobenzene	*(22)*	C_i^1	—	Pd—C 3.48 C—C 3.28, 3.29, 3.44	4.5	7.1	2.30	568	17.6	[63]
Bis(8-hydroxyquinolinato)copper(II)·Benzotrifuroxane	*(23)*	C_{2h}^5	—	Disordered	10	7.3	1.98	465	21.5	[64]
13,14-Dithia-tricyclo[8.2.1.1^{4,7}]tetra-deca-4,6,10,12-tetraene·Benzotrifuroxane	*(24)* • = S [b]	C_i^1	—	—	9.5 (for both rings)	—	1.98	—	—	[65]
Pyrene·Tetramethyl uracil	*(25)* • = N [c]	C_s^2	—	—	—	—	—	— No charge transfer		[66]

accurate determinations have been idealized to give molecules of the accepted regular shape.

All the crystals of the 1:1 complexes are formed from approximately plane-to-plane stacks of alternate donor and acceptor molecules, except the adduct of benzotrifuroxane and 13,14-dithiatricyclo[8.2.1.1.^{4,7}]tetradeca-4,6,10,12-tetraene [65] in which the paracyclophane-like aromatic has two plane-to-plane donor groups giving a stack similar to that of the 2:1 complex of *p*-chlorophenol and *p*-benzoquinone [46], in which two donor molecules alternate with one acceptor molecule.

There are three characteristic ways of packing together of the stacks in the crystals (Fig. 4), that can easily be

recognized from the crystallographic space groups. Type A occurs in the space group C_i^1 (No. 2) and requires that both molecules present have centers of symmetry. The crystal may also be regarded as built up from sheets containing donor and acceptor molecules in the ratio 1:1, with each donor molecule surrounded within the sheet by acceptor molecules and *vice versa*. Type B uses space group C_{2n}^5 (No. 14) and also requires that each molecule occupies a crystallographic symmetry centre. The structure is used on occasion by non-centrosymmetric molecules (*e.g.* in bis(8-hydroxyquinolinato)copper(II)/benzo-trifuroxane[64]) and disorder is observed. Type C requires a face-centered lattice, as in space group C_{2h}^3 or C_{2h}^6. The structure appears to be favored by non-centrosymmetric donor and acceptor molecules and is often associated with twinned or disordered crystals. Very many, probably the majority, of the crystals of $\pi-\pi$ complexes appear to be disordered or show complex super-lattice effects.

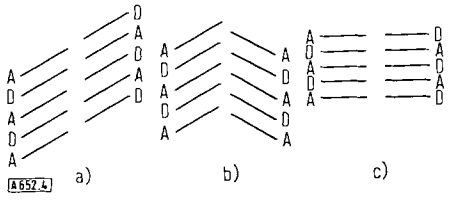

Fig. 4. Typical donor-acceptor stacks in $\pi-\pi$ complexes.

Examination of Table 5 suggests at first sight little system in the relative positions of donor and acceptor molecules. In only one example, *N,N,N',N'*-tetramethyl-*p*-phenylenediamine[42] are the aromatic rings exactly superposed in the eclipsed position. In *p*-iodoaniline/1,3,5-trinitrobenzene[58] which approximates most closely to *Mulliken*'s hypothetical case, the two benzene rings are not superposed, but the positions are in good agreement with the Mulliken prediction of an arrangement obtained by sliding one benzene ring one half a ring diameter over the other. A similar displaced system is found in seven out of the nine structures listed with a *p*-benzoquinone derivative as acceptor. In six of these complexes, the displacement approaches a whole ring diameter, and the overlap of the aromatic rings is very small. They have the common features that the highly polar quinone carbonyl group lies over the center of a benzene ring, with the C–O vector parallel to two C–C bonds of this ring, and that a C–O bond of the donor is similarly placed with respect to the quinonoid ring of the acceptor. It has been suggested[42] that this arrangement is taken by quinhydrone to satisfy the hydrogen bonding requirements of the crystal. However, it is observed in the absence of hydrogen bonding in bis(8-hydroxyquinolinato)palladium(II)/chloranil and in the absence of charge transfer forces in crystals of 1,4-naphthoquinone and its derivatives. It appears more likely that this arrangement is required to maximize the contribution of the highly polar groups to the dispersion forces. The structure of hexamethylbenzene/chloranil and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine/chloranil are exceptional. In the former the donor molecule is without polar groups, and the compound may be thought of as reverting to the *p*-iodoaniline/1,3,5-trinitrobenzene type. The latter compound in the solid state has absorption bands in the visible and ultraviolet region characteristic of the radical ions $(chloranil)^-$ and $(N,N,N',N'$-tetramethyl-*p*-phenylenediamine$)^+$[67] suggesting complete transfer of an electron from donor to acceptor and the possibility of major changes in structure as observed.

The relative orientations of donor and acceptor in tetracyanoquinodimethane (TCNQ) complexes resemble those in the *p*-benzoquinone compounds, the highly polar carbon-carbon double bond of the TCNQ molecule taking up a similar position to the quinone carbonyl group. The position of the carbon-carbon double bond relative to the aromatic ring of the donor is also similar to the donor in the TCNE complexes with naphthalene and pyrene. The charge transfer spectral absorption bands of pyrene/TCNE have been studied in some detail. Charge transfer is from the highest and next highest energy orbitals of the donor to the only available orbital of the acceptor. The two donor orbitals of the pyrene respectively require the carbon-carbon double bond of the TCNE molecule to lie parallel and perpendicular to the long axis of the molecule for maximum overlap. The observed position is said to be a compromise of these two opposing requirements[53]. It is, however, surprising that if charge transfer effects are the main orientating force, the TCNE molecule lies so far from the center of the pyrene molecule.

Complexes of 1,3,5-trinitrobenzene (TNB) have been reasonably thoroughly investigated. The acceptor is much less polar than the quinonoid compounds, and the structures are probably determined largely by charge transfer effects, modified to some extent by crystal packing requirements. The simplest example, *p*-iodoaniline/TNB[58] has been discussed. There are a number of examples of complexes of TNB (or picryl azide) with aromatic donors with two or more condensed ring

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systems. In all these compounds, the arrangement in the stack approximates to C-atoms 2, 4, and 6 of 1,3,5-trinitrobenzene being eclipsed with C-atoms 4, 5, and 10 of a naphthalene nucleus. The idealized arrangement approached in numerous compounds is not that claimed for naphthalene/TNB [42]. However, details of the naphthalene/TNB structure determination have not been published. Similar arrangements have been found in complexes of pyromellitic dianhydride [60,61] and for the 1,2,4,5-tetracyanobenzene (TNCB) molecule in the 1:2 complex of bis(8-hydroxyquinolinato)-copper(II) with TCNB [62] that is not interacting with the copper atom shown in the projection in Table 5.

Complexes of bis(8-hydroxyquinolinato)copper(II) and palladium(II) are one of the few groups of complexes where one donor has been taken with a number of acceptors. The system is complex. The donor is a highly polarized system and acceptor molecules appear attracted to the C–O bond in the donor. Further interaction between the copper atom of the donor and the acceptor molecule has been observed in complexes with TCNB [62] and benzotrifuroxane [64].

It has been claimed [42] that "where charge transfer might be expected to be more significant in determining the structure (*e.g.* low ionization potential of the donor) the relative orientation and position of the components are such as to allow the maximum degree of overlap between their molecular π orbitals". The content of this statement implies that high electron affinity of the acceptor would also be acceptable as a criterion for maximum degree of overlap, and *N,N,N',N'* - tetramethyl - p - phenylenediamine/chlor - anil is quoted as the ideal case of maximum overlap.

The facts in Table 5 do not support this statement. Indeed the higher the electron affinity of the acceptor for a given donor *e.g.* in the 8-hydroxyquinolinate series, almost the contrary appears to be true. However, there are two further difficulties. One is the relative importance of dispersion forces in determining orientation. Most of the better electron acceptors are the more highly polar molecules, and the better donors are the most readily polarized molecules. Complexes between them are likely to be those in which dispersion forces assume the greatest importance. Indeed, complexes apparently of the plane-to-plane stacked donor-acceptor type are formed between a polarizable molecule and a polar molecule *e.g.* pyrene/tetramethyluracil [66], without there being any evidence for charge transfer effects. The other difficulty is that as yet there is no detailed theory which states which orbitals of the donor and acceptor are involved in charge transfer, and no one has produced a clear picture of the expected positions for maximum overlap, largely due to a neglect of the symmetry requirements governing the combination of states in equation (1). Indeed, the electronic structures of the more complex electron acceptor molecules are far from being fully understood.

Further, it is assumed that a short interplanar perpendicular separation is associated with a high relative importance of the charge transfer contribution to the intermolecular bonding. If the energy of the charge transfer band is taken to be an inverse measure of the contribution of charge transfer to the bonding energy, then it would be expected that a short interplanar perpendicular distance would be associated with charge transfer bands of low energy, that is, with donors of low ionization potential and acceptors of high electron affinity. In Table 5 there appears to be little correlation between perpendicular interplanar spacing and any of these factors. What correlation there is tends to suggest that short interplanar spacings are associated with molecules in which dispersion forces assume the greatest importance. Some of the shortest interplanar spacings between flat organic molecules are found in crystals of the highly polar barbituric acid derivatives including barbituric dihydrate with a spacing of 3·12 Å [68]. It is to be expected that there may be a correlation between interplanar spacings and the heat of formation and free energy of formation – measurements which take into account all factors in the binding energy. Unfortunately, those complexes for which free energies of formation *etc.* are known are not always those of known structure, and in any case these measurements are generally made in solution and the results may not apply to the solid state.

5. Conclusions

Stimulated by *Mulliken*'s first treatment of the theory of donor-acceptor complexes, and by the growing interest in electronic charge transfer processes in both biological and technological fields, the structure analysts have provided a great deal of information on an apparently rather random choice of donor-acceptor complexes. The choice of compounds has probably been determined by the availability of good single crystals rather than by a coordinated plan. Certain general structural features emerge, the linear groups in the donor-halogen $\sigma-\sigma$ complexes, the axial benzene/halogen $\sigma-\pi$ complexes, the quinone orientation and other recurrent arrangements in $\pi-\pi$ complexes. These features were not all predicted in earlier theoretical work, and to date their theoretical interpretation is largely unsatisfactory. The many physical investigations of molecular complexes since *Mulliken*'s theoretical work suggest that further significant advances in the understanding of charge transfer processes and structural principles in donor-acceptor systems will not be long delayed.

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Studies on the Adsorption of Gases on Clean Metal Surfaces with the Aid of Field-Emission and Field-Ion Microscope Techniques

BY W. M. H. SACHTLER [*]

Studies on the adsorption of gases such as xenon, hydrogen, nitrogen, and carbon monoxide on the surface of a single crystal of tungsten with the aid of field-emission and field-ion microscopy have, in the past few years, led to new, fundamental insights into chemisorption and heterogeneous catalysis. Important phenomena which were discovered and elucidated by these techniques include the pronounced face specificity of the adsorption, the fact that several different adsorption complexes of a gas are found on one and the same crystal face, and the rearrangement of the surface atoms through chemisorption. Many of the interpretations thus gained for the systems studied can also be generalized for other chemisorption complexes.

1. Introduction

A number of powerful methods are available for experimental studies concerning the adsorption of gases on solid surfaces. For instance, adsorption complexes can often be characterized by means of IR spectroscopy [1]. As soon as ordered surface structures are formed, they can be identified by their electron diffraction pattern, obtained by low-energy electron diffraction (= LEED) [2, 3]. In the case of adsorption on oxides, for instance, electron spin resonance [4, 5] provides valuable information on the adsorption complex if the adsorbate contains an odd number of electrons or if transition-metal ions with incompletely filled d-orbitals occur in the adsorbing surface. Furthermore, magnetostatic methods [6–8] can record the change in magnetization upon adsorption on para- or ferromagnetic solids. For adsorbing metals [9, 10] and alloys [11] the change in work function caused by adsorption gives important indications as to the character of the bond between adsorbent metal and adsorbate. The change in electrical resistance [12–14] of adsorbing metal films is another tool in studying adsorption phenomena.

As in the course of time evidence was gathered that a given gas may be bound in widely different ways on a given metal [15, 16], so that at a high degree of coverage several different adsorption complexes can be distinguished on one and the same surface, this led to a growing interest in methods providing information on single atomic events and enabling the adsorbing centers and the adsorption complexes to be characterized precisely. Two related methods, which can also be used in combination with each other, have proved particularly useful in solving such problems: field emission microscopy and field ion microscopy. In the following, the scope, the fundamental limitations, and difficulties of these methods will be outlined with regard to the special purpose of studying adsorption complexes; subsequently, results obtained will be discussed. (For a detailed account of the theory and the application of field emission microscopy and field ion microscopy the reader is referred to ref. [17–20].)

2. Field Emission (FE) Microscopy

The potential energy of an electron close to the surface of a neutral metal in the absence of external fields is schematically represented in Fig. 1 (curve 1). In the interior of the metal, at absolute zero, all energy levels up to the Fermi level are each filled by two electrons, all higher energy levels are empty.

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The energy of the Fermi level being lower than the energy of the electron *in vacuo* by an amount φ, there is no emission of electrons unless energy is supplied, for instance, by means of light quanta (photoelectric emission) or colliding corpuscles. At higher temperatures energy levels above the Fermi level are also filled, and it is then possible that electrons leave the metal surface.

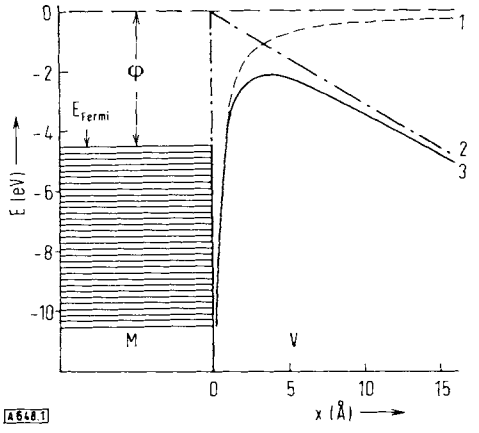

Fig. 1. Potential-energy diagram for an electron near a metal surface. M = metal, V = vacuum. 1) ($E = -e^2/4x$), no external field. 2) ($E = -eFx$), external field $F = 0.3$ V/Å. 3) potential resulting from superposition of curves 1 and 2 after application of external electric field F.

As soon as an external electric field F is applied, with its negative pole at the metal, the potential energy $-eFx$ (curve 2) is superimposed on the potential energy of the electron in the absence of a field. The resulting potential curve (curve 3) shows a maximum (Fig. 1). Evidently, an electron sufficiently far from the metal surface has a lower potential energy than inside the metal: thus, electron emission has become an exothermic process. Whether this process actually takes place is dependent on whether any electrons can be transferred from the left to the right of the potential barrier. Theoretically, this can be achieved in two ways:

1) across the potential barrier (process with positive activation energy);

2) through the potential barrier (quantum-mechanical tunnel effect).

At very low temperature and at field strengths of the order of 10^7–10^8 V/cm (0.1–1 V/Å) it is obviously only the latter possibility that is of interest. We will therefore restrict ourselves to a consideration of such tunneling effects in the following.

For a given metal the field electron emission – field emission for short – increases strongly with field strength. At equal field strength but for different metals it is greatest for the metal with the lowest work function. The relation between current density j, field strength F, and work function φ was derived – after simplifying assumptions – by *Fowler* and *Nordheim* [21].

After some further refinements the "Fowler-Nordheim equation" acquired the following form [22]:

$$j = \frac{1.54 \times 10^{-6}}{t^2(y)} \cdot \frac{F^2}{\varphi} \exp\left[-6.83 \times 10^7 \frac{\varphi^{3/2}}{F} \delta(y)\right], \qquad (1)$$

where $t(y)$ and $\delta(y)$ are functions of the variable:

$$y = 3.79 \times 10^{-4} \frac{F^{1/2}}{\varphi}, \qquad (2)$$

which are available in tabular form.

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The field strength at the surface depends both on the voltage applied, V, and on the geometry of the surface according to the relation:

$$F = \alpha V \qquad (3)$$

Essentially, α is inversely proportional to the radius of curvature, ρ, of the emitting surface. Hence, extremely high voltages are not necessary if the emitter has the form of a sharp tip with small ρ. In actual practice, chemical and electrochemical etching methods have been developed which enable metal tips to be made with a radius of curvature of the order of 10^{-5} cm. This typical form of the emitter not only renders it possible to reach the desired field strength at voltages that are easy to realize experimentally (several kilovolts but also leads to two additional consequences:

a) Because the equipotential curves are parallel to the tip surface and the electrons emitted follow the orthogonal trajectories through the equipotential curves a diverging beam of electrons is formed. Upon striking a fluorescent screen the electrons produce a strongly magnified image of the emitting surface. The magnification is given by the factor:

$$M = \frac{R}{\beta\rho}, \qquad (4)$$

where R is the distance between tip and screen and β (≈ 1.5) is a compression factor determined by the geometry. For $R = 15$ cm and $\rho = 10^{-5}$ cm the magnification factor M thus amounts to 10^6, which means that 1 mm on the screen corresponds to 10 Å on the surface. As early as in the thirties, these possibilities inspired *E. W. Müller* [22] to design the field emission microscope [23, 24], the principle of which is shown in Fig. 2.

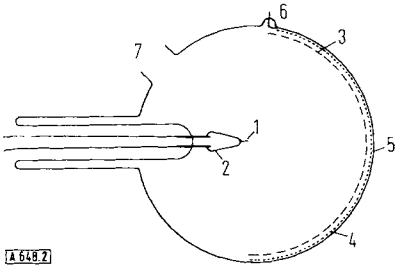

Fig. 2. Principle of the field-emission microscope.
1, metal tip. 2, heating loop. 3, fluorescent screen. 4, conductive coating. 5, glass envelope. 6, anode. 7, to vacuum.

Although in principle it is possible to increase the magnification factor to $M > 10^7$ – by using constructions with large R and small ρ – there is no point in doing so, because there is a fundamental limit to the resolving power. This is due to the fact that the probability of tunneling is greatest for those electrons which, before emission, are at the highest filled level. Since the electrons are distributed in the metal according to Fermi-Dirac statistics these electrons possess considerable energy also at absolute zero, so that after the emission the projectiles generally have a compo-

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[23] *E. W. Müller*, Physik. Z. *37*, 838 (1936).

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nent perpendicular to the field gradient, in addition to the component of motion in the direction of the applied field. The resulting unsharpness makes it impossible to realize a resolution in the range of atomic dimensions with the aid of field electrons. This is possible, however, with the field ion microscope, in which images are obtained with projectiles not subject to Fermi-Dirac statistics (see Section 3).

b) Since the radius of curvature ρ is smaller than the crystallites constituting the metal wire, the emitting tip is nearly always part of a *single crystal*. It is a known fact that macroscopic single crystals in thermodynamic equilibrium build up their surface in such a way that the crystal faces with very small Miller indices predominate, whereas the less stable faces only appear in the form of rounded edges and corners; for microscopic crystals, on the other hand, equilibrium is reached when the surface is the nearest approach to the spherical shape. Thus, the surfaces of the tips in the FE microscope contain, in addition to the stable and smooth faces, unstable and rough faces.

Since the effective work function φ_{hkl} is different for different faces[*], but, according to eq. (1), strongly influences the emission current, the electron-optical image of the tip shows a pattern of bright and dark areas corresponding to the distribution of local work functions on the surface. Since as a rule the crystal structure of the emitting metal is known, it is easy to recognize from the symmetry of the image to what crystal face a given area of the image corresponds.

Summarizing, it may be said that the FE microscope produces the strongly magnified electron-optical image of the surface of a well-defined single crystal, in which the brightness of each image point depends on the work function of the emitting crystal face. In addition, the current-voltage characteristic, which is easy to measure, can be analyzed quantitatively. The prospects for FE microscopy as a tool in studying adsorption on metals will now briefly be discussed:

1) As practically every adsorption leads to a change in work function – an increase or a decrease – the adsorption can be recognized and followed *visually* through the change in brightness of the image.

2) Quantitatively, every state of adsorption can be characterized by the parameters of the current-voltage characteristic. In this connection it is of practical value to replace the field strength in eq. (1) by the voltage according to eq. (3) and the current density j by its proportional current strength. To a good approximation, the F(owler)-N(ordheim) equation then acquires the form:

$$\log i\,V^{-2} = \log A - B\varphi^{3/2}V^{-1}. \qquad (5)$$

If the constant B is known and remains unchanged by the adsorption, the parameters log A and φ before as well as after the adsorption can conveniently be derived from the ordinate intercept and the slope of the F–N line, which is obtained by plotting log $(i\,V^{-2})$ against V^{-1}. The work function of the clean metal, φ_0, being known, constant B can be calculated from the F–N line of the clean metal. As both log A and φ generally have different values for the tip covered with an adsorbed gas and for the clean tip, any adsorbed state can be characterized by the two parameters:

$$\Delta \log A = \log A_{\text{covered}} - \log A_{\text{clean}} \qquad (6)$$

and:

$$\Delta\varphi = \varphi_{\text{covered}} - \varphi_{\text{clean}}. \qquad (7)$$

Although Δ log A is easily accessible experimentally, it is difficult to interpret theoretically; cf. the partly conflicting views of *Gomer*[20,58], *Van Oostrom*[29], and *Holscher*[49].

It is common usage to call the parameter Δ log A the pre-exponential factor, and the quantity $-\Delta\varphi$ (sometimes also $+\Delta\varphi$) the surface potential. According to classical physics the surface potential of a double layer should be related to the dipole moment μ and the number of dipoles n per cm^2 according to the Helmholtz equation[25]:

$$-\Delta\varphi = 4\pi n\mu, \qquad (8)$$

where μ is expressed in Debye units and the positive sign of μ applies for dipoles with the adsorbate positively charged with respect to the metal surface. For a surface built up of atoms the moment of the bonding dipole between metal atoms and adsorbate atoms may have different directions; then μ is the projection of the bonding dipole on the surface normal. For adsorptions where there are only very few atoms on the metal surface the model of the Helmholtz double layer derived from classical physics loses validity.

3) At a low degree of coverage the adsorbate will generally not be distributed uniformly over the total surface, but will be concentrated on some preferred crystal faces. Visually this face specificity of the adsorption can be recognized by the fact that at incipient adsorption the brightness of many crystal faces changes considerably, whereas the images of other faces do not, at first, change. As the adsorption proceeds, the brightness ratio of two crystal faces may vary greatly, in some cases even repeatedly be inverted.

4) Quantitatively, for any crystal face with the Miller indices (*hkl*), the face specificity is characterized by the parameters Δ log A_{hkl} and $\Delta\varphi_{hkl}$. This, however, can only be done in a reliable way with the aid of a variant of the FE microscope, the probe-hole tube. It differs from the type already described in that there is in the fluorescent screen a minute hole behind which are mounted a Faraday cage collector and a number of auxiliary electrodes. In this way the partial emission current of a particular surface element is diaphragmed out of the total beam and can thus be measured. As this branch current also obeys the F–N equation, it is possible to determine the parameters log A_{hkl} and

[*] The work functions determined with the aid of the FE microscope refer, not to charge-free infinity, but to points which are still close to the surface and which, with respect to similar points close to another crystal face, have a finite potential. It is therefore not possible to create a *perpetuum mobile* by removing an electron from the metal through one crystal face and re-introducing it through another face.

[25] *J. H. de Boer*: Elektronenemission und Adsorptionserscheinungen. J. A. Barth, Leipzig 1937, p. 50.

φ_{hkl} both before and after the admission of gas for that (*hkl*) face whose emission beam enters the Faraday cage. *Müller*[26,27], *Smirnov* and *Shuppe*[28], *Van Oostrom*[29], and *Holscher*[30] have devised variants which enable the emission beam from any face to be directed into the Faraday cage. This can be realized by means of magnetic deflection of the electron beam or by mechanical shifting of the emitter, for instance, with the aid of a vacuum-tight stainless-steel bellows (cf. Fig. 3).

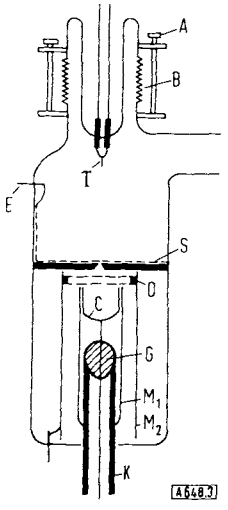

Fig. 3. Field emission probe-hole tube, according to *Holscher* [30]. A, adjusting screw. B, vacuum-tight, stainless-steel bellows. C, collector. D, double grid. E, metal-in-glass seal (connected electrically with the fluorescent screen). G, glass pressing. K, kovar tube. M_1 and M_2, molybdenum cylinders. S, fluorescent screen. T, tip (field cathode).

5) The *heat of adsorption* $-\Delta H$, particularly the face-specific heat of adsorption $-\Delta H_{hkl}$ of a given gas on a given crystal face of the metal considered can be measured with the FE microscope, which in this respect is unrivaled. In principle the $-\Delta H_{hkl}$ values can be determined both by equilibrium measurements and, kinetically, by measuring the activation energies E_{des} and E_{ads} for desorption and adsorption. In the former case use can be made of the thermodynamic equilibrium relation:

$$\frac{\theta^z}{(1-\theta)^z p} = \exp\frac{\Delta S}{R} \cdot \exp\left(-\frac{\Delta H}{TR}\right) \qquad (9)$$

where θ is the degree of coverage, p the equilibrium pressure, ΔS the adsorption entropy, and z the degree of dissociation; R and T have their usual meanings. If it is possible to estimate θ, z, and ΔS theoretically, ΔH can be calculated from a pair of p and T values with the aid of eq. (9).

Another way is simply to start from the assumption that points of equal brightness correspond to the same value of θ and to find experimentally the p, T pairs that correspond to the same emission. Eq. (9) is then written as an adsorption isochor:

$$\ln p = \text{const} + \frac{\Delta H}{RT} \text{ (for } \theta = \text{const)} \qquad (10)$$

from whose slope $-\Delta H$ is calculated.

For the FE determinations of heats of adsorption that have so far become known, however, use has been made of the kinetic method, which is based on the relation between caloric and kinetic quantities:

$$-\Delta H = E_{des} - E_{ads} \qquad (11)$$

For systems in which the adsorption is not an activated process ($E_{ads} = 0$) the problem reduces to that of determining the activation energy of the desorption. This is measured, for instance, by first establishing a certain degree of coverage at a low temperature, then rapidly raising the temperature to a value that can be measured accurately, and measuring the time during which the emission current and thus the brightness of the surface element under consideration change to the value for the clean surface. Again the evaluation can be carried out in either of two ways: either no assumption is made as regards the activation entropy and E_{des} is determined from the temperature dependence using Arrhenius' law, or use is made of the absolute rate theory and a physically acceptable value for the activation entropy of the desorption is inserted in the general rate equation. In the former case the activation energy of the desorption is given by:

$$E_{des} = -R \cdot \frac{d \ln r_{des}}{d(1/T)} \qquad (12)$$

where r_{des} is the rate of desorption measured in arbitrary units. In the latter case the general equation:

$$r_{des} = \frac{kT}{h} \exp\frac{\Delta S^*}{R} \exp -\frac{E_{des}}{RT} \qquad (13)$$

(molecules per adsorption site per second) is valid. For the ideal limiting case $\Delta S^* = 0$ eq. (13) passes into the well-known Frenkel equation[31]:

$$E_{des} = RT \ln (kT/h)\tau \qquad (13a)$$

where k and h are the Boltzmann and Planck constants respectively, and τ is the half-life value of the desorption process (in seconds). In many cases the two methods for determining E_{des} are about equally accurate; but there are also systems for which the assumption $\Delta S^* = 0$ is impermissible[32].

6) The probe-hole technique mentioned under 4) makes it possible to single out from the emission beam very small regions which may correspond to an emitting area of 10×10 atoms. With such small regions, evidently, the building-up and disintegration of the adsorption layer can no longer be described as continuous processes, but represent a sequence of *discrete*

[26] *E. W. Müller*, Z. Physik. *120*, 26 (1943).
[27] *E. W. Müller*, J. appl. Physics *26*, 732 (1955).
[28] *B. G. Smirnov* and *G. N. Shuppe*, Ž. techn. Fiz. *22*, 973 (1952).
[29] *A. G. J. van Oostrom*, Thesis, Amsterdam University, 1965.
[30] *A. A. Holscher*, J. chem. Physics *41*, 579 (1964).
[31] *J. Frenkel*, Z. Physik *26*, 117 (1924).
[32] *L. A. Pétermann*, Nuovo Cimento, Suppl. *5*, 364 (1967).

single steps of individual molecules landing or jumping off. Fig. 4 shows a graph – determined with the aid of *Holscher*'s probe-hole tube – of an emission current as a function of time at a residual gas pressure of 10^{-8} torr.

Fig. 4. Emission current versus time plot of a probe-hole experiment. Object: tungsten (110) region. Gas: nitrogen (10^{-8} torr). 300 °K, 340 V, current 10^{-13} to 10^{-12} A.

It is clearly seen that every landing of a gas molecule causes a jump in the emission current. As these measurements do not obey the rules of statistics their reproducibility is necessarily limited.

7) Under 5) mention was made of the possibility of performing *kinetic measurements* with the aid of the FE micoscope. This possibility is not restricted to adsorption and desorption, but also refers to the diffusion of adsorbed atoms over the tip surface.

Gomer [20] and *Ehrlich* directed a beam of gas sideways on to a tip that was cooled to a very low temperature. The emission image clearly showed that only the side of the tip facing the gas source was covered with an adsorption layer. As soon as the temperature was raised to a level at which surface diffusion was possible the adsorbate spread over the total surface at a rate that could be observed and measured.

It appears [33, 34] that in diffusion certain paths are preferred. Extensive investigations of surface diffusion, in which the hopping energy was also determined, were reported by *Gomer* [20], *Ehrlich* [19, 33], and *Drechsler* [34–36]; the last-mentioned author also investigated the dependence of the hopping energy on the field applied.

Other kinetic investigations deal with the desorption process. They do not, however, concentrate on the determination of E_{des}, but mainly on the dependence of the rate of desorption on the degree of coverage, and, hence, on the order of the reaction.

For instance, *Ehrlich* [19, 33] finds that the desorption of β nitrogen from tungsten (see under 8)) is a second-order reaction and concludes from this that the nitrogen must be on the surface in the form of atoms, since for molecularly adsorbed nitrogen the desorption would be expected to be of the first order.

It should be pointed out, though, that an experimentally found relation between rate of desorption and degree of coverage can only be evaluated in this simple way if it is absolutely certain that the activation energy and the activation entropy of the desorption are truly constant, *i.e.* are not dependent on the degree of coverage as well. If they should be, the resulting exponential dependence of the rate on the degree of coverage obscures the actual influence of the reaction order. Unfortunately, systems in which the heat of adsorption and the activation energy and entropy of the desorption are really constant are extremely rare. To what extent these quantities may in fact depend on the degree of coverage has been illustrated very strikingly by results obtained by *Mars*, *Scholten*, and *Zwietering* [37] for the nitrogen/iron system.

8) Often the heat of adsorption varies with the degree of coverage, not continuously, but in discrete steps. This means that the same gas is present on the surface in several discrete "states". If the temperature of a metal covered with gas is uniformly increased, the simultaneous presence of different states is recognized by the fact that the desorption occurs, not uniformly, but for instance in discrete eruptions. The most weakly bonded state is, of course, desorbed at the lowest temperature. Such states can also be recorded without a FE microscope, for instance, by kinetic pressure/time measurements [38–40]. *E.g.*, the α, β, and γ states of nitrogen on tungsten have been distinguished in this way. Furthermore, all physical quantities that are measurably changed through chemisorption are suitable for characterizing the simultaneous presence of several states of adsorption. In particular, the changes in electric resistance [16], in work function of thin metal films, and in magnetization of disperse metal-on-carrier systems have proved the coexistence of several states of adsorption for various metal/gas systems [40]. Nevertheless, with all these methods the question remains whether the various states must be assigned to different crystal faces or whether they can coexist on one and the same face. In this respect the FE microscope is superior to the above-mentioned methods, because it is at once established visually to what crystal face an irregularity in one of the adsorption-dependent parameters corresponds. To anticipate the most important result: coexistence of several states on one and the same crystal face is indeed possible [42].

3. Field Ion (FI) Microscopy

As already mentioned the resolving power of the FE microscope is fundamentally limited by the fact that the electrons in the metal obey Fermi-Dirac statistics, on account of which they possess, also at low temperature, considerable kinetic energy, which is undirected in space. Improved resolving power can only be expected if the image on the fluorescent screen is produced by projectiles whose kinetic energy perpendicular to the applied field is substantially smaller than that of the metal electrons emitted. This is the case for ions generated, by field ionization, from atoms which have

[33] *G. Ehrlich*, Proc. third int. Congr. Catalysis, Amsterdam *1965*, 113.

[34] *M. Drechsler*, Z. Elektrochem., Ber. Bunsenges. physik. Chem. *58*, 334 (1954).

[35] *M. Drechsler*, Z. physik. Chem. N.F. *6*, 272 (1956).

[36] *M. Drechsler* and *R. Vanselow*, Z. Kristallogr., Kristallgeometr., Kristallphysik, Kristallchem. *107*, 161 (1956).

[37] *P. Mars*, *J. J. F. Scholten*, and *P. Zwietering*: The Mechanism of Catalysis. Elsevier, Amsterdam 1959, p. 66.

[38] *G. Ehrlich*, J. appl. Physics *32*, 4 (1961).

[39] *G. Ehrlich*, J. chem. Physics *34*, 29 (1961).

[40] *G. Ehrlich*, Trans. New York Acad. Sci. *101*, 722 (1963).

[41] *W. M. H. Sachtler* and *L. L. van Reijen*, J. Res. Inst. Catalysis, Hokkaido Univ. *10*, 87 (1962).

[42] *W. J. M. Rootsaert*, *L. L. van Reijen*, and *W. M. H. Sachtler*, J. Catalysis *1*, 416 (1962); Z. Elektrochem., Ber. Bunsenges. physik. Chem. *66*, 722 (1962).

been cooled to very low temperatures. *E. W. Müller* [18,43] succeeded in realizing this idea with the FI microscope, the principle of which is shown in Fig. 5. Outwardly, the FI microscope resembles the FE microscope. The main differences are that the field is of reversed polarity and its strength is higher by about an order of magnitude, that the tip is cooled, for instance, with liquid hydrogen, and that the tube is filled with gas, usually helium at a pressure of 10^{-3} torr.

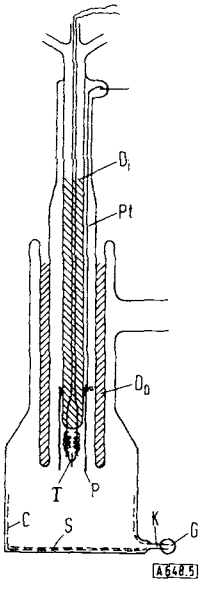

Fig. 5. Principle of the field-ion microscope.
S, fluorescent screen. C, conducting layer. D_i, inner Dewar. D_0, outer Dewar. T, tip. P, polished metal cylinder. K, kovar tube. Pt, platinum wire. G, glass pearl.

Near the surface the helium atoms are exposed to a field of such high strength that an electron can tunnel from a helium atom to a vacant energy level inside the metal. The He^+ ion thus generated is accelerated by the electrical field towards the fluorescent screen, where it produces an image point.

For an understanding of the image it is essential to know that near the surface the equipotential lines follow the atomic profile; at a greater distance the atomic roughness has been levelled out and the equipotential lines have become smooth. Consequently, the potential gradient above the atomic cores is larger than that above the interstices. At correct adjustment – the best image voltage – the ionization probability is much greater for gas atoms above the atomic cores than above the interstices. Therefore, the resulting image shows the surface atoms (as e.g. in Fig. 6). A prerequisite is, of course, that the paths of ions produced above two neighboring metal atoms do not overlap. This is realized by cooling the gas and the tip to very low temperatures.

We shall not go into details of the imaging process, because on account of the great importance of the method for metal science numerous publications have appeared on the subject. With regard to the special purpose of the study of adsorption complexes the following points are important:

[43] *E. W. Müller*, Z. Physik *131*, 136 (1951).

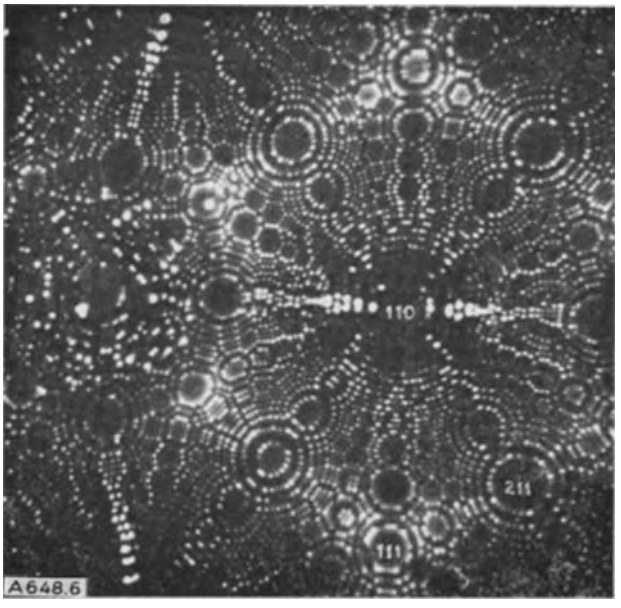

Fig. 6. Field-ion pattern of an ordered tungsten surface, field-evaporated at 20 °K and 10.5 kV.

Under normal operating conditions the adsorption process suffers from serious interference. Gas molecules with a permanent or induced dipole moment are accelerated towards the tip. The partial pressure prevailing in the vicinity of the metal tip may become so high that the tip becomes covered with layers of liquefied or crystallized gas. This fact was utilized by *Inghram* and *Gomer* [44] and by *Beckey* [45,46] to study condensed phases with the field-ion mass spectrometer.

In addition, molecules with a permanent dipole moment or with anisotropic polarizability are oriented in the field, so that dipole vector and field vector are opposed to each other.

Finally, gas molecules with a low ionization potential are already ionized – by the tunnel effect – before they reach the tip and are thus removed because ionization is at once followed by acceleration of the ion away from the tip.

All three effects are also of importance for the adsorption layer. At the voltages usually applied in the helium-filled tube to obtain good imaging of the tip, ionization is predominant in the neighborhood of the surface, since all other gases have a lower ionization potential than helium. Hence, when the field is applied only very few gas molecules are left that succeed in crossing the ionization zone and reaching the metal surface. But also particles that were adsorbed before the voltage was applied or those which are adsorbed at the back of the tip and subsequently diffuse to the image region are strongly affected by the field applied. Many of them are also ionized through the tunnel effect and torn off as ions; this process is known as *field desorption*. But also particles which, at the field strength prevailing at the surface and in the absence of

[44] *M. Inghram* and *R. Gomer*, J. chem. Physics *22*, 1279 (1954); Z. Naturforsch. *10a*, 863 (1955).

[45] *H. D. Beckey*, Z. Naturforsch. *14a*, 712 (1959).

[46] *H. D. Beckey*, Bull. Soc. chim. belges *73*, 326 (1964).

an "image gas", just escape field desorption can be torn off at imaging conditions. This phenomenon is called *promoted field desorption.* Its physical cause has not yet been satisfactorily explained. Various possibilities are being considered. For instance, it has been pointed out [47] that the electron liberated by field ionization acquires some kinetic energy on its short path from the site of ionization to the metal surface, so that the surface is in fact bombarded by electrons. Greater still is the energy of secondary electrons, which are generated when the He^+ ions hit the fluorescent screen and are then accelerated towards the tip surface. The bombardment of the tip by neutral helium atoms must also be considered [48]. As it is preferably helium atoms with a small velocity component normal to the tip surface that undergo field ionization, the non-ionized helium atoms are no longer in Maxwell-Boltzmann equilibrium, but have a higher effective gas temperature. Thus, they are potential projectiles provoking desorption. Finally, the possibility has been suggested [49] that colliding helium atoms may form short-lived complexes with the adsorbed atom species, which complexes, on account of their relatively low ionization potential, are thought to be very effectively torn off from the tip through field desorption. Which of these explanations is the nearest approach to reality will not be discussed here; suffice it to say that the *promoted field desorption* has been substantiated by reliable experiments – a point of importance for the items to be discussed in the following. In evaluating FI-microscopic images it should be borne in mind that the surface is cleaned by promoted field desorption within a time that is considerably shorter than the minimum time required for producing an image on the fluorescent screen.

For many purposes this implies an advantage. Because field desorption and promoted field desorption continually clean the surface, comparatively strongly contaminated helium can also be used without the surface being poisoned. For the investigator, however, who wishes to study the adsorption of gases on metals, it is a great drawback that the method destroys its object of investigation, *i.e.* the adsorption complex, within an extremely short period of time.

In the past few years, however, two new points of view have come to the fore, which have opened up novel perspectives for the study of adsorption problems by FI microscopy:

1) On the basis of theoretical considerations it was pointed out some considerable time ago [40,41] that an adsorption layer in which the surface atoms remain in their original places in the lattice does not necessarily represent the energetically most favorable state. When, for instance, the bond between metal and adsorbate is a strongly polar one, an energetically more favorable state might possibly be attained through the metal atoms leaving their places in the lattice, which results in another arrangement with optimum coordination of positive and negative ions.

That such rearrangements are actually possible follows from the fact that metals can corrode and from numerous results obtained at elevated temperature [50 to 53]. Whether they also occur at low temperature depends on the activation energy of the process. This energy cannot be predicted exactly, but several years ago the present author pointed out [41,53] that the activation energy should decrease with increasing degree of coverage, as adsorption of gas X_2 on metal M would be attended not only by the destruction of X–X bonds and the formation of M–X bonds, but also by a considerable degree of weakening of the M–M bonds of the surface atoms.

Rearrangements of this kind can be demonstrated with the FI microscope [54,55]. If the gas to be adsorbed reaches the metal tip while no external field is applied and the conditions required for imaging (admission of helium, cooling the tip to the temperature of liquid hydrogen, application of a field) are only applied after evacuating, the majority of the adsorbed atoms will be removed through promoted field desorption, but those metal atoms which during the action of the gas had left their places in the lattice cannot return to them, because at the temperature of liquid hydrogen they are insufficiently mobile. The field ion images of the tip before and after the contact with gas are then different. Even if the metal atoms removed from their places in the lattice are also torn off the surface by promoted field desorption, the vacant sites left by them are visible in the ion image [49,56].

If, however, rearrangement does not occur and the promoted field desorption is complete, the ion images before and after the action of the gas are the same. In this case it is essential that the tube can also be operated as an FE microscope, so that it can be judged from the emission characteristic whether adsorption has in fact occurred.

2) The removal of adsorbed particles upon adjustment of the imaging conditions need not always be complete. If the adsorption is accompanied by atom rearrangements, atoms of the adsorbate can be favorably embedded in the surface and thus escape the influence of the field and, hence, of promoted field desorption. This at once raises the question as to what is the behavior of adsorbed non-metal atoms on the surface of a metal crystal under the conditions of FI microscopy. *Ehrlich* [19,33,57] had assumed that such atoms should

[47] *G. Ehrlich* and *F. G. Hudda*, Philos. Mag. *8*, 1587 (1963).

[48] *O. Nishikawa* and *E. W. Müller*, J. appl. Physics *35*, 2806 (1964).

[49] *A. A. Holscher*, Thesis, Leiden University, 1967.

[50] *S. Z. Roginskiĭ. I. I. Tetryakov*, and *A. B. Shekter*, Doklady Akad. Nauk SSSR *91*, 881, 1167 (1953); *O. V. Krylov* and *S. Z. Roginskiĭ*, *ibid.* 1353.

[51] *J. N. Wilson, H. H. Voge, D. P. Stevenson, A. E. Smith*, and *L. T. Atkins*, J. physic. Chem. *63*, 463 (1959).

[52] *K. Tamaru*, Trans. Faraday Soc. *55*, 824 (1959).

[53] *W. M. H. Sachtler* in: Trans. third int. Vacuum Congr. 1965. Pergamon Press, Oxford 1966, Vol. 1, p. 41.

[54] *E. W. Müller* in: Structure and Properties of Thin Films. Wiley, New York-London 1959, p. 523.

[55] *S. Nakamura* and *E. W. Müller*, J. appl. Physics *36*, 3634 (1965).

[56] *A. A. Holscher* and *W. M. H. Sachtler*, Discuss. Faraday Soc. *41*, 29 (1966).

[57] *G. Ehrlich* and *F. G. Hudda*, J. chem. Physics *36*, 3233 (1962).

be visible in the ion image as additional bright dots. But *Holscher*[49] pointed out that theoretically it is more likely that metalloid atoms appear as blurred "nebulous patches" or even obscure the metal atoms immediately underneath. The predictions of theory in this respect being too vague, an important research object for FI microscopy is thus outlined. It is to be expected that clarifying the question of how non-metal atoms are imaged will, at the same time, shed a new light on the problem of the bond character in chemisorption. In particular *Holscher*'s finding[49] that chemisorbed nitrogen atoms appear in the ion image as "nebulous patches" seems to confirm the present author's opinion that the chemisorption bond is a localized one and that through chemisorption the atoms of the metal surface are deprived of their typical metal character and thus no longer contribute to the collective properties of the metallic state[41, 53].

4. Related Methods

Some attention should now be given to a few techniques related to field emission microscopy, which can also provide important information on adsorption problems. For instance, *Menzel* and *Gomer*[58] and *Ermrich*[59] used the FE microscope to study the phenomena induced by electron bombardment of the adsorption layer; these topics include the appearance of new states of adsorption and the question of the effective cross-section of adsorbed molecules. Other investigators have concentrated on field desorption, and succeeded in identifying mass-spectrometrically the atoms or atom complexes torn off by the field. In this connection special mention must be made of the work of *Inghram* and *Gomer*[44], *Schmidt*[60], and *Block*[61]. Through utilization of the time of flight principle the sensitivity of the mass-spectrometric methods has in the meantime been increased to such a degree that *Müller*[62] recently announced a single-atom mass spectrometer and reported the first results obtained with it.

Another important technique is that of field evaporation[63], as it is the only means to produce surfaces that are both chemically pure and have nearly all atoms at ideal lattice sites.

Finally, we shall briefly deal with the important role of field cathodes in investigations in which the electrons emitted are decelerated by a retarding field so that their kinetic energy can be measured. Because the electrons are emitted by the tunnel effect, they need not overcome a potential barrier and consequently have – after compensation of the accelerating voltage by a retarding field – exactly the same energy as before the emission. If the temperature of the emitter is 0 °K the highest-energy electrons have exactly the energy of the Fermi level. Such electrons are able to penetrate into the surface of a metallic collector only if its potential is higher than that of the emitter by at least φ_{coll}, *i.e.* the work function of the collector.

Two important quantities can be determined experimentally by this method. *Henderson* and *Dahlstrom*[64] had tried to measure the limiting voltage at which the field-emitted electrons just manage to enter into the collector and thus the work function of the collector, φ_{coll}. The method is independent of the work function of the emitter, but requires excellent electron optics. The latter also applies for the second quantity that can be determined by retarding field measurements, *i.e.* the energy distribution of the electrons. It is characterized by the half-width, whose dependence on the temperature, the work function of the emitter, φ_{em}, and the constant B is known (see eq. (5)). If both the half-width and the slope of the F–N line are known, two equations are available which contain the two unknown quantities B and φ_{em}, and the two parameters can therefore be calculated.

The retarding field method thus enables the absolute values of the work functions of both the emitter, φ_{em}, and the collector, φ_{coll}, to be determined. *Young* and *Müller*[65] used it in particular to measure the energy distribution of the electrons and φ_{em}. *Van Oostrom*[29] combined the retarding-field method with the probe-hole technique and thus determined the work functions of various crystal faces, φ_{hkl}. *Holscher*[66] further developed the possibilities of the retarding-field method to determine the work function – and thus also the change in work function upon gas adsorption – of a collector and used it to study thin metal films deposited by evaporation under ultra-high vacuum conditions. This method is, in several respects, superior to the conventional techniques for determining work functions and surface potentials (photoelectric emission, thermal emission, contact potentials). In particular, if a movable collector is used it is possible to scan very small areas of the collector surface with the aid of a narrow electron beam; in this way slight inhomogeneities are detected. It is even possible to measure an entire alloy system if care is taken that the concentration of one alloy component possesses a lateral gradient along the collector surface.

5. Examples

The possibilities, offered by the methods described in Sections 2–4, of studying adsorption phenomena and the results thus obtained will now be illustrated. Suitable examples are the physisorption of xenon and the chemisorption of carbon monoxide, nitrogen, and hydrogen on tungsten. The fact that tungsten is preferred in most investigations is due to this high-melting metal being particularly convenient to handle; it is easy to clean by annealing and is sufficiently hard, so that there is no risk of the tips being torn off at high field strengths. It should be stressed, however, that metals

[58] *D. Menzel* and *R. Gomer*, J. chem. Physics *41*, 2211, 3329 (1964).

[59] *W. Ermrich*, Thesis, Technische Hochschule Aachen, 1967.

[60] *W. A. Schmidt*, Thesis, Freie Universität Berlin, 1962; *R. Vanselow* and *W. A. Schmidt*, Z. Naturforsch. *22a*, 717 (1967).

[61] *J. Block*, Z. Naturforsch. *18a*, 952 (1963); Z. physik. Chem. N.F. *39*, 169 (1963).

[62] *E. W. Müller*, Paper, 14th Field Emission Sympos., Washington D.C. 1967.

[63] *D. G. Brandon*, Philos. Mag. *14*, 803 (1966).

[64] *J. E. Henderson* and *R. K. Dahlstrom*, Physic. Rev. *45*, 764A, (1934).

[65] *R. D. Young* and *E. W. Müller*, Physic. Rev. *113*, 115 (1959).

[66] *A. A. Holscher*, Surface Sci. (Amsterdam) *4*, 84 (1966).

with greater ductility, such as platinum or nickel, are also suitable; *Gomer*[67] has even studied mercury crystals in the form of whiskers grown on tungsten.

5.1. The Tungsten / Xenon System

As shown in Section 3, it is not possible, at the present state of knowledge, to study this system with the FI microscope, because the ionization potential of xenon is considerably lower than that of any gas suitable as an imaging gas. For the latter purpose the choice is limited as it is necessary that the imaging gas does not condense at the low temperature required ($\approx 20\,^{\circ}K$) and a pressure of 10^{-3} torr. The FE results of *Ehrlich* and *Hudda*[68,69] are essentially in excellent agreement with those of *Rootsaert*, *Van Reijen*, and *Sachtler*[42]. At low temperature the adsorption is definitely face-specific, contrary to the conventional opinion that physisorption is a phenomenon of low specificity for the adsorbent.

Because adsorbed xenon strongly reduces the work function of tungsten and the brightness in the FE image is consequently increased considerably the adsorption can conveniently be followed visually.

The photographs of Fig. 7 illustrate an experiment in which xenon is adsorbed, at 10^{-5} torr, on a tungsten tip which after having been annealed is cooled at 78 °K.

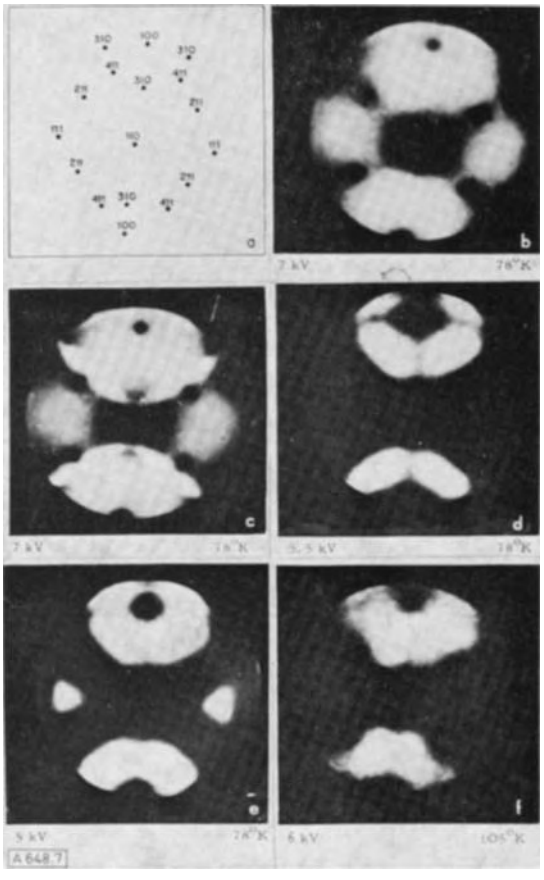

Fig. 7. Adsorption of xenon on tungsten at 78 °K.
a, positions of crystal faces. b, pure tungsten. c–e, increasing coverage with xenon. f, desorption at 105 °K.

At incipient adsorption (Fig. 7c) the areas between the dark (100) and (211) faces are occupied first – strikingly, with a sharp diffusion front, starting from the edge onwards. Visual observation, which cannot be shown photostatically, suggests similarity to a carpet being rolled out from the edges of the (211) faces. The area covered is denoted as the (411) area, after the indexing of its center; this does not mean to say, though, that this area is a smooth crystal face, but it refers to the fact that the configuration of the atoms in this area is essentially that of the (411) faces.

The physical cause underlying the phenomenon of the "unrolling carpet" is clear. The vast (111) and (211) faces serve as capturing areas for xenon. Part of the gas atoms striking these faces are reflected elastically; those that are retained are bonded loosely, so that at the prevailing temperature these atoms can move rapidly across the faces. As soon as they move over the edges into a (411) area they are at once precipitated, because there the heat of adsorption is higher and the rate of diffusion lower; that is why these areas are occupied from the edges onwards. As long as the (411) areas are still incompletely covered they act as "pumps" for xenon which is loosely adsorbed on the neighboring faces; accordingly, these faces are initially covered with xenon to only a very slight extent.

That this explanation is correct has been substantiated by *Ehrlich*'s measurements at 20 °K[19]. At this temperature adsorbed xenon can no longer move about freely; consequently the (411) areas and the (111) faces are, from the beginning, occupied at a comparable rate (the rates need not be exactly the same, because the sticking coefficients may be different), and the phenomenon of the unrolling carpet does not occur.

As soon as at 78 °K the (411) areas are completely covered with xenon they no longer act as "pumps"; the faces with the next highest heat of adsorption are then filled. Fig. 7d shows the state in which the (411) areas have just become more or less completely filled. In the mean time their emission has increased to such a degree that the acceleration voltage had to be reduced to avoid halation of the image and the other faces now appear dark. The apparent darkness is therefore only an indirect consequence of xenon adsorption. The state of coverage of the "second-best" areas ((111) faces and their immediate surroundings) is shown in Fig. 7e. Continued supply of xenon does not bring about any further change of the emission phenomena; hence, as far as can be observed visually, the areas appearing as dark patches are not covered with xenon. Unfortunately, no probe-hole measurements have yet been made, this being the only way to decide whether the F–N parameters of the apparently bare areas are really identical with those of the same areas before admission of xenon. From the F–N line for the total emission it appears that xenon adsorption causes the average work function of tungsten to be lowered by 1.4 eV.

When the tip temperature is increased to 105 °K the (111) faces are rapidly, the (411) areas more slowly freed from xenon. The rates and eq. (13a) and (11) afford a heat of adsorption of 7.5 kcal/gat (8–9 kcal/gat[68]) for the (411) areas and of 5 kcal/gat (5 kcal/gat[68]) for the (111) faces.

The absolute value of the surface potential and the face specificity of the heat of adsorption are particularly interesting on account of their generalizability. That adsorbed xenon reduces the work function of tungsten had already been demonstrated experimentally by *Mignolet*[70] by contact potential measurements. This finding is in agreement with the view that the sign of the surface potential ($-\Delta\varphi$) must be identical with that of the difference ($\varphi-\psi$), with φ standing for the work function of the adsorbing metal and ψ for

[67] *R. Gomer*, J. chem. Physics *28*, 457 (1958).
[68] *G. Ehrlich* and *F. G. Hudda*, J. chem. Physics *30*, 493 (1959).
[69] *G. Ehrlich*, Brit. J. appl. Physics *15*, 349 (1964).
[70] *J. C. P. Mignolet*, Recueil Trav. chim. Pays-Bas *74*, 685 (1955).

the Mulliken electronegativity of the gas adsorbed[71,72]. It was not known, however, whether the FE microscope would give the same value as the other methods, for it was feared that the electric field applied would polarize the adsorbed atoms and that an induced dipole moment would thus be imposed upon the natural dipole moment of the adsorption bond. Since in the FE microscope the tip is negative and the screen positive, the induced dipole moment would have to have its negative pole directed outwards away from the metal. Since the adsorption dipole of the W–Xe bond is in a direction opposite to that of the induced dipole, it would be expected that the FE microscope would measure a lower surface potential than *e.g.* the contact potential method used by *Mignolet*[70]. The results show that this is not so; the FE value of 1.4 eV is even slightly higher than the value of 1.14 eV found by *Mignolet*. The difference can be explained by the different averaging methods. Hence, it would seem that the natural bond dipole of the adsorption bond is only slightly affected by the field of 0.4 V/Å. This conclusion is very important with regard to the suitability of FE microscopy for the study of adsorption complexes.

The heats of adsorption measured reveal that in thermodynamic equilibrium at 78 °K and at a low degree of coverage (so that the Xe atoms can freely choose their places) the ratio of the degrees of coverage of the two faces under consideration should be θ_{411}: $\theta_{111} = 10^7$:1, which is in agreement with the observation that the (111) faces remain practically empty until the (411) areas are filled. The face specificity of the heat of adsorption is apparently *not* due to the differences in local work function. On the contrary, since the electrons of the adsorbed xenon are polarized towards the metal it might have been expected that adsorption would be energetically most favorable in the areas of the highest work function, which is not confirmed by the experiments; the work function is highest for the (110) faces.

The preference for the (411) areas, on the other hand, is easy to understand upon considering the geometry of the adsorption centres. In the (411) areas atomic configurations of the type shown in Fig. 8 are predominant. They contain "troughs" in which a xenon atom fits exactly; a xenon atom in such a trough is in contact with six tungsten atoms at a time. No other crystal face of tungsten shows adsorption centers with so high a coordination number. Hence, the results support the hypothesis that for physisorption the strength of the adsorption bond largely depends on the number of nearest neighbors with which the adsorbed atom at an adsorption site is in contact. This principle even allows a quantitative prediction to be made regarding the heat of adsorption of xenon to be expected on other crystal faces, which is experimentally confirmed for the (111) faces – the only ones for which measured values are available.

[71] *W. M. H. Sachtler* and *G. J. H. Dorgelo*, J. Chim. physique Physico-Chim. biol. *54*, 27 (1957).

[72] *J. J. Broeder, L. L. van Reijen, W. M. H. Sachtler*, and *G. C. A. Schuit*, Z. Elektrochem., Ber. Bunsenges. physik. Chem. *60*, 838 (1956).

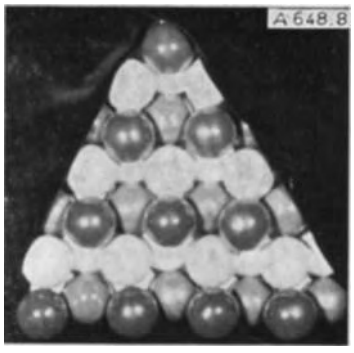

Fig. 8. Geometry of the (411) areas of tungsten.

As is known, physisorption is often used to determine the surface area of solid bodies. It is then important to know the area required per atom adsorbed. In the literature there are serious discrepancies on this point. For instance, for krypton values from 14.6 to 21 Å^2/atom are given[73]. These discrepancies become less surprising if they are considered in the light of the results discussed in this section, for these results suggest that the apparent area requirement per Xe atom is determined by the arrangement of the adsorption centers and, hence, may be different both for different crystal faces and for different metals. In this connection mention should be made of results obtained by *Ricca*[74].

5.2. The Tungsten/Carbon Monoxide System

There are few systems which have been examined as extensively as the W/CO system and for which the interpretations of almost equal experimental results are so widely divergent[19,33,49,56,57,75–83]. The consensus of opinion is that at temperatures up to a few hundred degrees Centigrade no appreciable dissociation of the CO molecule occurs and that at low temperature at least three types of chemisorbed carbon monoxide can be distinguished, to which at higher pressure and very low temperature physisorption must be added. These types can be distinguished by the desorption kinetics as well as by the parameters $\Delta\varphi$ and $\Delta \log A$.

Furthermore, it is commonly agreed that at least some parts of the adsorption process have an appreciable activation energy.

[73] *Z. Knor* and *V. Ponec*, Collect. czechoslov. chem. Commun. *26*, 961 (1961).

[74] *F. Ricca* and *A. Bellardo*, Z. physik. Chem. N.F. *52*, 318 (1967).

[75] *R. Gomer*, J. chem. Physics *28*, 168 (1958).

[76] *L. Swanson* and *R. Gomer*, J. chem. Physics *39*, 2813 (1964).

[77] *R. Gomer*, Discuss. Faraday Soc. *41*, 14 (1966).

[78] *A. A. Bell* and *R. Gomer*, J. chem. Physics *44*, 1065 (1966).

[79] *J. W. May* and *L. H. Germer*, J. chem. Physics *44*, 2895 (1966).

[80] *B. J. Hopkins* and *S. Usami*, Nuovo Cimento, Suppl. *5*, 535 (1967).

[81] *T. E. Madey* and *J. T. Yates jr.*, Nuovo Cimento, Suppl. *5*, 535 (1967).

[82] *J. Anderson* and *P. J. Estrup*, J. chem. Physics *46*, 563, 567 (1967).

[83] *G. Ehrlich*, Discuss. Faraday Soc. *41*, 7 (1966).

The state created upon adsorption of CO, at 77 °K, by clean tungsten is clearly distinct from the one resulting on a tip covered with CO at 300 °K and subsequently cooled to 77 °K. On the other hand, the state observed at 300 °K is independent of the route, *i.e.* independent of whether the adsorption is effected at 77 °K and the temperature is subsequently raised to 300 °K or whether the virgin tip is covered with CO at 300 °K (cf. Fig. 9).

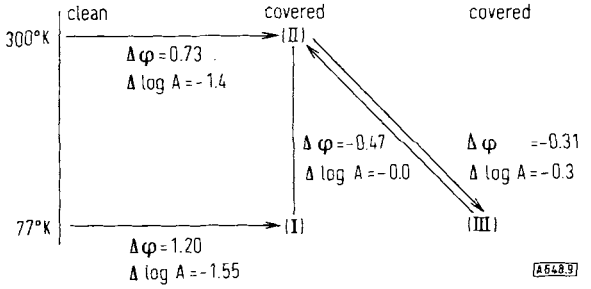

Fig. 9. FE results for the W/CO system [56].
$\varphi_0 = 4.50$ eV; $\log A_0 = -5.5$.

Significant differences of opinion, however, appear in the interpretation of the FI images. In *Ehrlich*'s opinion, all tungsten atoms remain in their places during chemisorption, and he postulates that chemisorbed CO molecules which escape promoted field desorption show up in the FI image as bright dots. *Holscher* and *Sachtler*, on the contrary, advance arguments according to which:

1) the great majority of molecules adsorbed on an undisturbed surface are removed by promoted field desorption and thus do not appear in the FI image;

2) chemisorption of CO, particularly at high coverage and elevated temperature, leads to rearrangement of the W atoms;

3) those CO molecules which manage to escape promoted field desorption (hence, in particular those which, after rearrangement, are embedded in the surface) do not produce bright dots in the FI image, but, on the contrary, reduce the ionization probability for impinging helium atoms and thus lower the image contrast.

To prove the first allegation there is the observation [49, 56] that at a low degree of coverage and low temperature the FI image cannot be distinguished from that of the clean tungsten, although the F–N parameters for this state, which were measured immediately before the image was taken, show unambiguously that the surface was covered with appreciable quantities of carbon monoxide before application of the imaging voltage. Since, however, the heat of adsorption decreases with increasing degree of coverage, it cannot be understood why at a low degree of coverage the strongly bonded CO molecules should be removed quantitatively by promoted field desorption, and at a high degree of coverage, under the same conditions, the much more weakly bonded CO molecules should not be torn off.

If the first allegation is correct the second can hardly be evaded, as the considerable disturbance of the FI image after CO adsorption – particularly at a high degree of coverage or with adsorption at room temperature – must be due to a physical cause (cf. Fig. 10a and b).

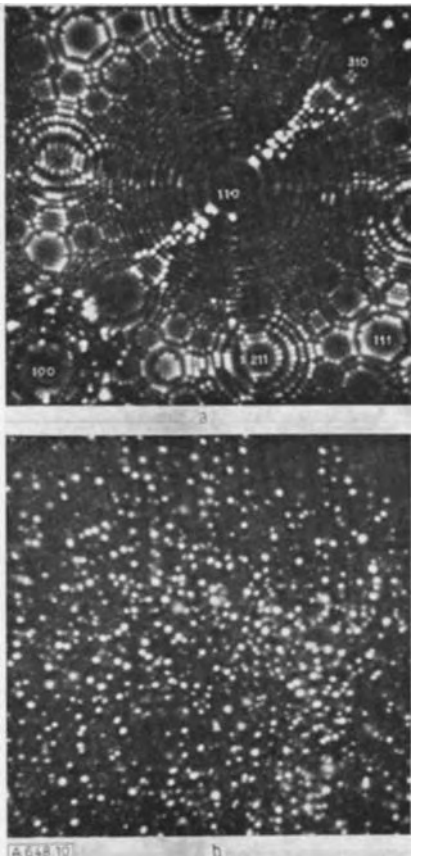

Fig. 10. Comparison of FI images of tungsten (a) before and (b) after chemisorption of CO at 300 °K. Images at 77 °K and at 8.05 and 9.6 kV, respectively.

An independent argument for the second allegation is the increase of the disturbance observed in the FI image with increasing degree of coverage and rising temperature. It is precisely what is to be expected for a rearrangement process, whose activation energy must, of course, be positive and decrease with increasing degree of coverage, if it is true that the metal-metal bonds inside the surface are progressively weakened as the adsorption proceeds. If, on the other hand, adsorbed molecules were directly responsible for the additional dots of light it would rather be expected that the number of these dots would decrease with rising temperature.

A further proof of the second allegation is supplied by an experiment in which after chemisorption the metal atoms of the surface are carefully removed by field evaporation. If it is true that metal atoms leave their places in the surface during chemisorption they should leave behind as many vacancies. At not too low temperatures these vacancies will move into the interior of the crystal through an atom located at some depth hopping into the free place. Accordingly, chemisorption would inject vacancies into the crystal. If afterwards the surface atoms are removed by field evaporation and layer after layer is thus carefully "peeled off" until an undisturbed surface is again exposed, the number of lattice planes indirectly disturbed by chemisorption can be counted.

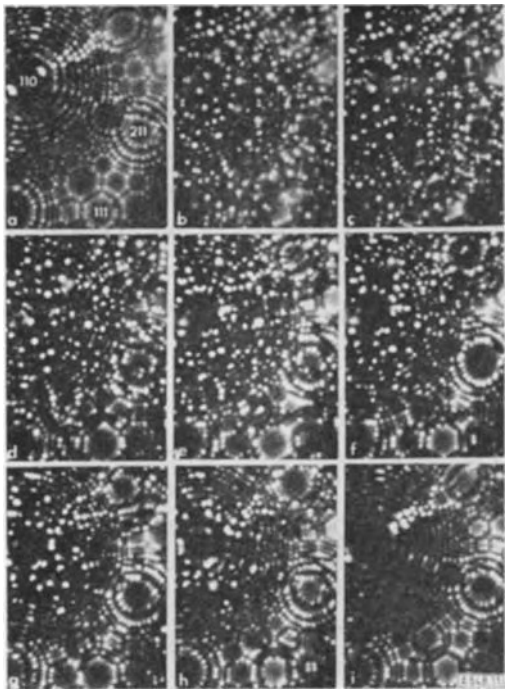

Fig. 11. Field desorption and field evaporation of surface layers after chemisorption of CO on tungsten at 300 °K.

The first picture of Fig. 11 shows the original tungsten surface, the second the state immediately after chemisorption. Subsequently, the field strength was increased stepwise (the photographs were taken at equal field strength, however). Accurate analysis reveals that four layers of tungsten had to be "peeled off" to uncover another undisturbed surface (see last picture). Hence, the lattice disturbances injected by chemisorption had, at 300 °K, migrated into the crystal to a depth of four layers.

We shall not go further into the third allegation – that chemisorbed molecules produce, not bright dots, but perhaps diffuse patches – because an extensive account of the subject will appear elsewhere [84]. Suffice it to say that this allegation follows from theoretical considerations and was confirmed experimentally in particular for the W/N_2 system; for this system diffuse "nebulous patches" were demonstrated that could be removed through field desorption.

If all the phenomena observed on the W/CO system are taken together, this leads to a new, logical, classification of chemisorption phenomena superseding the classification by state (with the Greek alphabet as labeling parameter). For chemisorption we distinguish:

a) Adsorption on an undisturbed crystal surface (*chemi-adsorption*);

b) A rearrangement of atoms, following a) and creating a highly stable state of favorable mutual coordination. On account of its fundamental similarity to corrosion this process is called *surface corrosion or corrosive chemisorption* [41].

c) As in the course of process b) metal atoms or ions which were first covered during a) once more reach the surface, adsorption occurs again. The energetic incentive for this is the same as in adsorption on the cations in the surface of an oxide or chloride, in particular the tendency of these ions to surround themselves by an optimum number of ligands. Thus, this adsorption is called *ligand adsorption.*

An important point is that the transition (a) → (b) may occur before (a) has reached the state of complete coverage. As the activation energy for this transition has different values on different crystal faces, atomic reconstruction of different crystal faces does not, in general, take place simultaneously. The dipole moment projected on the normal to the surface is larger for (a) than for (b), because in (b) the dipoles are no longer perpendicular to the surface but possess a considerable tangential component. Indeed it was established experimentally that the work function decreases during the transition (a) → (b).

In the W/CO system the stable final state of surface corrosion (b) corresponds to the β state of the nomenclature used earlier. At 77 °K state (a) and physisorbed carbon monoxide predominate on the surface; at a high degree of coverage state (b) can just be detected. At 300 °K, on the other hand, states (b) and (c) are predominant.

5.3. The Tungsten/Nitrogen and Tungsten/Hydrogen Systems

The chemisorption of nitrogen on tungsten was investigated in several ways [19,29,30,33,49,57,66,83–86]. As with the W/CO systems, the FI images obtained after chemisorption at room temperature show very little order; the disturbance at 77 °K is even more pronounced than with CO and seems to depend, not only on the degree of coverage, but also on the rate at which the nitrogen was transferred to the tungsten surface. And once again the results that were practically equal are interpreted in different ways by two authors. *Ehrlich* [57] assumes that the chemisorbed nitrogen atoms themselves appear in the image as bright dots; *Holscher* [49], on the contrary, believes that it can be shown that these dots are produced by tungsten atoms after rearrangement, the argumentation being similar to that used for the W/CO system. Again, the stable state, which in *Holscher*'s opinion is created by surface corrosion, corresponds to the β state of the earlier terminology.

The impression may be that surface corrosion occurs with the chemisorption of any gas by any metal at room temperature. But this is not justified, as is illustrated by the tungsten/hydrogen system. In this system chemisorption does not bring about any changes in the image [49]. This refutes the suspicion that the effects found for nitrogen and carbon monoxide may not be brought about by chemisorption at all, but rather by some peculiarity of FI microscopy. Strictly speaking, the very fact that in the W/H_2 system any rearrangement fails to come about is an important argument in favor of the assumption that the chemisorption of N_2 or CO is accompanied by

[84] *A. A. Holscher* and *W. M. H. Sachtler*, Proc. Battelle Meeting 1968, in press.

[85] *T. A. Delchar* and *G. Ehrlich*, J. chem. Physics *42*, 2686 (1965).

[86] *T. Oguri*, J. physic. Soc. Japan *18*, 1280 (1963); *ibid. 19*, 83 (1964).

surface corrosion. For, while tungsten is capable of forming a stable nitride with nitrogen and a stable hexacarbonyl with carbon monoxide, a tungsten hydride does not seem to be stable. From this point of view the absence of corrosion phenomena can be understood. For chromium, which is homologous to tungsten and of which a hydride of low stability – Cr_7H_2 – is known, the remarkable fact has been established that the hydride formation is not attended by a real rearrangement of the metal atoms; the chromium lattice is only slightly expanded – just as in the case of hydrogen adsorption by palladium the lattice is not broken down but only widened. Indeed, according to *Pauling*, the stability of these hydrides is largely due to the metal-metal bonds. Hence, on the basis of the same chemical arguments that lead us to expect a rearrangement of the tungsten atoms for the W/N_2 and W/CO systems a similar rearrangement is excluded for the W/H_2 system. Thus, the experimental findings confirm the expectation also for this system.

The W/H_2 and W/N_2 systems were investigated with the aid of FE microscopy [29,30,42,86–89]. Only for the W/N_2 system have probe-hole measurements been performed, and these produced a result which was at first amazing: nitrogen chemisorption causes the work function of the tungsten on many crystal faces to be increased, on others to be lowered. *Oguri* [86] as well as *Holscher* [30,49], *Van Oostrom* [29], and *Delchar* and *Ehrlich* [85] arrived at this experimental result. Although the $\Delta\varphi_{hkl}$ values reported by the various authors differ, the difference in sign on different crystal faces is no longer a point of discussion.

The interpretation of this finding is still a speculative one. In general it is assumed that it is not the elementary bond dipole proper, but the orientation of the dipoles with respect to the surface normal that is different. According to whether the nitrogen is above or below the surface the component of this vector in the direction of the surface normal has a different sign.

This opinion is shared also by *Ehrlich* [85], who rejects the rearrangement of atoms. He assumes that nitrogen atoms on the rough metal surfaces can penetrate into the "electron gas" without being sterically hindered by the tungsten atoms, which remain in their places. To reconcile this assumption with the results *Delchar* and *Ehrlich* have to invoke a number of postulates; for instance, the (100) face is to be considered a smooth one, the (211) face a rough one; moreover, the nitrogen atom must be the positive, the tungsten atom the negative pole of the elementary bond dipole, although on the basis of electronegativities the opposite would be expected. Besides, this picture would lead to serious difficulties if it were applied, for instance, to the adsorption of hydrogen on tungsten or other metals.

The experimental results can, in our opinion, be interpreted in a more convincing manner if the possibility of surface corrosion is taken into account. That this corrosion may lead to the normal component of the dipole moment vector being reduced has already been established for the W/CO system. It is not difficult to imagine for N_2 – whose chemisorption, unlike that of CO, is dissociative – that during surface corrosion nitrogen atoms will even occupy places beneath the tungsten atoms. As already mentioned, the activation energy for these rearrangements must be face-specific. If the simplest assumption is made, viz. that the rearrangements will occur soonest on those crystal faces where each tungsten atom has the smallest number of nearest (tungsten) neighbors, it can be understood that it is the (100) faces and the (611) areas where the W–N bond dipoles are first seen "from behind". These bond dipoles are polarized as $W^{\oplus}-N^{\ominus}$, in accordance with the electronegativity rule discussed in Section 5.1 [71,72]: $(-\Delta\varphi) \approx (\varphi-\psi)$.

6. Concluding Remarks

Investigations with the aid of the FE and the FI microscope have provided fundamental contributions to the understanding of adsorption and heterogeneous catalysis. After many years of qualitative speculation, concepts like face specificity, adsorption states, and atom rearrangements have become accessible to exact measurements. Considering that the available experimental material mainly refers to a single metal and a small number of inorganic adsorbates it is not difficult to predict that further research on these problems will provide a wealth of valuable information.

Experimental difficulties are dwindling. During the past decade the ultra-high vacuum technique has developed into a standard method for the study of chemisorption on metals. Direct-current sources of sufficient stability as well as image intensifiers – the latter as a by-product of space research – are now commercially available. Liquid hydrogen is available in many places, as it is also required for other research purposes. (For that matter, all results discussed in the present article have been obtained *without* an image intensifier, and FI images of only slightly reduced quality can also be produced at the temperature of solid nitrogen.)

The further development of this field of research is retarded by theoretical rather than by experimental problems. This can be illustrated, for instance, by the fact that studies on the same adsorption system by different investigators lead to practically the same experimental results, which are often interpreted in widely different ways. Considering the poor theoretical basis underlying these interpretations this is not surprising. Therefore, a survey of the application of FE and FI microscopy to research on chemisorption by metals can hardly end otherwise than by making an appeal to theoretical physics. Even the theory of the electron work functions is highly unsatisfactory and far from capable of making quantitative statements. For the work functions of alloys both theoretical starting points and experimental data are lacking [111].

[87] *T. W. Hickmott*, J. chem. Physics *32*, 810 (1960).
[88] *R. Gomer* and *R. Wortman*, J. chem. Physics *23*, 1741 (1955).
[89] *R. Wortmann*, *R. Gomer*, and *R. Lundry*, J. chem. Physics *24*, 161 (1956).

Far more serious for FE microscopy is the fact that the work function is a quantity which can only be defined macroscopically and which, like the surface potential and the Helmholtz equation, loses its meaning if – as is done with the probe-hole technique – the adsorption of a single atom on a minute face element consisting of only a few atoms is considered. It is also doubtful whether the theory of the metallic state can be applied to surfaces largely covered with a metalloid adsorbate. As is known, there is much to be said for the supposition that the surface atoms are demetallized through adsorption [41, 53, 49, 90].

For FI microscopy, in which the individual surface atom plays an even more predominant role than in FE microscopy, the question is raised as to whether the band model of the metallic state may still be applied. What is certain is that the Sommerfeld approximation of the quasi-free electron is an unsuitable starting point, as in this simplest model the parameters of the atoms are amalgamated to those of the band, whereas FI microscopy, conversely, resolves the metal continuum into discrete atoms. A description in terms of the band model, therefore, is acceptable only if it is based on approximations in which the atom cores embedded in the "electron gas" are explicitly considered.

[90] *K. D. Rendulic* and *Z. Knor*, Surface Sci. (Amsterdam) 7, 205 (1967).

It should be borne in mind that all theories of the metallic state have primarily been designed for the interior of the three-dimensional metal. *Dowden* [91] and *Bond* [92] are of the opinion that extrapolation to the metal surface is most promising if it is based on approximations taking into account the spatial orientation of the metal bonds. From this point of view, the models formulated by *Goodenough* [93] and *Trost* [94], in which the spatial orientation of the bonds in the metal is regarded as a consequence of the crystal field, are of particular interest.

As long as no molecular orbital theory of the metal surface or even a theory of the surface demetallized through chemisorption is available, the physicochemist must, of necessity, continue to use the rather crude theoretical tools with which FI microscopy has reached its present, impressive, degree of development.

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German version: Angew. Chem. *80*, 673 (1968)

[91] *D. A. Dowden* in: Coloquio sobre Quimica Fisica de Procesos en Superficies Solidas. Libreria Cientifica Medinaceli, Madrid 1965, p. 177.

[92] *G. C. Bond*, Discuss. Faraday Soc. *41*, 200 (1966).

[93] *J. B. Goodenough*: Magnetism and the Chemical Bond. Interscience, New York 1963.

[94] *W. R. Trost*, Canad. J. Chem. *37*, 460 (1959).

On the Chemistry of Clay[**]

BY U. HOFMANN[*]

Kaolinite, illite, chlorite, montmorillonite, and vermiculite are among the most important of the clay minerals. Cations are embedded between the silicate layers and on the basal faces of the crystals. Whereas only the cations on the outer faces are exchangeable in the first three of the above minerals, those between the layers can also be replaced by others in montmorillonite and vermiculite. These characteristics and the ability of montmorillonite and vermiculite to undergo intracrystalline swelling and to form inclusion compounds are responsible for the industrial importance of kaolin and clay. The structure of halloysite is particularly interesting, since the silicate layers in this case are rolled up to form tubes. The possible role of the clay minerals as catalysts in the formation of petroleum and in the beginning of life is finally discussed.

1. Form and Crystal Structure of Some Clay Minerals

Only 40 years ago, practically nothing was known about the clay minerals. The reasons for this are that their crystals are so small that they cannot be observed under the optical microscope and that a clay or kaolin is generally a mixture of several minerals. The discovery of the clay minerals was only made possible by X-ray interferences, and the electron microscope soon afterward made it possible to observe their crystals. The clay minerals are very numerous, but we shall deal here only with a few of the important ones.

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[**] Based on a plenary lecture to the General Meeting of the Gesellschaft Deutscher Chemiker in Berlin, September 1967.

1.1. Electron Micrographs

The electron micrograph of a well formed kaolinite, which is the principal clay mineral in kaolins, is shown

in Figure 1. The crystal platelets, which are often hexagonal, have a diameter of about 5000 Å and a thickness of about 500 Å.

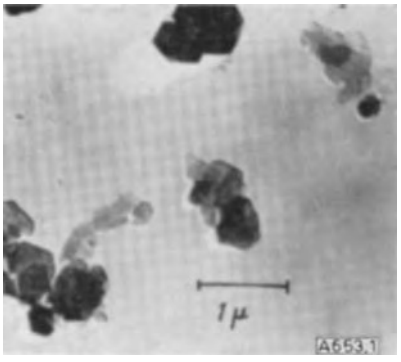

Fig. 1. Electron micrograph of a kaolinite, shadowed with chromium at an angle of 20°.

Figure 2 shows the electron micrograph of a kaolinitic clay, which is characterized, above all, by the presence of very small and very thin crystal platelets that are mostly no longer hexagonal. Their average diameter is 1200 Å and their average thickness 250 Å.

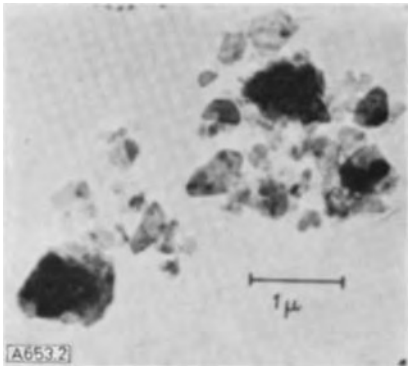

Fig. 2. Electron micrograph of a kaolinitic clay.

Figure 3 shows the electron micrograph of a micaceous clay mineral often known as illite. This mineral rarely occurs in high concentrations, but is often present in clays and sometimes in kaolins, and is particularly frequently the clay mineral present in arable soil. The crystals are irregularly shaped, and are often very small and very thin.

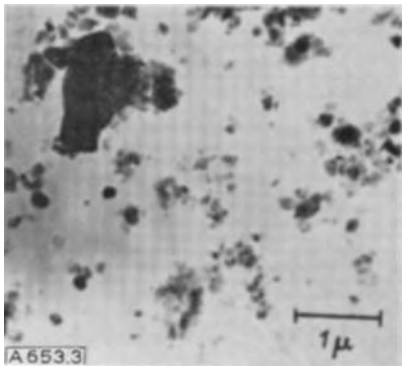

Fig. 3. Electron micrograph of an illite.

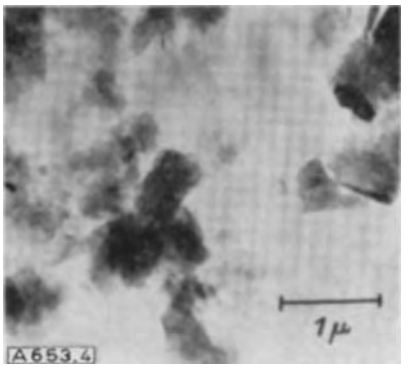

Fig. 4. Electron micrograph of a chlorite.

Figure 4 shows the electron micrograph of a chlorite, which occurs in high concentrations *e.g.* in shales. Chlorite also occurs as the clay mineral in arable soils. The crystals are generally thin lamellae whose diameters are not very small, and which have an irregular outline.

1.2. Crystal Structures

The crystals of the clay minerals mentioned above are platelets and, accordingly, have a layer structure. Figure 5 shows the crystal structure of kaolinite. The structure of the silicate layer was predicted by *Pauling* [1] as early as 1930; a (lower) tetrahedral layer of Si and O is condensed with an (upper) octahedral layer of Al and OH, thus giving the formula $Al_2(OH)_4[Si_2O_5]$. *Hendricks* [2] and *Brindley* [3] established the sequence of the stacked silicate layers, and suggested that the octahedral layer is bound to the tetrahedral layer above by hydrogen bonds to the O atoms.

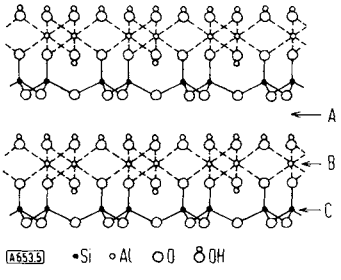

Fig. 5. Crystal structure of kaolinite. A: hydrogen bonds, B: octahedral layer; C: tetrahedral layer. b = 8.93 Å, distance between layers = 7.15 Å.

In fine-particle clay, the silicate layers of the kaolinite exhibit a parallel displacement in relation to one another. The clay is then known as the "fireclay type" [4]. This lattice disturbance is also observed, though to a smaller extent, in kaolins. It is intensified in particular by dry grinding.

[1] *L. Pauling*, Proc. nat. Acad. Sci. U.S.A. *16*, 578 (1930).

[2] *S. B. Hendricks*, Z. Kristallogr., Mineralog. Petrogr., Abt. A *95*, 247 (1936).

[3] *G.W. Brindley* and *K. Robinson*, Mineralog.Mag.J.mineralog. Soc. *27*, 242 (1946); *R. E. Newnham* and *G.W. Brindley*, Acta crystallogr. *9*, 759 (1956); *10*, 88 (1957); *G.W. Brindley* and *M. Nakahira*, Mineralog. Mag. J. mineralog. Soc. *31*, 781 (1958).

[4] *G.W. Brindley* and *K. Robinson*, Trans. Faraday Soc. *42 B*, 198 (1946); Trans. Brit. ceram. Soc. *46*, 49 (1947); *U. Hofmann*, Silikattechnik *8*, 224 (1957).

The micaceous clay mineral illite was extensively studied in 1937 by *Hofmann* and *Maegdefrau*[5] and by *Grim*[6]. Its structure can be derived from that of coarsely crystalline mica[7,8]; the silicate sheet consists of two tetrahedral layers with the vertices of the tetrahedral pointing inward, these two layers being joined by an octahedral layer (Figure 6). Some of the Si atoms in the tetrahedral layers are replaced by Al atoms, thus giving the silicate sheet a negative charge, which is neutralized by potassium ions situated between the sheets. Al in the octahedral layer may also be replaced by Mg, Fe^{II}, Fe^{III}, *etc.*

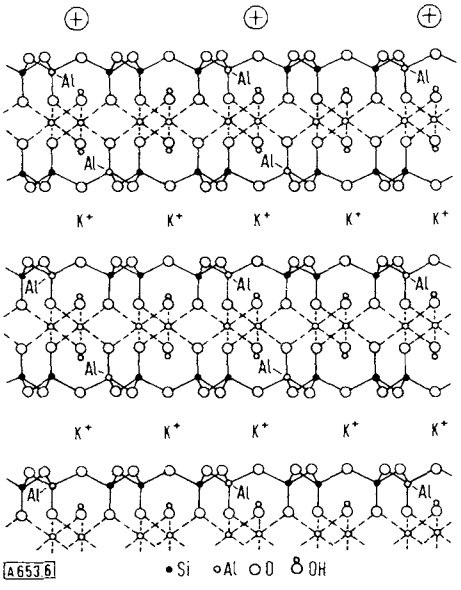

Fig. 6. Crystal structure and cation exchange of mica. Top: a free basal surface with exchangeable cations (⊕); the K ions of the two inner layers are not exchangeable.

Illite is much more finely crystalline than the coarse mica (cf. Fig. 3). It generally has a lower content of potassium ions, as well as distortion of the lattice by parallel displacement of the silicate sheets, so that it can often be indexed as orthorhombic[5]. If the octahedral layer contains mainly trivalent ions such as Al^{3+}, the mineral is described as "dioctahedral", while if this layer contains mainly bivalent ions such as Mg^{2+}, the mineral is "trioctahedral".

Chlorite consists of an alternation of micaceous silicate sheets with magnesium hydroxide or aluminum hydroxide sheets[1,9]. As in illite, the chemical composition may be varied by the replacement of Si by Al and of Mg by Al, Fe^{II}, Fe^{III}, *etc.* The micaceous silicate sheets and the hydroxide sheets are probably oppositely charged and held together in this way. Hydrogen bonds from the hydroxide sheets to the O atoms of the tetrahedral layers may also contribute to the bonding between the layers. Most chlorites are close to the trioctahedral type, though dioctahedral types also occur.

The crystal structure of montmorillonite[10] is shown in Figure 7; the structure of the silicate layers is the same as in mica sheets. An interesting characteristic of montmorillonite is its ability to absorb water (according to the water vapor pressure) between the silicate sheets, with simultaneous unidirectional intracrystalline swelling, perpendicular to the sheets. This intramolecular swelling also occurs with other polar liquids.

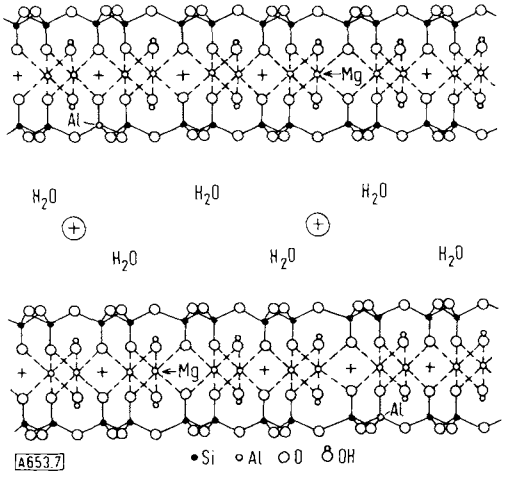

Fig. 7. Crystal structure and intracrystalline swelling of montmorillonite. ⊕ = exchangeable cations; *b* approx. 9 Å; distance between layers approx. 10—20 Å (15.5 Å).

Montmorillonite is occasionally found in clays and kaolins. Clays having high montmorillonite contents are called bentonites. The cations in the tetrahedral and octahedral layers may be replaced in the same way as in micas. Montmorillonite with a high iron content is known as nontronite, whereas the trioctahedral form with a high magnesium content is called saponite or hectorite[11]. As a result of intracrystalline swelling, the silicate sheets lose their orientation with respect to one another, and one then obtains only the interferences of the distance between sheets (001) and the cross-lattice interferences (*hk*) of the individual silicate sheets.

Vermiculite corresponds to a trioctahedral montmorillonite, though its crystals are much larger, occasionally having diameters of up to many cm, and the crystal lattice is more regular. Vermiculite containing no iron is called batavite[12].

Illites having high iron contents are green, and are known as glauconite or seladonite; they are the pigment of veronese green. The Mössbauer spectrum of a glauconite containing 15 % of iron calculated as Fe_2O_3 and 1 % as FeO[13] showed only the γ absorption of Fe^{III} in the octahedral arrangement, and, in agreement with the chemical analysis, no Fe^{II}. Fe^{III} in the octahedral layer possibly colors the mineral green. The same is true of green nontronite, chlorite, and many others.

[5] *E. Maegdefrau* and *U. Hofmann*, Z. Kristallogr., Mineralog. Petrogr., Abt. A *98*, 31 (1937); *E. Maegdefrau*, Sprechsaal Keram., Glas, Email *74*, 369 (1941).

[6] *R. E. Grim*, *R. H. Bray*, and *W. F. Bradley*, Amer. Mineralogist *22*, 813 (1937).

[7] *L. Pauling*, Proc. nat. Acad. Sci. USA *16*, 123 (1930).

[8] *W. W. Jackson* and *J. West*, Z. Kristallogr., Mineralog. Petrogr., Sect. A *76*, 211 (1930); *87*, 160 (1933).

[9] *K. Robinson* and *G. Brindley*, Proc. Leeds philos. lit. Soc., sci. Sect. *5*, 102 (1948); *G. W. Brindley*, *B. M. Oughton*, and *K. Robinson*, Acta crystallogr. *3*, 408 (1950).

[10] *U. Hofmann*, *K. Endell*, and *D. Wilm*, Z. Kristallogr., Mineralog. Petrogr., Sect. A *86*, 340 (1933).

[11] *H. Strese* and *U. Hofmann*, Z. anorg. allg. Chem. *247*, 65 (1941).

[12] *Armin Weiss* and *U. Hofmann*, Z. Naturforsch. *6b*, 405 (1951).

[13] *U. Hofmann*, *E. Fluck*, and *P. Kuhn*, Angew. Chem. *79*, 581 (1967); Angew. Chem. internat. Edit. *6*, 561 (1967).

Table 1. Formulas of some clay minerals.

Mineral	Formula
Kaolinite	$Al_2(OH)_4[Si_2O_5]$
Illite (micaceous clay)	$\approx K^+_{\sim 0.7}\{(Al_2, Mg_3, Fe^{III}_2, Fe^{II}_3)(OH)_2[Si_{3.3}Al_{0.7}O_{10}]\}^{0.7-}$
Montmorillonite	$\approx \{(Al_2, Mg_3, Fe^{III}_2, Fe^{II}_3)(OH)_2[Si_{3.6}Al_{0.4}O_{10}]\}^{0.4-} + 0.4\ M^+$
Vermiculite	$\approx \{(Mg_3, Al_2, Fe^{II}_3, Fe^{III}_2)(OH)_2[Si_{3.35}Al_{0.65}O_{10}]\}^{0.65-} + 0.65\ M^+$
	octahedral layer tetrahedral layer

The structure of halloysite is discussed in Section 1.4. The formulas of the clay minerals are summarized in Table 1.

1.3. Exchangeable Cations

All clay minerals contain exchangeable cations. *Weiss* [14] found that in very finely cleaved micas and in illite, only the potassium ions on the free basal planes are exchangeable. Within the limits of accuracy, the quantity of exchangeable cations agrees quantitatively with the quantity of potassium ions between two silicate sheets in the interior of the crystal. These potassium ions cannot be exchanged. Cation exchange at the edges of the silicate sheets is normally improbable, and may be disregarded (cf. Fig. 6).

The exchangeable cations in nature are mostly calcium and magnesium ions (action of hard water).

The chemical analysis of kaolinite agrees to within the limits of accuracy with the formula, and no substitution of ions that might lead to a negative charge on the crystals has been detected. *Weiss* [15] was able to dissolve kaolinite crystals from the basal surface (octahedral layer) with ammonium fluoride solution. The cation-exchange capacity, based on the original quantity of kaolinite, remained unchanged. It therefore appears that exchangeable cations are practically confined to the basal surface, where the tetrahedral layer is exposed. It is possible that only this one outermost silicate layer carries a negative charge as a result of substitution of its ions.

Weiss [16] has drawn up a table of minerals that in principle contain the same silicate layers. The series extends from pyrophyllite and talc, with the formulas $Al_2(OH)_2Si_4O_{10}$ and $Mg_3(OH)_2Si_4O_{10}$ respectively, in which there are no cations between the silicate layers, to the micas. An extract from this table is shown in Table 2.

Intracrystalline swelling is observed in clay minerals having a medium cation density between the silicate layers. It is caused by the hydration of these cations, which draw the water in between the silicate sheets. If there are no cations between the silicate sheets, the mineral cannot swell. Moreover, if the cation density between the sheets is too high, as *e.g.* in muscovite, the Coulomb forces between the cations and the silicate layers are too great; these forces hold the sheets together, and no swelling takes place. The silicate sheets are held together particularly strongly by potassium ions (see *e.g.* vermiculite). Potassium ions are less strongly hydrated than sodium ions or alkaline earth metal ions, and their size is such that they fit very well into the 12-coordination offered them by the O atoms of the two tetrahedral layers [17].

Table 2. Intracrystalline swelling of layer silicates (after *A. Weiss* [16].

Mineral	Equiv. cations per formula unit [a]	Layer distance (Å) with: Alkaline earth ions dry	Alkaline earth ions in H_2O	K^+-Ions dry	K^+-Ions in H_2O	Na^+-Ions dry	Na^+-Ions in H_2O
Pyrophyllite, Talc	0	constant 9.2					
Montmorillonite	0.24–0.5	11.5	20	10	∞	10	∞
Vermiculite	0.65	11.5	14.5	10	10	10	15
Illite	0.7	—	—	10	10	—	—
Muscovite	0.8–1.0	—	—	10	10	—	—

[a] $(M^{III}_2, M^{II}_3)(OH)_2[(Si, Al)_4O_{10}]$

Alkaline earth metals ions allow only limited swelling in water; up to four layers of water are incorporated in montmorillonite, and up to two layers in vermiculite. Sodium and potassium ions give infinite swelling

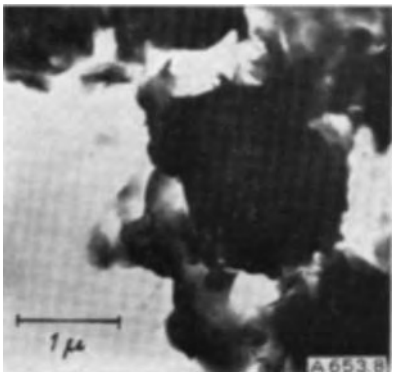

Fig. 8. Electron micrograph of a montmorillonite having exchangeable alkaline earth ions.

[14] *Armin Weiss*, Z. anorg. allg. Chem. *297*, 257 (1958).

[15] *Armin Weiss*, Z. anorg. allg. Chem. *299*, 92 (1959).

[16] *Armin Weiss*, *G. Koch*, and *U. Hofmann*, Ber. dtsch. keram. Ges. *32*, 12 (1955); *U. Hofmann*, Kolloid-Z. *169*, 58 (1960).

[17] *Armin Weiss*, Lecture to the Chemical Society Heidelberg, Jan. 23, 1968.

in montmorillonite, *i.e.* the crystal separates into individual silicate layers.

Figure 8 shows the electron micrograph of a montmorillonite having exchangeable alkaline earth ions; as usual, the sample was prepared from a suspension. In the suspension, the silicate layers move toward one another and dry in such a way that their original outline is indistinct.

The electron micrograph of a freeze-dried montmorillonite gel having exchangeable sodium ions gives a picture of the type shown in Figure 9. Owing to the intracrystalline swelling, the silicate sheets had separated singly or a few at a time. In the gel they form a framework structure with water trapped in its cavities. The silicate layers are flexible, and can be folded like silk ribbons.

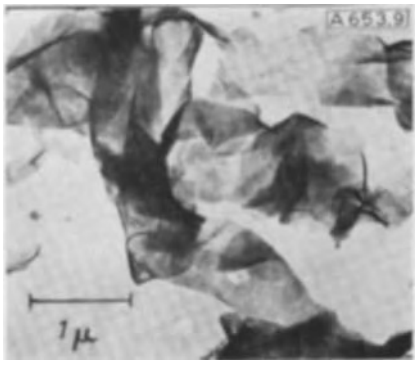

Fig. 9. Skeletal structure of a freeze-dried gel of montmorillonite having exchangeable sodium ions.

If a suspension of a montmorillonite with exchangeable sodium ions is evaporated to dryness for examination in the electron microscope, a film of flat silicate layers is obtained.

Table 3 shows that the content of exchangeable cations in kaolinite, chlorite, and illite increases with decreasing thickness of the crystal platelets. In montmorillonite and vermiculite, the cations between the silicate layers can also be exchanged.

Table 3. Content of exchangeable cations (M^+) in the clay minerals.

Mineral	M^+ (mequiv/100 g)
Kaolinite	1—20
Chlorite	3—40
Illite	10—50
Montmorillonite	60—130
Vermiculite	100—170

1.4. Halloysite

Halloysite occurs in two forms, one having a high and the other a low water content. In the form with the high water content, $Al_2(OH)_4[Si_2O_5]\cdot 2\,H_2O$, [$d(001)$ = 10.1 Å], the kaolinite and water layers alternate. The water is eliminated at about 50 °C to give the form having the low water content [$d(001)$ = 7.3 Å], which consists only of kaolinite layers ($Al_2(OH)_4[Si_2O_5]$) [18]. The crystal structure [19] of the highly hydrated halloysite is shown in Figure 10.

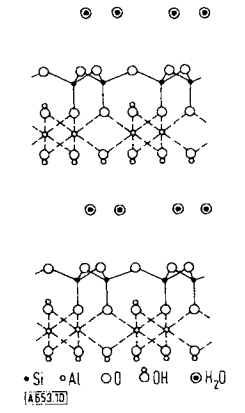

Fig. 10. Crystal structure of the highly hydrated form of halloysite. Distance between layers = 10.1 Å.

The electron micrograph of halloysite having a low water content (Fig. 11) shows fine needles. A needle shape can also be discerned in the highly hydrated halloysite by means of replicas. Closer examination shows that the needles are in fact tubes [20], smaller tubes often being inserted in larger ones. The tubes are most clearly seen in surface replicas [21, 22]; carbon

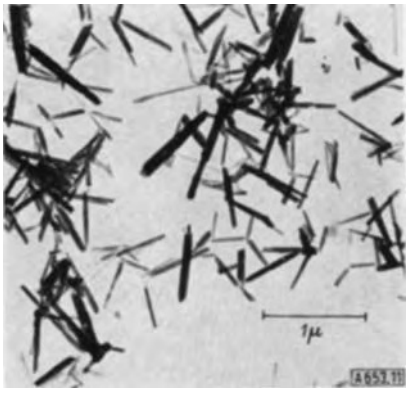

Fig. 11. Electron micrograph of halloysite.

is vaporized onto a piece of halloysite, and the halloysite is subsequently dissolved out with hydrofluoric acid. Halloysite tubes remain embedded in the carbon layer, and it is occasionally possible to see them very clearly in end view (Fig. 12).

It can be seen from Table 4 that the outside diameter as found under the electron microscope gives a smaller calculated surface area if the tubes are assumed to be

[18] *U. Hofmann, K. Endell,* and *D. Wilm,* Angew. Chem. *47,* 539 (1934).

[19] *U. Hofmann,* Kolloid-Z. *69,* 356 (1934); *S. B. Hendricks,* Amer. Mineralogist *23,* 295 (1938); *G. Ruess,* Mh. Chem. *76,* 168 (1946).

[20] *T. F. Bates, F. A. Hildebrand,* and *A. Swineford,* Amer. Mineralogist *35,* 463 (1950).

[21] *T. F. Bates* and *J. J. Comer,* Proc. 3rd Nat. Conf. Clays and Clay Minerals, Nat. Acad. Sci., Washington 1955, p. 1; *Th. Nemetschek* and *U. Hofmann,* Z. Naturforsch. *16b,* 620 (1961).

[22] *U. Hofmann, S. Morcos,* and *F. W. Schembra,* Ber. dtsch. keram. Ges. *39,* 474 (1962).

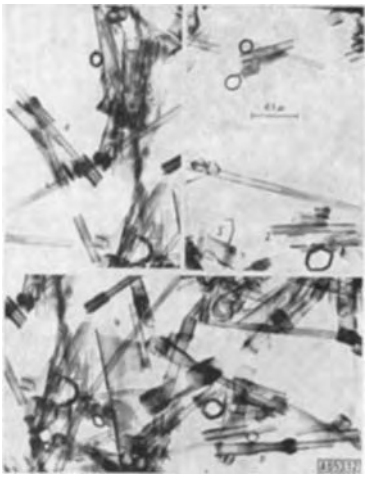

Fig. 12. Electron micrograph of a surface replica of Stolberg halloysite. 1, 2, and 3: tubes inserted one inside another; 4: rolled-up tube; 5: example of a tube in cross section.

solid than that found by nitrogen adsorption measurements (BET, AREAmeter), better agreement being obtained if the inside diameter is taken into account [23].

Table 4. Specific surface areas of halloysites.

Sample	Full needles (Calc.) (m^2/g)	BET (m^2/g)	AREAmeter (m^2/g)	Tube (Calc.) (m^2/g)	Outer radius (Å)	Inner radius (Å)
Argile Djebel I fine	35.2	49.4	49.7	47.9	243	69
Argile Djebel I coarse	33.4	52.1	51.7	44.7	252	68
Djebel Debar I fine	37.9	61.2	53.7	51.4	226	64
Djebel Debar I coarse	39.4	55.6	56.2	54.0	213	61
Novo Bdro Jugoslav.	28.2	45.9	41.1	36.5	309	77
Span. "kaolin" Marocco	33.6	46.8	47.0	40.6	256	59
"kaolin" from Ceylon ($r < 3\ \mu m$)	14.7	22.3	20.6	19.7	557	112
Bergnersreuth ($r < 10\ \mu m$)	23.1	29.7	30.5	29.7	381	93
Lawrence, Illinois	25.8	36.6	39.2	31.1	342	66

These tubes are probably formed as follows. An individual kaolinite silicate layer is formed first, but this layer carries a negative charge as a result of substitution of its ions, and it also carries exchangeable cations. The hydrated cations prevent the formation of hydrogen bonds and hence also combination with another silicate layer. In the single silicate layer, the *a* and *b* axes along the tetrahedral layer (8.95 Å) are theoretically greater than the *a* and *b* axes of the octahedral layer (8.65 Å). In the kaolinite crystal, the hydrogen bonds brace the octahedral layers against the tetrahedral layers of the adjacent silicate layer, and so keep the crystal planar. In halloysite, on the other hand, the individual kaolinite-like silicate layers are able to roll up into a spiral tube, taking with them a layer of water between the silicate layers as a result of the hydration of the cations (Figure 13) [22, 24].

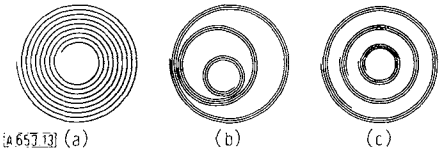

Fig. 13. Cross section through the spiral of the halloysite tube. (a) Highly hydrated form; (b) low water content form; (c) low water content form, silicate layer broken into three tubes.

[23] *R. Reingraber*, Dissertation, Universität Heidelberg, 1968.

[24] Unpublished work by *A. Weiss*.

Kaolinite that has been split into extremely thin layers *via* inclusion compounds can be rolled into halloysite-like tubes by careful treatment [25].

The *b* axis of the kaolinite lattice generally becomes the fiber axis for the halloysite tube.

If the water is driven out of the highly hydrated form of halloysite, the spirals roll up more tightly. They occasionally split in the longitudinal direction to give narrow halloysite tubes inside wider tubes.

Halloysite has a higher cation-exchange capacity in the high-hydration than in the low-hydration state, since some of the cations in the latter are shut in. The content of exchangeable cations is generally between 5 and 30 mequiv/100 g of mineral.

1.5. Dimensions of the Crystals of the Clay Minerals

To determine the average diameter $\bar{d}$ of the crystal platelets of kaolinite and illite, about 1500 crystal platelets were measured in the electron micrograph of each kaolin or clay.

The specific surface area *O* of the clay mineral crystals has been determined by adsorption of nitrogen at its boiling point as described by *Brunauer, Emmett*, and *Teller* (BET method). The best preparations for this purpose are those obtained from gels by freeze-drying, the nitrogen evidently penetrating into the gaps between the crystals of the clay mineral. However, the determination is meaningful only if there is no intracrystalline swelling of the mineral, since the inner surface is not reached in the adsorption of nitrogen. The same area is obtained on determination by the adsorption of phenol from decalin solution.

The thickness *h* of the crystal platelets can be determined from the surface area and the diameter [26]:

$$h = (2\bar{d}^3/\bar{d}^2)/((\rho \cdot O \cdot \bar{d}^3/\bar{d}^2)-4)$$

The density ρ was taken to be 2.6 g/cm³. It is assumed in this equation that the thickness *h* is proportional to the average diameter $\bar{d}$ for any clay mineral crystal. If the calculation is carried out by another equation, in which all particles are assumed to have the same average thickness *h*, the values obtained for the average thickness are smaller. However, the assumption made for the equation given above is more probable.

The results agree very satisfactorily with the average thickness found by measurement of the shadow in the electron micrograph after oblique shadowing. Though the method used for the calculation of the thickness is not very accurate,

[25] *J. Russow*, Dissertation, Universität Heidelberg, 1965.

[26] *U. Hofmann, H. P. Boehm*, and *W. Gromes*, Z. anorg. allg. Chem. *308*, 143 (1961); *U. Hofmann et al.*, Ber. dtsch. keram. Ges. *44*, 131 (1967).

this comparison shows that the value obtained is approximately correct, and is too high rather than too low. It can be seen from Table 5 that kaolins are coarser than clays.

Table 5. Average diameter $\bar{d}$ and average thickness $\bar{h}$ of the crystals of kaolins and clays.

Material	$\bar{h}$ (Å)	$\bar{h}$ (Å)
Very coarse kaolin	7000	1500
Very fine kaolin	2500	340
Very coarse clay	2000	500
Very fine clay	1000	150

1.6. Activities of the Exchangeable Cations

When kaolin is liquefied with soda, calcium ions in the kaolinite are replaced by sodium ions, and sparingly soluble calcium carbonate precipitates out. A bentonite is activated in the same manner.

The cation exchange involves an equilibrium, which is clearly discernible even when a sparingly soluble salt is formed. The equilibrium in the aqueous solution can be described *e.g.* as follows:

$$\text{Ca-kaolinite} + 2\ Na^+ + C_2O_4^{2-} \rightleftharpoons \text{Na}_2\text{-kaolinite} + CaC_2O_4$$

The existence of an equilibrium can be demonstrated by shaking a sodium kaolinite with an excess of calcium oxalate in water. Calcium kaolinite and $Na_2C_2O_4$ are formed. Alternatively, when sodium kaolinite is shaken with $BaSO_4$, a barium kaolinite and Na_2SO_4 are obtained [27].

The concentrations or activities of the Na and oxalate ions in the above equilibrium can be determined in the separated aqueous solution. If a known quantity of $Na_2C_2O_4$ has been added to a pure calcium kaolinite, it is also possible to determine the position of the equilibrium. The activity of the Ca ions in the solution can be calculated from the solubility product of the sparingly soluble calcium oxalate and the measured activity of the oxalate ions. The activity in this case is equated to the activity of the Ca ions which remain on the kaolinite.

Table 6 shows the activities of cations on a clay mineral that is covered half with the cation in question and half with Na ions. These activities are one or more orders of magnitude lower than the activities of the same cations over the sparingly soluble salt in pure water.

This method naturally cannot be used to find the activity, in pure water, *e.g.* of the Ca ions on a kaolinite whose exchangeable cations have been completely replaced by Ca ions. However, the curves in Figure 14 show that even when 90 % of the exchangeable cations are calcium, the activity of the Ca ions is still very low. Exchangeable K, Mg, Ca, Ba, and La ions bound on clay minerals form compounds that are more sparingly soluble than, or roughly as sparingly soluble as $K[B(C_6H_5)_4]$, MgF_2, $CaC_2O_4 \cdot H_2O$, $BaSO_4$, and $La_2(C_2O_4)_3 \cdot 9\,H_2O$ respectively.

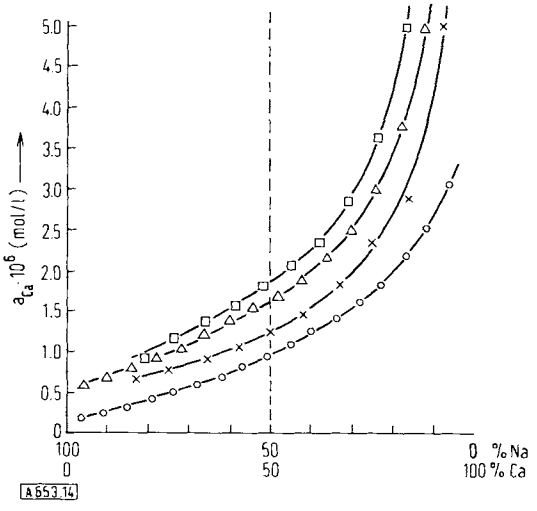

Fig. 14. Activity a_{Ca} of exchangeable calcium on clay minerals as a function of the covering ratio Na:Ca. ---- activity at a covering ratio of 1:1; -□-□-: glauconite (R); -Δ-Δ-: illite; -×-×-: kaolinite; -O-O-: glauconite (U.S.A.).

Table 6. Effective activities of the exchangeable cations on clay minerals.

Clay mineral	Electrolyte	Sparingly soluble compound	Activity of cation (mole/l) in the sparingly soluble compound in pure H_2O	Activity of cation (mole/l) on the clay mineral half covered with the cation and half with Na
K-kaolinite	$Na[B(C_6H_5)_4]$	$K[B(C_6H_5)_4]$	$1.82 \cdot 10^{-4}$	$5_{.0} \cdot 10^{-5}$
K-illite	$Na[B(C_6H_5)_4]$	$K[B(C_6H_5)_4]$	$1.82 \cdot 10^{-4}$	$3_{.2} \cdot 10^{-5}$
Mg-kaolinite	NaF	MgF_2	$1.25 \cdot 10^{-3}$	$1_{.65} \cdot 10^{-6}$
Mg-illite	NaF	MgF_2	$1.25 \cdot 10^{-3}$	$3_{.00} \cdot 10^{-6}$
Ca-kaolinite	$Na_2C_2O_4$	$CaC_2O_4 \cdot H_2O$	$4.5 \cdot 10^{-5}$	$1_{.25} \cdot 10^{-6}$
Ca-illite	$Na_2C_2O_4$	$CaC_2O_4 \cdot H_2O$	$4.5 \cdot 10^{-5}$	$1_{.65} \cdot 10^{-6}$
Ba-kaolinite	Na_2SO_4	$BaSO_4$	$1.00 \cdot 10^{-5}$	$1_{.4} \cdot 10^{-7}$
Ba-illite	Na_2SO_4	$BaSO_4$	$1.00 \cdot 10^{-5}$	$2_{.7} \cdot 10^{-7}$
La-kaolinite	$Na_2C_2O_4$	$La_2(C_2O_4)_3 \cdot 9\,H_2O$	$2.3 \cdot 10^{-6}$	$2_{.84} \cdot 10^{-10}$
La-illite	$Na_2C_2O_4$	$La_2(C_2O_4)_3 \cdot 9\,H_2O$	$2.3 \cdot 10^{-6}$	$4_{.00} \cdot 10^{-10}$

The higher the activity of the cation, the more readily is it exchanged. The lower the activity, on the other hand, the more readily is the cation taken up by the clay mineral. This is clearly shown when *e.g.* an ammonium kaolinite is treated with equivalent solutions of two cations and the ratio of the exchanged cations determined. The order of the activities of the cations corresponds to the Hofmeister series.

$$Na \gg K > Mg > Ca > Ba > La$$

It must be assumed that, unlike the Na ions, K, Mg, Ca, Ba, and La ions simply form a diffuse cloud around the clay mineral crystal.

If a natural kaolin or clay covered with Ca and Mg ions is to be covered with Na ions and then washed until free from salt, it is not advisable to use a sodium salt that gives sparingly soluble Ca and Mg salts, since the sparingly soluble salt would react again with the sodium ions during washing. On the contrary, a large excess of a sodium salt that gives soluble Ca and Mg salts should be used, these salts then being washed out with the excess of sodium salt.

[27] *U. Hofmann* and *W. Burck*, Angew. Chem. *73*, 342 (1961); *H. Friedrich* and *U. Hofmann*, Z.anorg.allg.Chem. *342*, 10 (1966).

1.6.1. Acid Strength of Exchangeable Hydrogen Ions

Clay minerals are attacked by acids. The best method of covering a clay mineral with exchangeable hydrogen ions is to use a strongly acidic cation exchanger [28]. Clay minerals containing the readily exchangeable Na ion react particularly well. The H-clay mineral can be titrated with CO_2-free sodium hydroxide, potassium hydroxide, or barium hydroxide solution in polyethylene containers under nitrogen with the quinhydrone electrode.

It can be seen from Figure 15 that the H-clay minerals react as acids, though they are less acidic than equivalent acetic acid [29]. (However, the value given by the titration is the average pH value of the clay mineral suspension. The concentration of H_3O ions is undoubtedly much greater immediately adjacent to the surface of the clay mineral.)

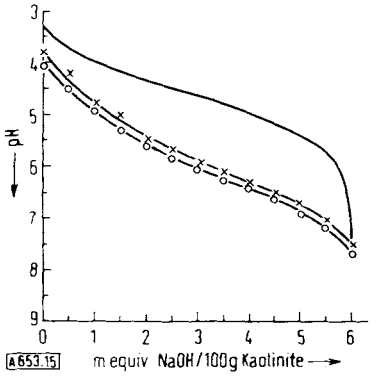

Fig. 15. Neutralization curves. ——: 0.01 N CH_3COOH + 0.1 N NaOH; -x-x-: 1.0 mequiv of H-kaolinite/100 ml of H_2O + 0.1 N NaOH; -O-O-: 0.1 equiv of H-kaolinite/100 ml of H_2O + 0.01 N NaOH.

2. Formation of the Clay Minerals

It seems probable from geological observations and from the synthesis of clay minerals in the laboratory [11,30] that these minerals are formed from aqueous solution.

Kaolinite, $Al_2(OH)_4[Si_2O_5]$, is formed by the weathering of feldspar, *e.g.* $K(AlSi_3O_8)$, in the presence of water containing acid, *e.g.* CO_2. The alkali metal and alkaline earth metal ions liberated are carried away; the excess SiO_2 is also carried away, or forms cristobalite or quartz in the course of time.

Kaolins generally occur in primary deposits. The rock often contains only 30 % of kaolinite, the remainder being quartz, feldspar, mica, *etc.* Clays are generally found in secondary deposits, to which they have been carried by water. Apart from kaolinite (usually of the fireclay type), they contain illite and montmorillonite, as well as quartz, iron oxide, calcium carbonate, humus, *etc.* Clays often contain clay minerals in high concentrations.

The formation of a kaolinite crystal can be explained as follows. A silicate sheet is formed first. The second silicate sheet then grows with its octahedral layer toward the tetrahedral layer of the first sheet, and with formation of hydrogen bonds. The crystal thus grows layer by layer until the concentration of foreign ions in the mother liquor becomes so high that the last silicate layer receives a negative charge as a result of ion substitution. This silicate layer binds exchangeable cations, the hydration of which prevents the formation of hydrogen bonds and hence the growth of a new silicate layer. Consequently, the crystal can grow no further.

A hypothesis proposed to explain the formation of halloysite tubes was described in Section 1.4.

Illite is formed by weathering of potassium feldspar and of micas if the potassium ions cannot be removed from the mother liquor. The weathering of feldspars yields roughly equal quantities of sodium and potassium ions. Ground water, however, contains *e.g.* only 4 mg of potassium ions/l as compared with 30 mg of sodium ions/l, and sea water contains 11 g of sodium ions/l as opposed to only 0.3 g of potassium ions/l. The potassium content of land plants is not sufficient to account for the missing potassium ions, particularly since much of it is recycled between the soil and the plants. The potassium ions have in fact been consumed by the formation of illite and other micas containing potassium.

As a result of weathering in the soil, illite provides the additional potassium required by land plants. Potassium feldspar is less common in soil and is coarser (0.1 to 0.01 mm diameter) and so weathers more slowly.

Montmorillonite results from the weathering of volcanic ashes in the presence of sodium ions, which promote the intracrystalline swelling. Bentonite deposits also contain vitreous weathering residues. The Lower Bavarian bentonite deposits may owe their existence to the impact of the great meteorite in the Tertiary, which formed the giant crater at Nördlingen in the Alb. The crater has a diameter of 20 km. The flying "volcanic" ash was carried south-eastward by the wind, collected in the Lower Bavarian basin, and changed into bentonite.

Investigation of the sediments in the sea around the mouths of large rivers led many workers to believe that montmorillonite sedimented first and then gradually changed into illite [31], taking up potassium ions from the sea water and increasing the negative charge on the sheets *e.g.* by substitution of magnesium for aluminum in the octahedral layer.

3. Properties and Use of Kaolin and Clay

Kaolins are generally washed before use to reduce the content of quartz, feldspar, and mica. Clays are usually worked without being washed. Coarse kaolins

[28] *K. Frühauf* and *U. Hofmann*, Z. anorg. allg. Chem. *307*, 187 (1961).

[29] *H. Friedrich* and *U. Hofmann*, Z. anorg. allg. Chem. *342*, 20 (1966).

[30] *W. Noll*, Z. Kristallogr., Mineralog. Petrogr., Sect. A *48*, 210 (1936); *S. Henin* and *O. Robichet*, C. R. hebd. Séances Acad. Sci. *236*, 517 (1953); *S. Caillére*, *S. Henin*, and *J. Esquevin*, *ibid. 237*, 1724 (1953); *H. Harder*, Naturwissenschaften *54*, 613 (1967).

[31] Cf. *W. v. Engelhardt*, Geol. Rdsch. *51*, 475 (1961).

are not very plastic, and for this reason the coarser grades are not used in ceramics. They are used as fillers for paper, as brightening fillers for plastics, as vehicles for insecticides, and for the preparation of ultramarine.

3.1. Plasticity

Kaolins and frequently clays are not worked alone in ceramics, but are mixed *e.g.* with quartz and feldspar for the manufacture of porcelain. Kaolins and clays containing a suitable quantity of water are plastic, *i.e.* they can be shaped, often into thin-walled vessels. They retain the shape of the vessel or model after being formed, and harden on drying.

There is unfortunately no satisfactory method of measuring the plasticity of clays. One method that is widely used is the Pfefferkorn method [32], in which the water content of a wet clay that is flattened to a given thickness by a falling plate is measured. Another method is *Cohn*'s method in which a rod must sink into a wet clay at a given speed, the water content of the clay then being determined. Thus, both of these methods involve the measurement of the water content of the wet clay at a given resistance to deformation.

Clays that are too wet or too dry have lower plasticities. The best method would be to measure the strength of a wet clay at a deformability that corresponds to the most plastic state [33]. Unfortunately, however, the strength cannot yet be determined with sufficient accuracy in the plastic state, since the clay flows. The potter's thumb is therefore still often the measuring instrument used in practice.

Pure quartz sand is fairly plastic in the moist state; the water adheres to the surface of the quartz sand and holds the quartz grains together by its surface tension. When dried, however, the quartz sand becomes mobile, since the only contact between the grains is at points. Clay or kaolin coats the quartz and feldspar grains with its crystal platelets, so providing large contact areas both in the wet and in the dry states, which give the wet mix its strength. The quartz in Figure 16, however, contains only a small quantity of clay, such as is present *e.g.* in a casting sand produced with bentonite. In a plastic ceramic mass, the interstices between the quartz grains are also filled with clay or kaolin platelets.

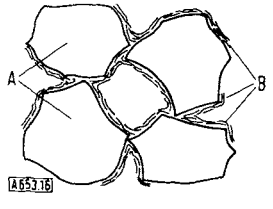

Fig. 16. Binding of quartz sand (A) by clay (B).

[32] *F. Zapp*, Ber. dtsch. keram. Ges. *34*, 12 (1957).

[33] *E. Scharrer* and *U. Hofmann*, Ber. dtsch. keram. Ges. *35*, 278 (1958); *U. Hofmann*, Keram. Z. *14*, 14 (1962).

The better the clay or kaolin conforms, the more plastic is the mixture. The flexibility of the platelets is therefore important. Clays are more plastic than coarse kaolins, but less plastic than fine kaolins.

According to *Weiss* [34], a coarse kaolin can be made very plastic by incorporation of compounds, such as urea, that break hydrogen bonds between the layers. By careful treatment, the kaolinite crystal can then be split into very thin lamellae and the compound added can finally be removed. The Chinese probably prepared their kaolin in this way during the Sung dynasty (960 to 1279) for the production of egg-shell porcelain. They obtained the inclusion compound by allowing decomposing urine to act on kaolin.

Ceramic objects are formed either freehand or on potter's wheels, which were known as early as 3000 B.C. Alternatively a slip may be cast in porous plaster-of-Paris molds; the action of the exchangeable cations can be seen in this case [35]. A plastic clay can be liquefied to a slip without changing its water content by the addition of a small quantity of soda and/or water glass.

In the natural or washed state, kaolin or clay generally contains exchangeable alkaline earth metal ions from the hardening constituents of water or from the flocculation with calcium hydroxide after washing. Soda enters into an equilibrium with the alkaline earth metal ions of the kaolinite or clay mineral, with exchange of sodium ions and precipitation of alkaline earth metal carbonate. Water glass reacts in a similar manner. The alkaline reaction of soda or water glass is necessary for the liquefaction only if the clay or kaolin also contains exchangeable hydrogen ions as a result of contact with acid soil water, *e.g.* humic acid.

Alkaline earth metal ions carry a double positive charge. They cannot completely screen the negative charges on the surface of the clay mineral crystals [35,36]. The negative potential extends outward between

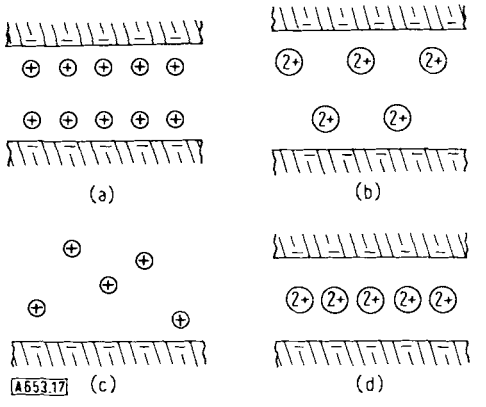

Fig. 17. Saturation of the negative surface charge of the clay minerals by monovalent cations (*e.g.* Na^+) and by divalent cations (*e.g.* Ca^{2+}). (a) Monovalent cations, better charge neutralization, screening of the surfaces; (b) divalent cations, poorer charge neutralization, inadequate screening of the surfaces; (c) diffuse cation cloud over the surface; (d) divalent cations, better charge neutralization by combination of two layers.

[34] *Armin Weiss*, Angew. Chem. *75*, 755 (1963); Angew. Chem. internat. Edit. *2*, 597 (1963).

[35] *U. Hofmann*, Silikattechnik *8*, 224 (1957); *W. Czerch*, *K. Frühauf*, and *U. Hofmann*, Ber. dtsch. keram.Ges. *37*, 255 (1960).

[36] *Armin Weiss*, Kolloid-Z. *158*, 22 (1958); *U. Hofmann*, *ibid.* *169*, 58 (1960); *U. Hofmann*, *E. Scharrer*, *W. Czerch*, *K. Frühauf*, and *W. Burck*, Ber. dtsch. keram. Ges. *39*, 125 (1962).

the alkaline earth metal ions (Fig. 17b). Clay mineral crystals therefore adhere to one another *via* two layers of water lying between them (Fig. 17d). The adhesion occurs, not only between faces, but also between faces and edges. This structure, which resembles a house of cards, is shown in a greatly exaggerated form in Figure 18a. Because of the water layers between them, the platelets can be displaced in relation to one another and subsequently become fixed again in their new position. This is the explanation of the plastic deformability and the dimensional stability.

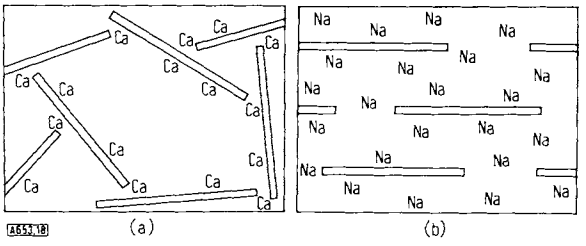

Fig. 18. (a) Plastic structure in the presence of Ca ions; (b) slip in the presence of Na ions (schematic section).

Sodium ions are monovalent, and can screen the negative potential of the clay mineral surface much more effectively. They are also strongly dissociated in water, and form a cation cloud around the clay mineral crystal (Fig. 17a and c). The clay mineral crystals repel one another and assume a parallel orientation, the clay thus becoming liquid. This is shown, again exaggerated, in Figure 18b.

When a slip is poured into the plaster mold, the porous plaster absorbs the water. It can be shown that the clay mineral platelets arrange themselves as nearly as possible parallel to the wall [37]. When the body becomes sufficiently thick, the remaining, unwanted slip is poured out of the mold.

Clay minerals containing exchangeable hydrogen ions also form a plastic mix, since they can form hydrogen bonds, and, since they can dissolve aluminum ions out of the octahedral layers of the crystals, these ions, as $Al(OH)^{2+}$, then act in the same manner as alkaline earth metal ions [38].

3.2. Action of Exchangeable Cations in Arable Soil

Owing to the alkaline earth metal ions normally present in arable soil, the clay minerals have the house-of-cards structure, giving the soil the desired loose and crumbly texture, so that it is permeable to water and to air. If the soil becomes flooded with sea water or if it is fed with too much potassium chloride, the alkaline earth ions are replaced by sodium or potassium ions, which liquefy the clay mineral skeleton in the presence of water having a low electrolyte content. Since the clay mineral platelets are now parallel to one another, the soil can contract to a very dense state on drying, and the fertility of the soil decreases or disappears. It then takes a considerably long time for the alkaline ions to be replaced by the hardening constituents of water. When the soil is fed with moderate amounts of potassium chloride, the clay minerals take up potassium ions as part of their complement of exchangeable ions and prevent them from being washed out of the soil, so that they are available for the plants.

3.3. Dry Bending Strength

Plastic clay mixes consist essentially of the solid particles and water; they contain practically no air. On drying, the water is removed, the clay shrinks, and air pores are simultaneously formed; the smaller the number of pores or the greater the solid content of the material, the higher is the dry bending strength [39].

In clay, the small platelets lie in the interstices between the large platelets in the house-of-cards structure of the plastic mix. The differentiation between small and large platelets is not so pronounced in kaolins, and the interstices between the large platelets are consequently not so well filled. This is shown exaggeratedly in Figure 19. On drying, therefore, the clays give higher densities, higher solid contents, and higher dry bending strengths than the kaolins.

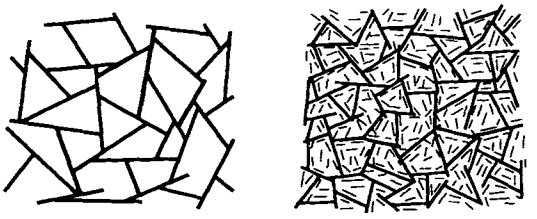

Fig. 19. House-of-cards structure in (a) kaolin and (b) clay (in section).

The dry materials obtained by slip casting have particularly high densities because of the parallel arrangement of the platelets; consequently, higher dry bending strengths are obtained by casting than by shaping of the same plastic material.

Table 7. Plasticity and dry bending strength as a function of the nature of the exchangeable cations (purified Zettlitz kaolin, 6.5 mequiv of exchangeable cations/100 g).

Exchangeable cations	Pfefferkorn plasticity (g H_2O/100 g dry kaolin)	Dry bending strength (kg/cm²)	Solids (Vol.-%)
Na^+	43.5	30	61
K^+	47	18	58
Ca^{2+}	46.5	16.3	59
Ba^{2+}	47.3	10.2	57
La^{3+}	50.6	8.4	54

[37] *A. Dietzel* and *H. Mostetzky*, Ber. dtsch. keram. Ges. *33*, 115 (1956).

[38] *K. Frühauf* and *U. Hofmann*, Z. anorg. allg. Chem. *307*, 187 (1961).

[39] *U. Hofmann*, *W. Czerch*, and *E. Scharrer*, Ber. dtsch. keram. Ges. *35*, 219 (1958); *U. Hofmann*, *E. Scharrer*, *W. Czerch*, *K. Frühauf*, and *W. Burck*, *ibid. 39*, 125 (1962); *U. Hofmann*, *F. W. Schembra*, *M. Schatz*, *D. Scheurlen*, *H. Friedrich*, and *J. Dammler*, *ibid. 44*, 131 (1967).

Halloysite has a given dry bending strength at a lower solids content than kaolinitic and illitic kaolins and clays. This is in agreement with the fact that a skeleton constructed from tubes (halloysite) can be made lighter for a given strength than can a skeleton constructed from plates (kaolinite and illite).

The effect of the exchangeable cations on the dry bending strength and the plasticity is shown in Table 7. The higher the water content of a kaolin for a given degree of flattening in the Pfefferkorn tester, the lower is the dry bending strength.

3.4. Use of Vermiculite

When vermiculite takes up potassium ions, it loses its capacity for intramolecular swelling; hence potassium ions are more readily exchanged in vermiculites that were previously swellable. Since this behavior is even more pronounced with rubidium and cesium ions, vermiculite is therefore used in the treatment of nuclear fuels to remove ^{137}Cs ions (half life 30 years) from solution.

Vermiculite forms fairly large crystals. When swellable vermiculite with one to two layers of water between the silicate layers is rapidly heated, the water between the layers cannot escape quickly enough. It boils and forces the silicate layers apart, so that the vermiculite swells. If the crystals have a small diameter *e.g.* 1 mm or less, they give worm-like structures, from which the name vermiculite is derived. Crystals greater than 1 cm in diameter give a very loose material having a bulk density of *e.g.* only 100 g/l. The material retains its loose structure up to about 1000 °C. It is a good packing material, and can also be used as a thermal insulator.

3.5. Use of Montmorillonite and Bentonite

Montmorillonite is generally used in industry in the sodium form [40]. Na-montmorillonite exhibits infinite swelling in water, forms very thin lamellae, and so disperses extremely readily in a wet clay. Sodium montmorillonites are sometimes found in nature. However, they can also be obtained by reaction of the more abundant natural alkaline earth metal montmorillonites in the moist state with soda, which leads to the equilibrium mentioned.

In spite of its high plasticity and dry bending strength, little use is made of bentonite in ceramics, since it usually contains some iron in its lattice and so has a brownish to reddish color after firing.

However, 5 % of bentonite is sufficient to make a casting sand sufficiently strong in the wet or dry state, while the permeability to gases is still excellent (cf. Fig. 16).

Sodium montmorillonite gives a suspension a high viscosity. At about 10 wt-% of montmorillonite, the suspension thickens to a gel at rest (thixotropy). This affords a good, strong drilling mud and at the same time, the montmorillonite lamellae seal off the wall of the borehole and prevent the drilling mud from flowing into the rock. Owing to the supporting and sealing effect on the wall, a bentonite suspension is introduced into the slits cut out in slit wall construction before the concrete is poured in.

The use of montmorillonite for the removal of radioactive ^{137}Cs ions from solutions during the treatment of nuclear fuels in nuclear power stations is also being considered [41]. In order to encase the cesium ions in an insoluble ceramic product, it would then only be necessary to fire the montmorillonite.

Still better exchange is obtained with long-chain organic ammonium ions. (These ions even cause intramolecular swelling in illite or muscovite [14,42], though this takes some weeks to occur.) One such montmorillonite is supplied in organic solvents under the name "Bentone" as an additive for paint suspensions and for lubricating greases. Protamines, *e.g.* salmine, which has a high arginine content, are very readily exchanged. However, proteins are also exchanged in acidic solution *via* the basic amino acids [43]. Montmorillonite is therefore used to free wine and export ale from proteins and protein degradation products, which would otherwise flocculate on standing. Montmorillonite absorbs up to its own weight of protein. It is probable that only one end of the protein molecule with basic amino acids is incorporated between the silicate layers of the montmorillonite.

4. Clay Minerals as Catalysts

Clay minerals, particularly montmorillonite are good catalysts [43c,44]. For example, in the presence of air, montmorillonite oxidizes diphenylamine to the blue benzidinium ion or aniline to aniline black. Peptides are cleaved by montmorillonite. This led us to consider the formation of petroleum and of oil shale.

Oil shale contains clay minerals and "kerogen", an organic material, and affords a petroleum-like product on slow distillation. The earth probably contains four times as much potential oil in oil shale as it does free oil.

Evidence in favor of the biological origin of kerogen and petroleum is provided *inter alia* by the detection of porphyrins by *A. Treibs*. Proteins, fats, and possibly also carbohydrates from plankton, algae, and similar microorganisms change in the sludge at the bottom of the sea into gyttja as a result of H_2S-induced oxygen deficiency and into sapropel in the absence of oxygen.

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It is possible that petroleum is formed from sapropel, and kerogen from sapropel and gyttja [45]. Clay minerals simultaneously sediment into the sludge. The petroleum has emerged from the clay minerals in the course of time, and is now found in porous rocks such as sandstone.

Weiss and *Roloff* [46] have shown that hemin incorporated as a cation into the layer lattice of montmorillonite is stable up to about 300 °C, instead of only up to 200 °C as in the free state. However, clay minerals act as catalysts even above 200 °C on organic substances. Organic ammonium ions, which may be derived from decaying protein, change in the layer lattice of montmorillonite above 200 °C into a mixture of hydrocarbons that corresponds to petroleum and natural gas [47]. The same is true of protein incorporated into montmorillonite. Montmorillonite carrying organic ammonium ions also absorbs fats. The hydrocarbons are formed above 200 °C in every case.

Thus petroleum can be produced in the laboratory from organic ammonium ions, protein, and fats by the catalytic action of montmorillonite. Does this also happen in nature?

We have determined the clay minerals in a series of oil shales [48]. The older shales (Cambrian to Jurassic) contained illite and the younger shales (Jurassic to Middle Eocene) montmorillonite.

In the young Middle Eocene oil shale from Messel, the kerogen is at least partly situated between the silicate sheets of the montmorillonite.

Illites also have a large surface and can act as catalysts. However, the geological sequence suggests that the kerogen was initially formed in the montmorillonite and migrated slowly, while the montmorillonite changed into illite as a result of the absorption of potassium and an increase in the charge on the layers. The free petroleum may also have been formed from the kerogen of the oil shale.

When montmorillonite is heated with organic ammonium ions, an ammonium montmorillonite is formed; above 350 °C and in the absence of air, this changes into an H-montmorillonite [47]. The H ions migrate into the silicate layers, probably into the octahedral layer, and the montmorillonite, loses its intracrystalline swelling capacity, and like pyrophyllite and talc, can no longer swell.

In Trinidad asphalt we [48] found an unswellable layer silicate having a distance of 9.9 Å between the illite layers, but which contains only 0.34 K per formula unit. This may be a montmorillonite with 0.34 potassium ions that has lost the ability to swell because of the temperature of about 300 °C at which the kerogen was formed and driven out to form the asphalt.

It is also possible that montmorillonite or the clay minerals in general were involved as catalysts in the creation of life on earth. Three or four billion years ago, the earth probably had a "primordial atmosphere" of hydrogen, methane, ammonia, and water. The ultraviolet radiation from the sun (which was not absorbed by oxygen as it is now) and electric discharges cooperated in this atmosphere to form the components of the proteins and nucleic acids, *e.g.* formaldehyde, prussic acid, glycine, alanine, aspartic acid, adenine, and sugars. Algae and microorganisms have been detected in rocks as much as three billion years old [49]. The clay minerals, which existed even in the Precambrian, may have catalyzed the formation of "viable" compounds of high molecular weight [50].

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Antibiotics as Inhibitors of Nucleic Acid and Protein Synthesis[1]

BY G. HARTMANN, W. BEHR, K.-A. BEISSNER, K. HONIKEL, AND A. SIPPEL[*]

The antibiotics of the rifamycin, actinomycin, chromomycin, and anthracycline groups have been found to be specific inhibitors for the DNA-controlled synthesis of RNA[2] in vitro. Streptomycin, chloramphenicol, and puromycin can specifically suppress certain steps in the biosynthesis of proteins. The investigation of the mode of action of such substances may help us to gain a better insight into the transmission of hereditary information.

1. Introduction

Seven years ago *Reich*, *Franklin*, *Shatkin*, and *Tatum*[3] found that small concentrations of the antibiotic actinomycin in tissue cultures selectively suppress the synthesis of RNA whereas DNA and protein syntheses, on the other hand, remained temporarily almost unchanged. This discovery attracted great interest in connection with the intensive efforts being made to explain the nucleic acid and protein syntheses, since specific inhibitors had already been of great value in the elucidation of the individual reaction steps of other important metabolic chains.

Since then, many antibiotics have become recognized as inhibitors of processes that lead to the imprinting of genetic information[4,5], *i.e.* of processes that differ from normal enzyme reactions in that they involve information-carrying templates. Consequently, the inhibitors for this reaction include, not only those substances that attack the enzyme protein or antimetabolites that resemble the substrate, but also substances that inactivate the template. This has been confirmed by a number of experiments *in vitro*. The examples given in this article are confined to antibiotics whose chemical structures are known, and which directly inhibit the enzymatic polycondensation process.

2. Inhibition of Nucleic Acid Synthesis

2.1. Action of RNA Polymerase

The first step in the transfer of genetic information, which is contained in the base sequence of the DNA, to protein synthesis is the formation of single-strand RNA. Ribonucleoside triphosphate is polycondensed by the catalytic action of the enzyme RNA polymerase (EC 2.7.7.6) with DNA as a template to form RNA whose base sequence corresponds to that of the DNA template[6].

$$\begin{matrix} n_1\ \text{ATP} \\ n_2\ \text{UTP} \\ n_3\ \text{GTP} \\ n_4\ \text{CTP} \end{matrix} \xrightarrow[\text{RNA-Polymerase}]{Mg^{2+},\ \text{DNA}} \text{RNA} + (n_1 + n_2 + n_3 + n_4)\text{PP}$$

Experiments, which have mainly been carried out with RNA polymerase from *Escherichia coli*, have shown that the reaction proceeds in several steps[7–10]. The polymerase protein first adds onto the nucleic acid, which may be single-stranded or double-stranded (Fig. 1a), in a readily reversible manner.

$$\text{DNA} + \text{Enzyme} \rightleftharpoons (\text{DNA-Enzyme})$$

On double-strand DNA the synthesis begins with a strongly temperature-dependent induction phase, the DNA helix evidently having to be locally opened up ("melted") (Fig. 1b), whereas reaction proceeds immediately in the case of single-strand DNA.

A relatively high concentration of purine nucleoside triphosphate is necessary at the beginning of the re-

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[1] This article is based on a lecture to be delivered to the meeting of the Gesellschaft Deutscher Naturforscher und Ärzte in Heidelberg on October 8, 1968.

[2] The following abbreviations are used in this article: DNA = deoxyribonucleic acid; RNA = ribonucleic acid; tRNA = transfer ribonucleic acid; mRNA = messenger ribonucleic acid; GDP, ATP, UTP, GTP, CTP = 5′-ribonucleoside di- and triphosphates of guanine, adenine, uracil, and cytosine, dATP, dTTP, dGTP, dCTP = 5′-deoxyribonucleoside triphosphates of adenine, thymine, guanine, cytosine; PP = pyrophosphate; poly-d(A–T), poly-d(DAP–T) = double-strand DNA's whose individual strands have the base sequence -adenine-thymine- and -2,6-diaminopurine-thymine-; poly-dGdC, poly-dIdC = double-strand DNA's constructed from the single strands polydeoxyguanylic acid, polydeoxycytidylic acid, and polydeoxyinosinic acid; FM = *N*-formylmethionyl-; CCA = trinucleotide cytidylyl-(3′→5′)cytidylyl(3′→5′) adenosine.

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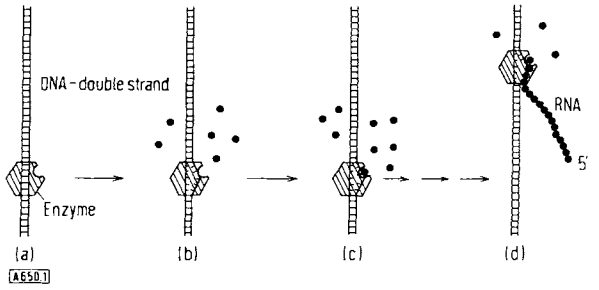


Fig. 1. Start of the DNA-controlled RNA polymerase on the DNA-double-strand. a) Addition of the enzyme to the DNA; b) "melting" of the DNA; c) DNA-enzyme-nucleotide complex; d) polycondensation to give RNA; • = ribonucleotides.

action. Formation of a stable DNA-enzyme-nucleotide complex takes place (Fig. 1c) and, possibly, for it cannot yet be established with certainty, a short RNA segment is also synthesized at this stage.

(DNA-Enzyme) + Nucleotide → (DNA-Enzyme-Nucleotide)

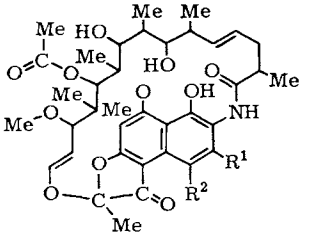
When the other nucleoside triphosphates are added, the synthesis of RNA proceeds with liberation of pyrophosphate, and the enzyme meantime moves along the DNA template (Fig. 1d) thus leading to the

(DNA-Enzyme-Nucleotide) + 4n 5'-Ribonucleoside triphosphate → (DNA-Enzyme-RNA) + 4n PP

formation of a DNA-enzyme-RNA complex [11], which dissociates under suitable conditions; the dissociation may be rate-determining for the reaction as a whole. The liberation of the RNA formed may be accelerated *in vivo* by the subsequent protein synthesis [12].

2.2. Rifamycins as Enzyme Inhibitors

Rifamycin B *(1a)*, its chemically modified derivatives [13–15] [*e.g. (1b)*], and the streptovaricins [16], which have a similar structure, are among the strongest inhibitors of the RNA polymerase from *E. coli.*; a concentration of only 3×10^{-8} M of rifampicin *(1b)* is sufficient to reduce the enzyme activity by half *in vitro* (Table 1). The action of the antibiotic is independent of the base composition and the secondary structure of the DNA used as the template [17–19].



Me = CH_3

(1a), R^1 = H, R^2 = O-CH_2-COOH

(1b), R^1 = -CH=N-N(piperazine)-N-CH_3, R^2 = OH

The inhibitor action is species-specific, since RNA polymerase from rat liver or from ascites cells is not inhibited [19, 20]; this offers interesting possibilities for application *e.g.* in virus research [18, 20a].

Table 1. Antibiotic concentrations for 50% inhibition of the DNA-controlled RNA and DNA polymerases from *E. coli*. Thymus DNA concentration in the RNA polymerase experiments 3×10^{-4} M, in the DNA polymerase experiments 1.3×10^{-4} M [17, 38, 44].

Antibiotic	50% inhibition of	
	DNA-Polymerase (M·10^5)	RNA-Polymerase (M·10^5)
Rifampicin	no inhibition	0.003
Actinomycin X_2	2	0.03
Echinomycin	3	0.3
Chromomycin A_3	2	0.03
Olivomycin	0.6	0.2
Mithramycin	3	0.2
Anthracycline:		
Ruticulomycin A	0.2	0.5
Nogalamycin	0.5	0.5
Cinerubin A and B	3	1
Daunomycin	2	3
Isoquinocycline	5	4

The rifamycins can exert their inhibiting action in full only on the free enzyme protein, the enzyme being protected to some extent, even by DNA, provided that the polymerase has had sufficient time to react with the DNA (cf. Fig. 1b). Much stronger and faster protection is provided by a combination of DNA with one or more nucleoside triphosphates. The antibiotic evidently has much less effect on the resulting initiation complex (Fig. 1c). If it is added after the start of the polycondensation with all four ribonucleoside triphosphates, no inhibition is observed up to the end of the synthesis and the dissociation of the reactants. The polycondensation is thus hindered only by the inhibition of the start of the reaction [19, 21].

The rifamycins [18, 19, 21], and the streptovaricins [22–24], which act in the same manner, are to be considered therefore as very selective inhibitors for the initiation of the DNA-controlled RNA polymerase of microorganisms.

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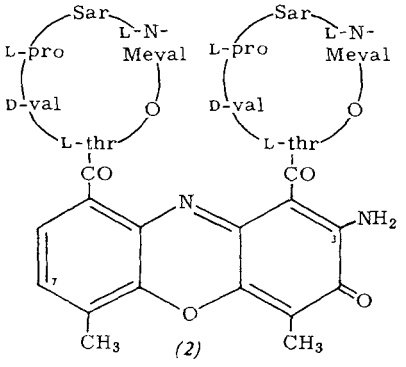
2.3. Inactivators of the Template

2.3.1. Actinomycin

In vitro experiments with the actinomycins *(2)* [25] and the structurally related echinomycin [26] showed some years ago that these antibiotics are strong inhibitors of the DNA-dependent RNA polymerase reaction [27, 28] (Table 1). This explained the specific suppression of RNA synthesis *in vivo* by actinomycin. The fact that the inhibiting action is independent of the source of



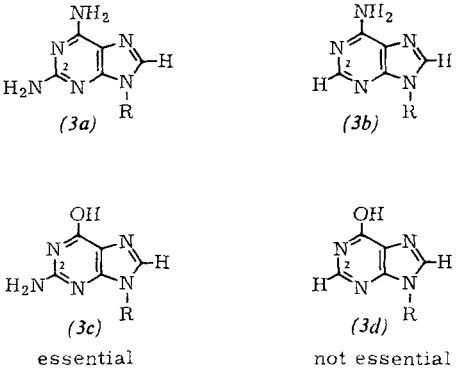
the polymerase preparation [29–31] is evidence that a reaction step is blocked that is independent of the nature of the protein.

Actinomycin does not influence the addition of the enzyme to the DNA (Fig. 1a), even at a concentration such that the overall reaction is almost completely blocked [7]. The point of attack of the antibiotic must therefore occur in a later step.

When DNA is present in excess, the degree to which the reaction is inhibited by a given quantity of actinomycin decreases with increasing DNA concentration. This indicates that the antibiotic reacts with the DNA, since the enzyme can then react with DNA that has not reacted with the antibiotic [32].

Further support for this being the case is afforded by the observation that the RNA polymerase reaction with RNA as the template is not affected by the antibiotic. Moreover, the inhibiting action is strongly influenced by the secondary structure of the DNA, since the RNA synthesis on denatured, *i.e.* largely unordered, DNA is scarcely affected by actinomycin.

The biochemical action of actinomycin also depends strongly on the base composition of the nucleic acid, *e.g.* the lower the guanine content of the DNA, the higher is the antibiotic concentration required for inhibition [27]. Particularly valuable information has been obtained from experiments with synthetic double-strand polydeoxynucleotides such as poly-d(A–T), poly-d(DAP–T), and poly-dGdC, whose sequences are also accurately read off by the polymerase. It was found that the RNA synthesis on poly-d(A–T) is completely unaffected by actinomycin, whereas the syntheses on poly-dGdC and poly-d(DAP–T) are totally suppressed. The action of the antibiotic is therefore entirely dependent upon the presence of a 2-amino grouping in the template, as in *(3a)* and *(3c)* [33].



for the action of the antibiotic (R = deoxyribose)

(3a): 2,6-diaminopurine nucleoside; *(3b)*: deoxyadenosine; *(3c)*: deoxyguanosine; *(3d)*: deoxyinosine.

The prevention of the attack on the DNA by actinomycin may be imagined as prevention of the reaction from proceeding along the template past the points with which the inhibitor has reacted. This is in agreement with the fact that actinomycin suppresses the polymerase reaction instantly, even when it is added only after the beginning of the reaction [34], and leads to the formation of short RNA chains [35].

2.3.2. Chromomycin

Chromomycin A_3 *(4)* [36] and the closely related antibiotics olivomycin and mithramycin [5] have been found to inhibit the RNA polymerase almost as strongly as actinomycin [37–39] (Table 1). The point of attack of these substances is probably again the double-strand DNA template, since the reaction with RNA as the matrix is not inhibited [28]. On the other hand, the action of chromomycin, like that of actinomycin, de-

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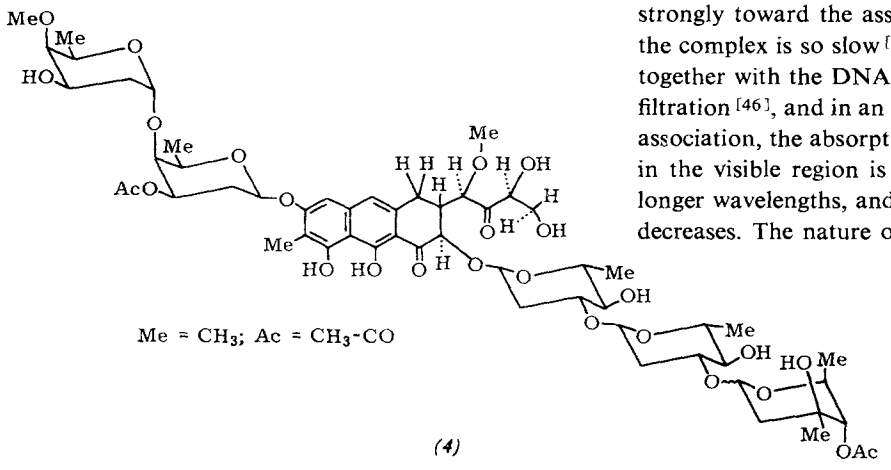

Me = CH_3; Ac = CH_3-CO

(4)

pends very strongly on the double-stranded state and on the guanine content of the DNA [39]. Experiments with synthetic polydeoxynucleotides (poly-d(A–T), poly-d(DAP–T), poly-dGdC, and poly-dIdC) have also shown that the presence of the 2-aminopurine grouping in the template is absolutely essential to the action of this group of antibiotics [28, 33]. In agreement with the hypothesis that these antibiotics also prevent the continuation of the enzyme reaction along the DNA, it is found that chromomycin inhibits the RNA synthesis immediately on addition [21].

2.3.3. Anthracyclines

The DNA-controlled RNA polymerase reaction is also inhibited by the anthracyclines [40] (*e.g.* daunomycin [41]) and related antibiotics (such as isoquinocycline [42]), the degree of inhibition being once again related to the inhibitor concentration by a hyperbolic function [37,43].

The anthracyclines, however, are distinctly less active than the other antibiotics discussed so far (Table 1). In contrast to actinomycin and chromomycin, the anthracycline antibiotics block the polymerase reaction even with RNA as the template; moreover, their action generally depends only slightly on the base composition of the DNA [28,44].

2.4. Blockage of DNA

2.4.1. Blockage with Actinomycin

The view that actinomycin and similar antibiotics act as template inhibitors is strongly supported by the observation that they can associate with DNA. The equilibrium of the complex is displaced so strongly toward the associate and the dissociation of the complex is so slow [45] that the antibiotic migrates together with the DNA on ultracentrifugation, on gel filtration [46], and in an electric field. As a result of the association, the absorption maximum of the antibiotic in the visible region is displaced by about 20 nm to longer wavelengths, and the extinction simultaneously decreases. The nature of the electric interactions that are responsible for this is not yet known [27]. It is interesting to note that actinomycin can associate, not only with DNA, but also with its degradation products such as apyrimidinic acid, simple oligonucleotides, purine nucleosides, and even β-naphthalenesulfonate; these associations are also accompanied by similar changes in the spectrum [27,45,47,48]. However, the associates differ clearly from the complex of actinomycin with native DNA, particularly in the position of the complex equilibrium and the much higher rates of association and dissociation [45,49,50].

If the inhibition of the RNA polymerase is assumed to be due to complex formation between DNA and the antibiotic, the association should exhibit the same features as the inhibitor action. This is in fact so. Thus in agreement with findings in the polymerase reaction, the antibiotic does not form a complex with single-strand or double-strand RNA [27,45].

The 2-aminopurine grouping as in *(3a)* and *(3c)*, which is essential in the DNA for the biological inhibiting action, is also necessary for complex formation with the antibiotic. The characteristic changes in the absorption spectrum occur only with poly-d(DAP–T) and poly-dGdC, and not with poly-d(A–T) or poly-dIdC [33,51]. Experiments with simple model compounds of actinomycin have shown that the specificity for the 2-aminopurine grouping is due to the chromophore of the antibiotic [45].

All the properties of the actinomycin-DNA associate can be explained on the assumption that on complex formation, the chromophore is inserted into the DNA helix horizontally above or below a guanine-cytosine base pair ("intercalation") [45, 51a].

The biological inhibiting action is probably determined by the rate of dissociation of the complex. The faster the associate can dissociate into free DNA and antibiotic, the shorter is the time during which the RNA

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polymerase is prevented from continuing the synthesis along the DNA template. It is found that the DNA complexes with biologically inactive actinomycin derivatives dissociate very rapidly, while the associates with active actinomycins dissociate only slowly [45]. The rate of dissociation of the actinomycin complex with denatured DNA, which is about ten times as high as that of the complex with native, double-strand DNA, is therefore probably responsible for the fact that the antibiotic inhibits the RNA polymerase to a much smaller extent on denatured DNA [52].

2.4.2. Blockage by Chromomycin

The ability of chromomycin to form a complex with DNA suggests that this inhibitor also acts by inactivation of the template [28, 52–56]; however, divalent metal ions such as Mg^{2+} must be added if the DNA preparation does not contain enough. The migration of the antibiotic with DNA in an electric field and on ultracentrifugation is explained by the position of the complex equilibrium

$$\frac{[\text{Chromomycin - DNA}]}{[\text{Chromomycin}]\,[\text{DNA}]} = 0.2 \times 10^6\ (\text{l/mole})$$

and the very low dissociation rate of the complex (half life approx. 110 min at 20 °C). As a result of the association, the absorption maximum of the antibiotic in the visible region is displaced by about 25 nm toward longer wavelengths. This should not be confused with the spectral changes observed on addition of heavy metal ions such as Cu^{2+} [5]. The nature of the electronic interactions is unknown.

The inhibitor properties of chromomycin are evidently determined by the complex formation with DNA, which exhibits the same features as the inhibition of the polymerase reaction. Thus the antibiotic forms associates only with DNA, and not with RNA. The observation that chromomycin has practically no inhibiting effect on the RNA synthesis on denatured DNA corresponds to the observation that chromomycin is bound to a much smaller extent on denatured than on double-strand DNA. This can be demonstrated particularly effectively with poly-dGdC. Unlike the double strand, the single strands poly-dG and poly-dC do not react with the antibiotic [44].

The DNA must contain the 2-aminopurine grouping as in *(3a)* and *(3c)* for the complex formation as well as for the inhibiting action. Experiments with synthetic polydeoxynucleotides gave results similar to those obtained for actinomycin. The specificity for the 2-aminopurine grouping is again due to the chromophore [44, 55].

The very low dissociation rate of the complex is undoubtedly very important to an understanding of the inhibition of RNA polymerase. The dissociation rates of the DNA complexes of chromomycin derivatives increase in order of decreasing enzyme-inhibiting action [52]. The chromomycin-DNA complex dissociates so slowly that it can be degraded with a mixture of deoxyribonuclease (EC 3.1.4.5), phosphodiesterase (EC 3.1.4.1), and phosphatase (EC 3.1.3.1) into smaller fragments containing chromomycin (sedimentation coefficient $s_D^{20} = 2.8 \pm 0.1$ S). The degradation stops with the formation of oligodeoxynucleotides having a guanine content of 33 mole-%. The base composition of the fragments indicates that they are double-stranded; they contain on average one bound chromomycin molecule per four pairs of bases. It can be seen from models that because of steric factors, this is the upper loading limit for the size of the antibiotic molecule, the strand segments encased by the antibiotic evidently being protected against attack by hydrolases [55].

2.4.3. Blockage with Anthracyclines

Anthracyclines also act as template inhibitors, probably because of their ability to associate with DNA. The complex formation is again accompanied by a displacement of the absorption maximum of the antibiotic in the visible range toward longer wavelengths [43, 54, 57]. However, measurements on the daunomycin-DNA complex have shown that the equilibrium is much less in favor of the complex than in the case of actinomycin, and depends strongly on the ionic strength [47, 57, 58]. This may be one reason for the low activity of these antibiotics (Table 1).

The absence of DNA-specificity in the enzyme-inhibiting actions is also found in the association, as is exemplified by daunomycin, which forms complexes, not only with DNA, but also with RNA, oligonucleotides, and mononucleotides [47, 57].

The low dependence of the inhibitor action on the base composition of the template is also seen in the associate formation, *e.g.* nogalamycin reacts almost as readily with poly-dGdC as with poly-d(A—T) [44].

2.5. Inhibition of DNA Polymerase

If the actinomycins, chromomycins, and anthracyclines act as template inactivators, they should also inhibit other reactions controlled by a DNA template, such as the DNA synthesis. The enzyme DNA polymerase (EC 2.7.7.7) catalyzes the polycondensation of deoxynucleoside triphosphates to form DNA on a DNA template in accordance with the equation

$$\begin{matrix} n_1\ \text{dATP} \\ n_2\ \text{dTTP} \\ n_3\ \text{dGTP} \\ n_4\ \text{dCTP} \end{matrix} \xrightarrow[\text{DNA-Polymerase}]{Mg^{2+},\ \text{DNA}} \text{DNA} + (n_1 + n_2 + n_3 + n_4)\text{PP}$$

the base sequence of the synthesized DNA corresponding to the sequence in the template. All antibiotics that act on the RNA synthesis by blockage of the DNA also inhibit this reaction (Table 1) [37, 38, 44] – only the

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rifamycins, which cannot associate with DNA, have no effect [17].

It is very striking that in many cases, the concentrations of base-specific inhibitors required to obtain a given effect on the DNA synthesis are much higher than those required for the same effect on the RNA synthesis (Table 1). The reason for this difference may be sought in the mechanisms of action of the two enzymes. On a partially degraded DNA helix, the purified DNA polymerase synthesizes preferentially

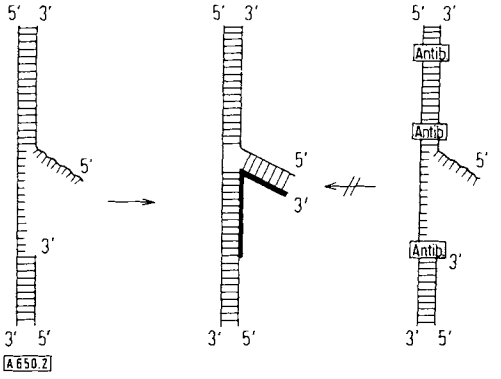

Fig. 2. Mode of action of DNA polymerase on the partly degraded DNA-double-strand and blockage of the reaction with antibiotics (Antib.) such as actinomycin or chromomycin [44, 59]. Bold continuous lines: newly synthesized strand segment.

the missing section along the remaining single strand by starting from the 3'-hydroxy end (Fig. 2). The result is the regeneration of a double strand that once more has its full biological activity [59].

The effects of actinomycin, chromomycin, and mithramycin, which are small in comparison with the inhibition of the RNA polymerase, may be explained by the observation that these give stable, slowly dissociating complexes only with the double strand. Since the enzyme begins to operate on the 3'-hydroxy end of the double strand, the antibiotics can block only the start of the reaction (Fig. 2). Inhibition can no longer be achieved merely by association with any point of a double strand, but requires specific blockage of the ends. Since antibiotics such as mithramycin associate statistically with the guanine residues in the double strand, a much higher inhibitor concentration is now necessary to suppress the reaction to the same degree as the RNA synthesis. The inhibition must depend on the guanine content of the DNA, since if there is no guanine in the end portion, the inhibitor cannot be bound there. This is in fact found [44] (Fig. 3a). It is also to be expected that part of the reaction cannot be suppressed even at very high antibiotic concentrations, since even in DNA having a high guanine content, some of the 3'-hydroxy ends are free from guanine.

The content of guanine-free ends decreases with decreasing adenine and thymine contents; consequently, the higher the guanine content of the template, the

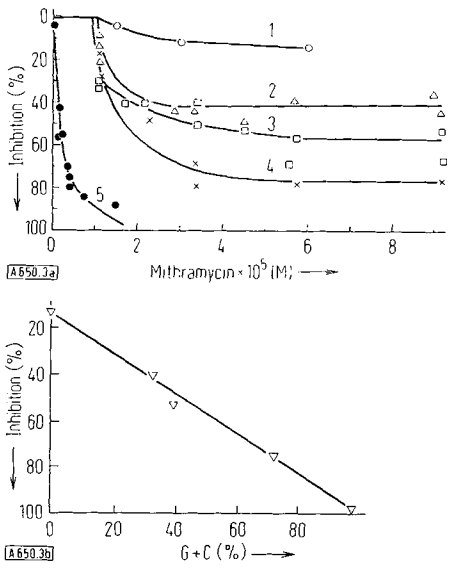

Fig. 3. a) Inhibition of the DNA polymerase reaction by mithramycin with various nucleic acids as templates [44]. 1: Poly-d(A—T), 2: T2-DNA, 3: calf thymus DNA, 4: DNA from *M. lysodeicticus*, 5: poly-dGdC. b) Dependence of the residual DNA polymerase activity at high mithramycin concentrations on the guanine + cytosine (G + C) content of the nucleic acid used [44].

greater is the degree to which the DNA synthesis can be inhibited. These predictions are confirmed by experimental results [44] (Fig. 3b).

As expected, the antibiotics having no pronounced base-specificity do not exhibit these peculiarities; they combine equally well with single-strand and double-strand DNA. Consequently, both DNA-controlled polymerase reactions are inhibited by anthracyclines in the same concentration range, and completely inhibited at higher concentrations (Table 1).

3. Inhibition of Protein Synthesis

3.1. Course of Protein Synthesis

Our knowledge of protein synthesis [60] is mainly based on the cell-free system from *E. coli*. In its essential features, however, it is also valid for other cells. It has been found that protein synthesis takes place on RNA-rich cell particles, the ribosomes, which are made up of two parts characterized by their sedimentation coefficients as 30S and 50S subunits (in the case of *E. coli*). The genetic information is transferred with the aid of mRNA. A number of soluble enzymes are also involved in the protein synthesis. The principal low molecular weight component required, apart from certain inorganic ions, is GTP. The amino acids must be present in the activated form of amino-acyl-tRNA esters. *e.g.* tyrosyl-$tRNA_{tyr}$ *(5)*. The information contained in the nucleotide code of the mRNA is read off from the ribosomes and transferred to the amino acid sequence of the protein being formed. Fig. 4 shows a highly

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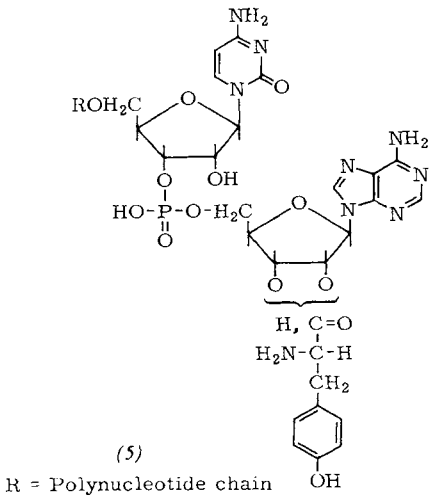

(5)

R = Polynucleotide chain

idealized picture of the reaction steps, the enzymological investigation of which is not yet complete.

Initiation: The *N*-formylmethionyl-tRNA(FM-tRNA$_F$) acting as the initiator first adds to the complex of a 30S ribosome subunit and mRNA. This reaction is enzyme-catalyzed, and is promoted by GTP [61,62] (Fig. 4a).

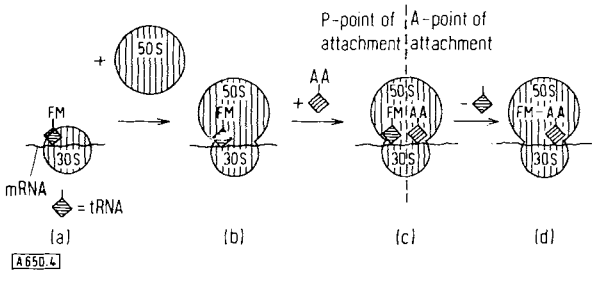

Fig. 4. Start of protein biosynthesis.

a) Addition of *N*-formylmethionyl-(FM)-tRNA to the complex of mRNA with the 30S ribosome subunit; b) addition of the 50S ribosome subunit; c) reading by addition of an amino-acyl-(AA)-tRNA to the A site of the ribosome; d) peptide transfer of the FM-tRNA bound to the P site onto the amino-acyl-tRNA added in step c. When the resulting peptidyl-(FM—AA)-tRNA has been moved to the P site and the mRNA moved in relation to the ribosome, processes c) and d) can be repeated.

Reading step: The 50S subunit adds to the complex formed in the initiation reaction to form the complete 70S ribosome with another point of attachment for activated amino acids [63] (Fig. 4b). The addition of the amino-acyl-tRNA to this point of attachment is very specifically dictated by the nucleotide triplets of the mRNA. Reaction occurs only with those activated amino acids that can interact with the mRNA section to be read off. This step determines the accuracy with which the genetic information is translated in the protein synthesis. The ribosome now carries a peptide-like activated residue (FM—tRNA$_F$) and an amino-acyl-tRNA. The P site on the ribosome (point of attachment of the peptidyl-tRNA) is distinguished from the A site (point of attachment of the amino-acyl-tRNA) (Fig. 4c).

Formation of the peptide linkage: The amino group of the activated amino acid (*e.g.* Tyr-tRNA$_{Tyr}$) attached to the A site is now enzymatically acylated by the *N*-formylmethionyl-tRNA bound to the P site.

$$\text{FM-tRNA}_F + \text{Tyr-tRNA}_{Tyr} \xrightarrow[\text{70-S-Ribosome}]{\text{attached to the}} \text{FM-Tyr-tRNA}_{Tyr} + \text{tRNA}_F$$

This reaction is enzymatically catalyzed by the peptidyl transferase located on the 50S ribosome subunit and results in the formation of the first peptide linkage with liberation of the tRNA residue of the initiator.

When the resulting dipeptidyl-tRNA has been moved to the point of attachment for peptidyl-tRNA and the mRNA moved forward, the process (reading step and formation of the peptide linkage) can be repeated. The peptidyl-tRNA takes over the role of the *N*-formylmethionyl-tRNA. In this way a long peptide chain is built up, one molecule of GTP per peptide linkage being hydrolyzed to GDP and phosphate [64].

Termination of synthesis: The reading process, and hence also the peptide synthesis, is brought to an end by an mRNA section containing a stop signal. The protein formed is released enzymatically from the terminal tRNA [65] and the ribosome dissociates again into its subunits.

Numerous antibiotics that can suppress this process on the ribosomes have recently been discovered and many of them can be distinguished by their effect on the 30S or 50S ribosome subunits, on the P or A site, or on the peptidyl transferase reaction [66–69]. Comparative studies indicate that the ribosomes of plants and bacteria clearly differ, particularly in the P sites [69].

We shall now consider the effects of antibiotics on the ribosome functions, taking streptomycin, chloramphenicol, and puromycin as examples.

3.2. Inhibitors of Protein Synthesis

3.2.1. Streptomycin

Addition of streptomycin in a concentration of 10^{-5} M to protein synthesis *in vitro* leads not only to a reduction of reaction but also to a distinct increase in error in the reading of the genetic information. With a synthetic mRNA consisting of an alternating sequence of the nucleotides UMP and GMP, the presence of streptomycin results in the incorporation of arginine

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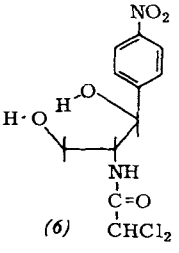
and serine into the polypeptide being formed, which normally consists entirely of cysteinyl-valine units. This and other observations indicate that the antibiotic interfers with the correct reading of the pyrimidine residues of the mRNA [70]. To find out more about the point of attack of streptomycin on the ribosome, the protein synthesis has been studied *in vitro* with genetically different ribosome subunits obtained from streptomycin-resistant or streptomycin-sensitive bacteria. It was found that the reading error in the presence of streptomycin is due to a protein of the 23S-ribonucleoprotein from the 30S ribosome subunit [71].

In agreement with this, other experiments have shown that streptomycin is bound to the 30S ribosome subunit [72], which must therefore be assumed to contain the primary point of attack. The reading errors and the decrease in protein synthesis that is also very often observed can be explained by the assumption that the configuration of the ribosomes is altered by streptomycin. The protein synthesis can still take place, but the high specificity of the interaction between the amino-acyl-tRNA and the mRNA on the ribosome is changed [73]. Thus streptomycin modifies the biological action of the template. Its effect is indicative of the active role of the ribosomes in the reading process.

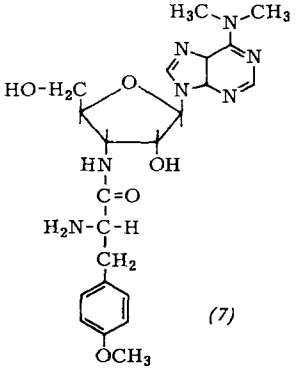
The changes caused by streptomycin in the amino acid sequence of the protein may not be confined to negative effects such as a decrease in the synthesis of an active enzyme. This has been very clearly demonstrated in the case of *E. coli* mutants that can no longer synthesize active ornithine transcarbamylase (EC 2.1.3.3). The addition of streptomycin to the culture medium reinitiates the synthesis of small quantities of the active enzyme [74]. In this case streptomycin is phenotypically equivalent to a suppressor mutation.

3.2.2. Chloramphenicol

The point of attack of many antibiotics on protein synthesis is in the 50S ribosome subunit. One antibiotic of this type is chloramphenicol *(6)* [75].



(6)



(7)

Experiments with the radioactively labeled antibiotic have shown that it is preferentially bound by the 50S subunit of the 70S ribosomes. This is observed only with the biologically active D(−)-*threo* isomer of the antibiotic. Thus the binding reaction exhibits the same stereospecificity as the inhibiting action on protein [76, 77].

Other antibiotics that also inhibit protein synthesis often interfere with the addition of chloramphenicol to the 50S subunit. This provides evidence of the point of attack of these antibiotics [66].

It is interesting to note that chloramphenicol, like some other inhibitors of protein synthesis, is species-specific in its action. Some types of cells that (like yeast or reticulocytes) contain 80S instead of 70S ribosomes cannot bind chloramphenicol [76]. The protein synthesis system with 80S ribosomes is accordingly insensitive to this antibiotic [78]. Ribosomes of different species can thus have different structures though their mode of action is fundamentally the same. This state of affairs is reminiscent of the different effects of rifamycins (and streptovaricins) on the RNA polymerases of different organisms [19, 20].

A clear indication of the mutual effects of the components in the ribosome complex is provided by the observation that the extent of the inhibiting action of chloramphenicol depends on the composition of the mRNA [79].

The manner in which chloramphenicol acts on the 50S ribosome unit has not yet been established; however, it may be concluded from results obtained with the antibiotic puromycin that it blocks the peptidyl transferase [80].

3.2.3. Puromycin

The addition of puromycin *(7)* to protein syntheses leads, not only to strong inhibition of the reaction, but also to the liberation of small peptide fragments [81]. The antibiotic is bound by an amide linkage of the amino group of its *O*-methyltyrosine residue with the carboxyl end of the peptide [82,83]. This is understandable in view of the structural resemblance of puromycin to the end portion of an amino-acyl-tRNA [*e.g.* tyrosyl-tRNA *(5)*] [84]. It acts on the A site of the ribosome, evidently as an inactive analog (antimetabolite) of an activated amino acid and in this role behaves as a competitive substrate for the peptidyl transferase and

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takes over the activated peptide residue, which is thus released from the ribosome [85]. The correctness of this

$$H_2N\text{-Peptide-CO-tRNA} + NH_2\text{-Puromycin} \xrightarrow{\text{Ribosome}} H_2N\text{-Peptide-CO-NH-Puromycin} + \text{tRNA}$$

view has been demonstrated with simple, chemically synthesized model compounds of puromycin, such as 2′(3′)-*O*-phenylalanyladenosine. Compounds of this type also act as acceptors for the transferred peptide in the peptidyl transferase reaction [86]. Since no interactions of a further tRNA with the ribosome or the mRNA are necessary in this case for the formation of a peptide linkage, the puromycin reaction is the isolated reaction step of the natural peptide formation. Addition of the initiator *N*-formylmethionyl-tRNA, which is the simplest peptide-like substrate of the P site, leads to the simple dipeptide *N*-formylmethionyl-puromycin [62].

Very simple model compounds of activated peptides, such as the trinucleotide cytidylyl(3′→5′)cytidylyl-(3′→5′)-2′(3′)-*O*-(*N*-formyl)methionyladenosine (abbreviation CCA–FM), are biochemically active substrates of the P sites. The compounds correspond to the adenosine end portion of the *N*-formylmethionyl-tRNA and with them the natural peptide formation can be caused to proceed on the 50S ribosome subunit with puromycin as the acceptor in accordance with the equation

$$\text{CCA–FM} + \text{Puromycin} \xrightarrow[\text{ethanol}]{\text{50S Ribosome}} \text{FM-Puromycin} + \text{CCA}$$

the product being *N*-formylmethionylpuromycin. This isolated peptidyl transferase reaction (fragment reaction) does not require the presence of GTP, tRNA, mRNA, the 30S ribosome subunit, or soluble enzyme. Ethanol, however, must be added [87–89].

Since chloramphenicol and some other antibiotics prevent this reaction, it may be concluded that the point of attack of these inhibitors is the peptidyl transferase [80,90].

4. Outlook

Caution must be exercised in drawing conclusions on the basis of *in vitro* experiments on the action of antibiotics that can lead to damage or death of the cell *in vivo*, since the nucleic acid and protein syntheses are related in a very complex manner, not only with each other, but also with other metabolic reactions in the cell. Cells of different types undoubtedly differ considerably in the degree and nature of the coupling. Thus it is not yet possible to predict the points in the cell metabolism at which even small disturbances in the transmission of the genetic information can have serious consequences. Finally, it is not possible *a priori* to rule out the possibility that the antibiotics in question inhibit other enzyme reactions. This will depend on the concentration of the inhibitor in the cell.

The biochemical importance of the antibiotics discussed here, as well as of many others, lies in the fact that owing to their widely differing modes of action, they are excellently suited for the investigation of the course of the important template-controlled processes in the transmission of genetic information.

It is particularly interesting to note that some inhibitors (actinomycin, chromomycin, streptomycin) are to some extent template-dependent, *i.e.* information-specific, in their action. It seems appropriate to compare these to the repressor proteins, which regulate the RNA synthesis in the cell [91]. Analogies of this nature have raised hopes of finding low molecular weight substances capable of permeating into cells, by means of which information-controlled syntheses (such as the multiplication of viruses in host cells) may be selectively suppressed. Inhibitors of this type could be of great interest in medicine.

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Replacement of Plasma by High Molecular Weight Substances[**]

BY W. APPEL AND E. BIEKERT[*]

In the course of the development work, natural and synthetic polymers were examined to see whether they were suitable for use as plasma substitutes. The criteria of a plasma substitute are discussed in this connection. The most important of the base substances used at present (dextran, modified gelatin, polyvinylpyrrolidone, and hydroxyethyl starch) are described, and a typical example of proven therapeutic value is discussed for each type.

1. Introduction

A group of medicaments that have grown in importance during recent years are substances whose aqueous solutions can be introduced directly into the blood stream in quantities of up to several liters. This "infusion therapy" may be used for widely different therapeutic purposes, such as the replacement of lost fluid, of salts, or of biological material, or for the introduction of nutrients, active substances, or drugs. The present article deals only with preparations intended to compensate for loss of blood. The development of these blood "substitute solutions" will be illustrated by the case of dextran, which has been extensively studied and is generally accepted as a plasma substitute.

The most satisfactory "blood substitute" is whole blood. However, blood transfusions, which have become routine operations in all hospitals (blood banks), have certain disadvantages. Though the fatality rate in blood transfusions, which was initially appreciable, has now been reduced almost to zero, even the most careful determination of blood groups and subgroups before the transfusion can never entirely rule out the possibility of incompatibility between the blood of the donor and that of the receiver. The greatest risk, however, is the transfer of pathogenic microorganisms, and 12–17.5% of all whole blood transfusions are followed by hepatitis that is directly attributable to the transfusion.

Since whole blood can only be stored for an average of about three weeks, in spite of stabilization with sodium citrate, blood plasma came into use as a substitute. Plasma, in the fresh, deep-frozen, aged (stored at 32 °C), and particularly freeze-dried states, is one of the most frequently used of the natural blood substitutes. In Switzerland, for example, lyophilized plasma from a single donor is often preferred, whereas aged pool plasma is preferred in the USA; only fresh plasma is used in Sweden. All forms of plasma, however, still carry the risk of hepatitis. The situation is improved to some extent by the use of pasteurized albumin solutions.

One important reason for the switch from whole blood to plasma was the recognition of the existence of the "shock syndrome". Of more than 100 forms of shock that have been described, the only form of interest in this connection is "hemorrhagic" shock, *i.e.* shock resulting from loss of blood. This is the syndrome of an acute hemodynamic disturbance due to such a severe loss of blood that the metabolic processes in important tissues are upset, with the result that functional, and later morphological, disturbances arise.

The use of plasma instead of whole blood is vindicated by the discovery that in cases of loss of blood, the important thing is not the replacement of the shaped blood elements (red and white blood cells and platelets), but the replacement of the lost volume of fluid.

The therapeutic requirement of ready availability, in sufficiently large quantities, of a substitute for lost liquid led to the further development of plasma substitutes. To satisfy the requirements of ready availability, *e.g.* for rescue operations in remote areas or for emergency treatment at the scene of an accident with restricted possibilities for blood-group determination, as well as availability in sufficiently large quantities for such situations as catastrophes or multiple accidents, make it essential that the solutions should have a reasonable storage life. It was only with the use of synthetic colloidal plasma substitutes with storage lives of several years that an adequate stock could be built up.

2. Requirements for Synthetic Colloidal Plasma Substitutes

We shall now discuss some of the properties that are required in a plasma substitute. There are as yet no known substances that satisfy all these requirements.

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[**] For a collection of the literature see: *U. F. Gruber*: Blutersatz. Springer-Verlag, Heidelberg 1968; *U. Behrens* and *M. Ringpfeil*: Mikrobielle Polysaccharide. Akademie-Verlag, Berlin 1964; *A. A. Bagdassarow* and *A. W. Guljajew*: Bluttransfusion. VEB Verlag Volk und Gesundheit, Berlin 1958; *H. Bürkle de la Camp*, Arch. klin. Chir. *273*, 258 (1953); *A. Grönwall*: Dextran and its Use in Collodial Infusion Solutions. Almqvist and Wiksell, Stockholm 1957; *W. Reppe*: Polyvinylpyrrolidon. Verlag Chemie, Weinheim 1954; *F. Patat*: Zur kinetischen Analyse von Enzymreaktionen. Die Bildung der Dextransucrase. Dechema-Monographien, Vol. 29, Verlag Chemie, Weinheim 1957; *D. Tourtelotte* and *H. E. Williams* in *Stainsby*: Recent Advantages in Gelatine and Glue Research. Pergamon Press, London 1957, p. 246.

1. Synthetic colloidal substances intended for use as plasma substitutes must have an adequate colloid-osmotic effect.

2. The colloid should be compatible and nontoxic. It must not be stored in the body, but should be excreted as such or after metabolic transformation. It must not influence or damage any organ, even on repeated administration. In particular, the colloid must not interfere with the kidney function, the performance of the heart, or the biosynthesis of plasma proteins in the liver, or lead to metabolic acidosis.

3. The plasma expander solution prepared from such a colloid should be capable of being administered in concentrations such that its colloid-osmotic pressure corresponds to that of normal blood plasma.

4. The viscosity of such a solution should permit easy intravenous application, and should not impose additional work on the heart muscle.

5. When administered by infusion following loss of blood, about 50% of the solution should remain in the blood stream for at least six, and preferably twelve, hours.

6. In the doses used, the solution should not affect the clotting of blood, and must not cause aggregation or lysis of red or white blood cells (erythrocytes or leucocytes). Above all, it must not interfere with the determination of blood groups.

7. It should not cause allergic reactions or fever. The solution should not have any antigenic action, cause any sensitization, or affect the resistance to infection. It must be sterilizable and free from contamination by viruses.

8. It must be possible to produce the solution fairly cheaply on the industrial scale with constant and fixed properties, and to store it for several years.

Since the use of a substance as a drug requires a constant quality guaranteed by the manufacturer, all drugs are subjected to rigorous final checks. In the case of colloids, these checks are largely based on the analytical methods of polymer chemistry. The purity requirements are particularly high for plasma substitutes, since these, unlike other drugs, must be administered directly into the blood stream in doses of 50 g or more. The purity of the other substances present is also important, *e.g.* the quality of the water used as the solvent, which is introduced into the blood stream in liter quantities. Industrial production depends on freedom from pyrogens, *i.e.* the absence of febrifacient bacterial metabolites, since the entire process must be carried out under sterile conditions. Sterilization of the final solution is not enough, since though any bacteria present would be killed, their metabolites would remain in the solution and would not be inactivated, so that they would still be capable of acting as pyrogens.

2.1. Terminology

The terminology includes a number of terms whose meanings partly coincide, such as blood substitutes, plasma substitutes, plasma volume expanders, or plasma expanders. It should be noted that the term "blood substitute" cannot be used of any synthetic substance, since there are as yet no true blood substitutes, *i.e.* nothing can replace the transport of oxygen by red cells (erythrocytes). The term "expander" should be confined to substances that give the effect of a volume greater than that actually introduced. Since the expander effect is time-dependent because of the elimination of the substance by the kidneys, no definition characteristic of these substances can be derived on this basis. The most suitable term in our opinion is "plasma substitute", which means solutions that normalize a diminished blood volume for a time after intravenous infusion, and can take the place of the plasma components of blood.

3. Physico-Chemical Characterization of Synthetic Colloids

The following discussion refers to all colloids that can be used as plasma substitutes. These colloids are mixtures of molecules having different molecular weights, which are characterized by the molecular weight distribution.

To determine this quantity, the polymeric mixture must be broken down analytically into more homogeneous fractions, and the concentrations and molecular weights of these fractions are subsequently determined. If the fractionation is sufficiently fine to give monodisperse fractions, all molecular weight determination methods give the same value. However, this is not usually the case; the resulting values are therefore known as average molecular weights $\overline{M}$. In the investigation of colloidal plasma substitutes, it is generally satisfactory simply to determine $\overline{M}$.

1. The weight average molecular weight $\overline{M}_w$

$$\overline{M}_w = \Sigma n_i M_i^2 / \Sigma n_i M_i$$

is obtained by methods that depend on the weight of the molecules present, *e.g.* by measurement of sedimentation (ultracentrifuge) or diffusion (light scattering). Both methods, and particularly the second, have proved valuable for routine measurements on colloidal plasma substitutes.

2. The number average molecular weight $\overline{M}_n$

$$\overline{M}_n = \Sigma n_i M_i / \Sigma n$$

is obtained by methods that depend on the number of molecules present. These include osmometry, chemical end-group analysis, and at low degrees of polymerization cryoscopic, ebullioscopic, and vapor pressure measurements.

The frequently used measurement of viscosity is not an absolute method. The viscosity average molecular weight $\overline{M}_v$

$$[\eta] = K \cdot \overline{M}^{\alpha}$$

is strongly dependent on other factors such as the degree of branching. The constants α and K in the above relationship ("Staudinger" equation) must be determined separately for each plasma substitute. $[\eta]$ in this equation is the intrinsic viscosity.

$\overline{M}_w$ and $\overline{M}_n$ have different values for polydisperse substances. The ratio $\overline{M}_w/\overline{M}_n$ gives an indication of the uniformity of the colloid. However, the plasma substitutes can only be accurately characterized by the molecular weight distribution.

The "rapid fractionation method" introduced by *Schulz*[1] is sufficient for practical purposes. In this case an upper and a lower fraction are separated and their weights and degrees of polymerization are determined. In the case of dextran, these values are determined by the A.D.M.P.D. method[*].

4. Historical Development of Plasma Substitutes

As early as 1667, *Denis* described a successful transfer of lambs' blood to human beings. However, this method was soon abandoned because of its serious side effects such as ague or hematuria[2]. Animal blood was again widely used for transfusions in 1870 and 1871 (*Landois*[3]) until it was realized that the side effects could only be reduced by the transfusion of homologous blood. It was later found that in cases of severe loss of blood, life can be saved, in principle, not only by the administration of blood, but, alternatively, by the intravenous application of a liquid. After *Landerer*'s first successful experiments on humans[4], infusions were carried out first with 0.9% sodium chloride solutions, which are isotonic with blood ("physiological saline"), and later with solutions of other electrolytes. This method has proved itself over the decades, and has enjoyed a recent vigorous revival in the USA. However, the use of electrolyte solutions is limited by the rapid elimination of these substances by the kidneys[5].

The search for better plasma substitutes became more pressing during the first world war. *Bayliss*, one of *Starling*'s co-workers, revived the animal experiments by *Ludwig* (1863) and *Morawitz* with gum arabic, and in 1916 he introduced gum arabic preparations as additives for electrolyte solutions[6]. Though these solutions, as expected, remain in the blood stream for a longer time, the foreign protein that is always present causes side reactions, so that this substance never became widely used. At about the same period, *Hogan*[7] (1915) and *Robertson*[8] (1918) tested gelatin as a plasma substitute. The difficulty of sterilization, the presence of allergens, and the fact that the substance is solid at room temperature made further development necessary, and a modified gelatin was finally introduced in 1962[9].

The use of preserved whole blood was extensive in the Spanish civil war and at the beginning of the second world war. Efforts, particularly in the USA, were then directed toward the development of plasma preparations (fresh plasma, stored pool plasma, dry preserved plasma, plasma fractions), as well as the testing of other natural polymers and the development of suitable synthetic polymers. These investigations led to polyvinylpyrrolidone (1943)[10], dextran (1947)[11], and the modified gelatins mentioned above (1962). A modified starch proposed by *Wiedersheim*[12] in 1957 is at present undergoing extensive clinical trials.

The most important and most interesting plasma substitutes are probably solutions of dextrans, modified gelatins, polyvinylpyrrolidone (PVP), and modified starch. One representative commercial preparation of each of these types will now be discussed in detail.

5. Dextrans

5.1. General

During the last century, the syrups in European sugar factories were frequently found to become slimy. This phenomenon was greatly feared because of the resulting serious disturbance of production. The polysaccharide character of the slime was recognized by *Vauquelin*[13], who described it as a variety of cellulose. In 1869 *Scheibler*[13] coined the name "dextran", because of the strong optical dextrorotation of the polysaccharide. *Pasteur*[13] demonstrated the microbial origin of dextran in 1861. In 1878 *Van Tieghem*[13] gave the dextran-forming microorganisms the generic name "Leuconostoc", since the bacteria, like the green algae nostoc, frequently link up to form long, but colorless, chains.

It was realized during the next few decades that the ability to synthesize polysaccharides is very widespread among microorganisms. In 1930, *Hucker* and *Pederson*[14] assigned most of the dextran-forming microorganisms to the family Coccaceae, species *Streptococcaceae*, genus *Leuconostoc*. The most important species are *L. mesenteroides* and *L. dextranicum*. They liberate fructose from cane sugar with formation of a polyglucoside, the degree of branching of which differs with the type of bacterium. Polymerization to form dextran is brought about by dextransucrase, an extracellular bacterial enzyme. Dextran can therefore also be produced by direct synthesis with a cell-free enzyme extract. The first work on this synthesis was carried out by *Hehre* and *Sugg*[14], who also recognized that the presence of sucrose is a necessary and sufficient condition for the formation of dextran.

In 1943, *Grönwall* and *Ingelmann*[11] in Sweden prepared a partly hydrolyzed, fractionated dextran having a molecular weight of about 100000, which largely satisfied the clinical requirements for a plasma substitute, particularly since the α-1,6-glucoside linkage in the linear dextran molecule cannot be cleaved by the α-amylase in the body. This "clinical" dextran rapidly grew in importance, and is now produced industrially.

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[1] *G. V. Schulz*, Makromolekulare Chem. *5*, 83 (1950).

[*] A.D.M.P.D.: American Defense Medical Purchase Description, U.S. Navy Supply Depot (Code 1051), 1965.

[2] According to *H. Weese*, Pharmazie *8*, 337 (1948).

[3] According to *H. Weese*, Lecture at the Med. Akademie Düsseldorf 1946.

[4] According to *H. Lampert*, Hippokrates *10*, 264 (1951).

[5] *E. H. Starling*, J. Physiology *19*, 312 (1895/96).

[6] *W. M. Bayliss*, Proc. Roy. Soc. (London), Ser. B *89*, 381 (1916).

[7] *J. J. Hogan*, J. Amer. med. Assoc. *64*, 721 (1915).

[8] *T. B. Robertson*, Brit. med. J. *477*, 691 (1918).

[9] *J. Schmidt-Thomé*, *A. Mager*, and *H. H. Schöne*, Arzneimittel-Forsch. *12*, 378 (1962).

[10] *G. Hecht* and *H. Weese*, Münchener med. Wschr. *I*, 11 (1943).

[11] *A. Grönwall* and *B. Ingelman*, Nordisk Med. *21*, 247 (1944).

[12] *M. Wiedersheim*, Arch. int. Pharmacodynam. Thérap. *111*, 353 (1957).

[13] According to *U. Behrens* and *M. Ringpfeil* (see p. 702, collected literature).

[14] *E. J. Hehre* and *Y. Sugg*, J. exp. Medicine *75*, 339 (1962).

5.2. Synthesis of Clinical Dextran

Whereas the strain *L. mesenteroides* B7E, *inter alia*, was formerly used for the synthesis of crude dextran, the strain B 512 F is now used almost exclusively. The enzymatic synthesis with partly or highly purified dextransucrose has not yet achieved any industrial importance, nor has the method devised by *Behrens* and *Ringpfeil*[13], in which sucrose is subjected to controlled bacterial polymerization with the addition of a small quantity of very uniform clinical dextran of the desired molecular weight as an initiator.

$$n\,C_{12}H_{22}O_{11} \rightarrow (C_6H_{10}O_5)_n + n\,C_6H_{12}O_6$$

Saccharose — Dextran — Fructose

Dextran is not formed after the manner of a phosphorylase-catalyzed reaction in which energy is supplied; the energy required for the synthesis is provided instead by the high-energy bonds of the sucrose. The enzymatic synthesis itself proceeds by the insertion mechanism[15]. The culture medium, which contains the nutrients necessary for the growth of the bacteria and the buffer substances needed to keep the pH value within the most favorable range, thickens in the course of a few days to a viscous mass, whose viscosity maximum coincides with the maximum yield. The native dextran is precipitated with methanol, ethanol, or acetone and then isolated. In the next step the dextran must be partly depolymerized. Acid hydrolysis is used almost exclusively in the industrial process; for special purposes, and in particular for the preparation of small quantities of highly fractionated dextrans, the native dextran can be degraded by ultrasonic radiation or enzymatically with dextranase.

The hydrolysis mixture has a very wide molecular weight distribution, and is unsuitable for clinical use. The product can be further fractionated by precipitation with ethanol or acetone, since the solubility of dextran in organic solvents decreases with increasing molecular weight. Both the absolute position and the width of the molecular weight distribution can be fixed by the choice of hydrolysis conditions (concentration and nature of the acid, temperature, pressure, time) and the precipitation conditions (alcohol concentration, time).

5.3. Chemistry, Structure, and Properties of Dextrans

Dextrans consist of a chain of glucose molecules joined by glycoside linkages (Fig. 1). Other linkages are also present in varying numbers, particularly between C (1) and C (3) or C (4). The degree of branching depends almost exclusively on the type of dextran-producing organism used. Native dextran has a molecular weight

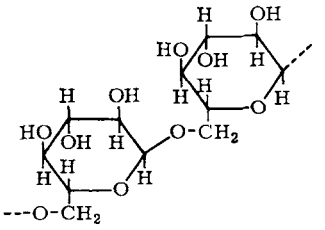

Fig. 1. Part of an unbranched dextran chain.

of 10^7–10^8, and exists in aqueous solution as an unoriented coil. A molecular weight of less than 10^6 in conjunction with a helical conformation has recently been discussed[16]. Native dextran forms highly viscous, structured solutions in water, and these solutions do not mix readily even with water.

Clinical dextran consists of filamentous molecules consisting of about 200–450 glucose units and with about 15–30 branching points. The molecules are electrically neutral, and are hydrated in aqueous solution. The filamentous arrangement of the chains allows high flexibility.

Table 1 shows physico-chemical data for two dextrans available for clinical use.

Table 1. Physico-chemical data for Macrodex® (dextran 60) and Rheomacrodex® (dextran 40) (Producers: Knoll AG, Ludwigshafen and AB Pharmacia, Uppsala).

	Macrodex®	Rheomacrodex®
Molecular weight		
Weight average $\overline{M}_w$	60000	40000
Number average $\overline{M}_n$	30000	25000
Viscosity average $\overline{M}_v$	50000	32000
Intrinsic viscosity $[\eta]$	0.230	0.190
1,6-Bonding (%)	> 93	> 93
$\overline{M}_w/\overline{M}_n$	2.0	1.6
Molecular weight distribution		
Higher peak fraction, 10%	< 110000	< 70000
Lower peak fraction	> 20000	> 15000

The molecular weight distributions of three dextran 60 preparations are shown in Figure 2, which illustrates the differences that can exist between nominally equivalent preparations. Table 2 shows the properties of Macrodex® and Rheomacrodex® infusion solutions.

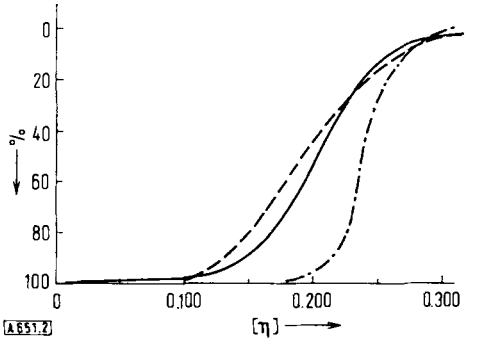

Fig. 2. Molecular weight distributions of three dextran 60 preparations.
ordinate: weight portion in %.
abscissa: intrinsic viscosity $[\eta]$

[15] *K. H. Ebert* and *F. Patat*, Z. Naturforsch. *17b*, 738 (1962).

[16] *K. H. Ebert*, Mh. Chem. *98*, 1128 (1967).

Table 2. Properties of infusion solutions of Macrodex® and Rheomacrodex® [a].

	Macrodex®	Rheomacrodex®
Concentration (%)	6	10
η_{rel} (37 °C)	*ca.* 3.4	*ca.* 5.4
Na^+ (m equiv./l)	154	154
Cl^- (m equiv./l)	154	154
Blood isooncotic concentration [b] (g/100 ml)	3.91	3.42
Oncotic pressure (mm H_2O)	920	2600
Water bonding capacity (ml H_2O/g dextran) [c]	25.6	29.2
pH	5.1–5.7	4.5–5.6
Titration acidity (ml 0.01 N NaOH/50 ml solution)	< 2.0	< 2.0

[a] Solutions with added glucose, sorbitol, or electrolytes are prepared for special purposes.

[b] The blood isooncotic concentration is that concentration of a substance that gives the same oncotic pressure as blood.

[c] Volume of water bound at the indicated concentration by a polymer molecule (dextran) that cannot diffuse through a semipermeable membrane.

5.4. Clinical Use

The clinical dextrans are designated dextran 20, 40, 60, 75, 80, and 120, according to their M_w values (20 = average molecular weight of 20000 *etc.*). The grades first commonly used in clinical work were dextrans 60, 75, and 80. Dextran 40 has also attained some importance in recent years, since it gives excellent results in the treatment of shock, particularly hemorrhagic shock.

This circulatory failure is largely due to disturbances of the microcirculation in the tissue and in the periphery. The inadequate perfusion that occurs in cases of shock is a result of aggregation of the red blood cells, and partly of the platelets; the capillaries are consequently "blocked", and the flow of blood reduced. Long persistence of this state can have catastrophic results (cell metabolism). Dextran 40 is able to break down these aggregates ("deaggregating action") and so improve or restore the blood supply in the peripheral blood vessels (flow improvement).

Recognition of the factors involved in shock greatly widened the scope of therapeutic methods. Possible applications include traumatic, toxic, protracted, hemorrhagic, and burn shock prevention and treatment of after-effects such as hepatorenal syndrome, oliguria, thrombosis, and fat embolism, and operations on cachectic or old patients, extracorporeal circulation, hypothermia, and vasular operations.

5.5. Biochemistry and Pharmacology of Dextrans

The greater part of a parenterally administered dose of dextran is eliminated by the kidneys. The renal threshold occurs at a molecular weight of about 50000. In the case of dextran 40, about 60% are eliminated in 6 hours and about 70% in 24 hours. The fate of the remaining dextran in the organism has been established with the aid of ^{14}C-labeled dextran. About 90% of the quantity infused are eliminated within 10 days, 64% in the urine and 26% as CO_2 in exhaled air. Approximately 2% appear in the feces.

Ebert et al. [17] recently carried out an enzymatic synthesis of dextran from ^3H-labeled sucrose. Hydrolytic degradation of the dextran with ultrasonic radiation gave the desired average molecular weight. The preparation was then divided into the clinical fractions.

Experiments with several types of animals showed, in agreement with literature data, that dextran is not stored in the body. Temporary storage, *e.g.* in the liver, skin, or kidneys, causes no pathological cell changes or disturbances of the organ function. Water was found as the metabolic end product in urine condensate and in the exhaled air. It should be mentioned, however, that these observations apply only to highly fractionated clinical dextran of an optimal molecular weight range, such as Rheomacrodex.

The enzymatic degradation of dextran by a dextranase (α-dextran-1,6-glucosidase) present in animal organs has also been detected in humans. *Saenko* and *Rosenfeld* [18] found dextranase in liver, kidneys, and spleen. Depending on the residence time of the dextran administered, partially degraded dextrans are formed first, and these are then completely degraded to glucose; thus enzymatic hydrolysis of α-1,3-linkages occurs. The enzyme can be induced in the liver by repeated doses of dextran and hydrocortisone. A dextranase activity has recently also been found in canine serum.

6. Gelatins

Pure gelatin solutions are unsuitable for infusion purposes. The first modified gelatin was a polyhydroxygelatin developed by *Campbell* [19] in 1951 (Gelifundol®). In 1954, *Tourtelotte* [20] prepared a depolymerized "modified liquid gelatin" containing succinic acid, which is marketed as Plasmagel®. Probably the most important gelatin preparation in Germany today is a urea-crosslinked, partly degraded gelatin described by *Schmidt-Thomé et al.* [9] in 1962 (Haemaccel®).

The gelatin in Haemaccel is obtained from bovine bone gelatin having an average molecular weight of about 100000. The gelatin molecules have a rod-like structure. The material is thermally degraded to polypeptides having a $\bar{M}_w$ of 12000–15000, which are crosslinked with isocyanate (Fig. 3).

A 3.5% aqueous Haemaccel solution (pH = 7.1) contains 145 mequiv of Na^+, 5.1 mequiv of K^+, 12.5 mequiv of Ca^+, and 162.5 mequiv of Cl^- per liter, and has an oncotic pressure of 350–390 mm H_2O. The molecules are approximately globular. The average half-life of such a solution is about 4 hours, the substance being eliminated largely unchanged by the kidneys. A minor portion may be enzymatically degraded by body proteinases of the cathepsin type; past experience suggests that it is not stored in the body. No

[17] *K. H. Ebert, G. Schenk,* and *R. Scholz,* Z. klin. Chem. u. klin. Biochem., in press.

[18] *A. Ss. Saenko* and *E. L. Rosenfeld,* 3rd Pan-Soviet Conference on the Chemistry and Metabolism of Carbohydrates, Moscow, 1963.

[19] *D. H. Campbell, J. B. Kowpfli, L. Pauling, N. Abrahamsen, W. Dandliker, G. A. Feigen, F. Lanni,* and *A. Le Rosen,* Texas Rep. Biol. Med. *9,* 235 (1951).

[20] *D. Tourtelotte,* 5e Congr. int. Transf. sangu, Paris 1954.

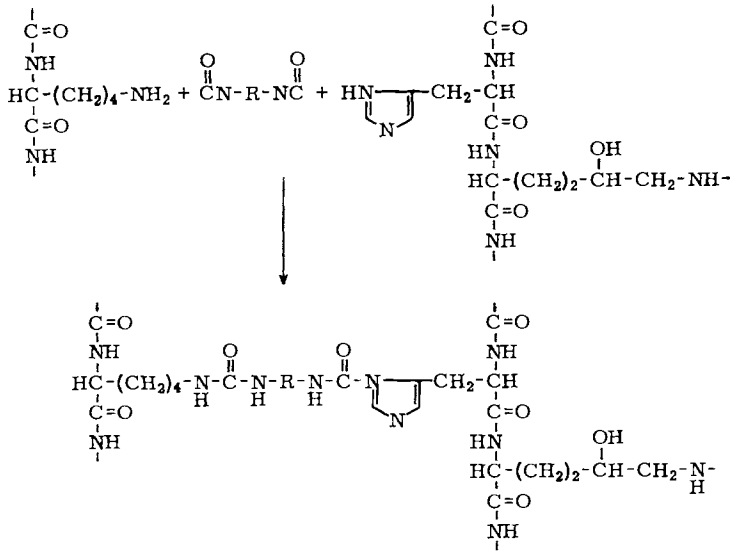

Fig. 3. Crosslinking of two peptide chain segments of bovine bone gelatin with diisocyanate.

Table 3. Physico-chemical data for Haemaccel (according to data provided by the manufacturer, Hoechst-Behringswerke, Marburg/Lahn).

Weight average mol. wt. $\overline{M}_w$	35000 [a]
Number average mol. wt. $\overline{M}_n$	15000 [21]
$\overline{M}_w/\overline{M}_n$	2.3
Relative viscosity η_{rel}	1.7–1.8
Isoelectric point, pH	4.5–5.0

[a] Determined from light scattering measurements and from sedimentation and diffusion constants.

disturbances of organ functions, blood clotting, or blood group diagnosis, antigenic action, or other general or local incompatibilities have been observed. For its effectiveness as a plasma expander *in vitro* and in animals, as well as therapeutic results, particularly in comparison with dextran preparations, the reader is referred to the special literature [21a]. So far as is known at present, gelatin derivatives do not cause deaggregation of erythrocytes and apparently have no effect on the microcirculation in the treatment of shock.

7. Polyvinylpyrrolidone

At the beginning of the second world war, many synthetic polymers were examined for use as plasma expanders. Extensive clinical tests showed that polyvinylpyrrolidone (PVP) was suitable, and this polymer was introduced into therapy in 1943 by *Hecht* and *Weese* [10] under the trade name Periston®. (PVP was also marketed for the first few years under the name Kollidon®.)

The starting material for the preparation of PVP is pyrrolidone, which is converted into *N*-vinyl-2-pyrrolidone by *Reppe* vinylation [21b] and polymerized to PVP. Some physico-chemical data for this substance are given in Table 4.

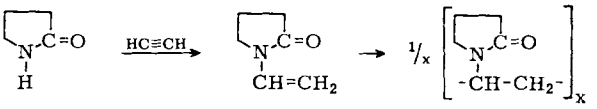

Table 4. Physico-chemical data for Periston® (from data provided by the manufacturer Farbenfabriken Bayer, Leverkusen, and by *Scholtan* [22]).

Weight average mol. wt. $\overline{M}_w$	25000–30000 [a]
Number average mol. wt. $\overline{M}_n$	15000 [21]
$\overline{M}_w/\overline{M}_n$	1.7–2.0
Relative viscosity η_{rel}	2.0
Highest molecular portion, $\overline{M}_w$	80000

[a] Determined from sedimentation and diffusion constants and from viscosities. Until 1952, Periston having $M_w = 50000$ was commercially available.

A 4% aqueous solution (pH = 6) contains 0.70 g of NaCl, 0.042 g of KCl, 0.05 g of $CaCl_2$, 0.0005 g of $MgCl_2$, and 0.025 g of $NaHCO_3$ per 100 ml of solution, and has an oncotic pressure of 670 mm H_2O. The filamentous molecules exist in the solution as coils having an average diameter of about 100 Å. The molecular weight distribution is shown in Figure 4.

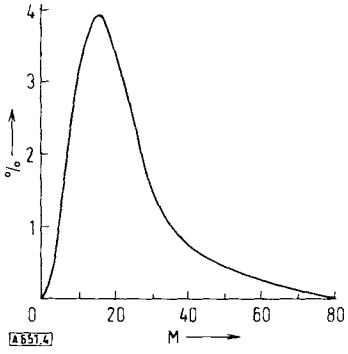

Fig. 4. Molecular weight distribution of Periston® according to information provided by the manufacturer.
Ordinate: weight portion in $\% \cdot 10^3$.
Abscissa: molecular weight $M \cdot 10^3$.

[21] *K. Granath* and *R. Strömberg*, Anaesthesist *17*, 224 (1968).
[21a] Cited by *U. F. Gruber* (see p. 702, collected literature).
[21b] See p. 702, collected literature.

[22] *W. Scholtan*, Makromolekulare Chem. *8*, 209 (1951); *36*, 162 (1960).

In spite of its good volume-expanding effect, PVP has now been pushed somewhat into the background, since objections have been raised to the use of completely synthetic polymers. A particularly significant question is that of the storage of PVP in the organism [23]. 80% of the material infused is eliminated by the kidneys during the first three days, the molecules with $\bar{M}_w < 30000$ being eliminated rapidly and those with $\bar{M}_w > 30000$ only slowly. Though *Hecht* and *Scholtan* [24] were able to show that in the case of the rabbit, the glomerulus filtrate even contains molecules with $\bar{M}_w = 150000$, *Ravin*, *Seligman*, and *Fine* [25] found ^{131}I-labeled PVP having $\bar{M}_w = 40000$ in the tissue. It seems clear that PVP cannot be degraded in the organism. The decisive question, which ultimately arises for all high molecular weight plasma expanders, is whether and to what extent storage in an organ can cause irreversible damage.

8. Hydroxyethyl Starch

Native starch is not suitable for use as the base for a plasma expander, since it is degraded too rapidly by the α-amylase in the blood serum. Of several starch derivatives that have been tested, the best appears to be hydroxyethyl starch, which was proposed by *Wiedersheim* [12] in 1957.

The starting material is not the amylose, but the highly branched amylopectin of starch from plants such as maize, grain, or millet, and particularly "waxy sorghum-starch". Millets and maizes in which the amylopectin content of the starch is higher than 90% instead of the usual 75% have been cultivated. The purified amylopectin is partly degraded to the desired degree of hydrolysis with dilute hydrochloric acid, and the neutralized mixture is treated with dilute sodium hydroxide and ethylene oxide until about 90% of the glucose molecules have been substituted.

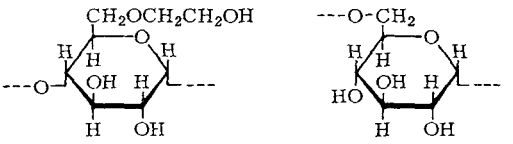

Fig. 5. Hydroxyethyl starch unit (left) and dextran unit (right).

Figure 5 shows a hydroxyethyl starch unit and a dextran unit. Some physico-chemical properties of hydroxyethyl starch are shown in Table 5.

Table 5. Physico-chemical data for hydroxyethyl starch, after *Schoch* [26] and *Cerny et al.* [27].

Weight average mol. wt. $\bar{M}_w$	435000 [a]
Number average mol. wt. $\bar{M}_n$	96000 [b], 71000 [b,c]
Intrinsic viscosity $[\eta]$ in 0.9% NaCl-solution	0.248
Molecular weight distribution	91500–497000
	76000–769000 [c]
$\bar{M}_w/\bar{M}_n$	4.5–6.1
Degree of substitution	0.80–0.83

[a] From light scattering measurements.

[b] From osmotic measurements.

[c] Different batch.

9. Conclusion

The decades of work on the transfer of the functional organ "blood" are not so well known to the public as their importance would merit. However, the difficulties are comparable (though different in nature) to those involved in skin, kidney, or heart transplants. The plasma substitute problem may now be regarded as largely solved. The therapeutic success of plasma substitutes speaks for itself – the number of people who owe their lives to solutions of this type cannot be estimated. Furthermore, the use of synthetic colloidal plasma substitutes has provided stimuli that have led to successful cures in quite unexpected fields.

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Translated by Express Translation Service, London

[23] *J. Lindner*, Verh. dtsch. Ges. Pathol. *44*, 272 (1960).

[24] *G. Hecht* and *W. Scholtan*, Z. ges. exp. Med. *130*, 577 (1959).

[25] *H. A. Ravin*, *A. M. Seligman*, and *J. Fine*, New England J. Med. *247*, 921 (1952).

[26] *T. J. Schoch*, 3rd Conference on Artificial Colloidal Agents, Nat. Acad. Sci. 1965, p. 16.

[27] *L. C. Cerny*, *C. A. Daniels*, and *R. C. Graham*, 3rd Conference on Artificial Colloidal Agents. Nat. Acad. Sci. 1965, p. 20.

The Cytogenetics of Human Tumors[**]

BY K. D. ZANG AND H. SINGER[*]

Chromosome changes can be observed in many tumors, suggesting that a connection exists between chromosome aberrations and tumor formation. A general introduction to the techniques and objectives of research in cytogenetics is followed by a discussion of the modern theories of the etiology of tumors, using human meningioma as an example. Meningiomas are relatively benign, slowly growing tumors of the meninges.

1. Introduction

Depending on the techniques involved and the aims of the particular research project, the field of work of the cytogeneticist lies between that of the chemist and molecular biologist on the one side, and that of the pathologist and anatomist on the other. The cytogeneticist also works with morphological structures, thereby obtaining information not accessible by purely histomorphological techniques about the fine structure of genetic material. This information, however, does not provide any evidence of the function of these structures. The aim of the geneticist to discover correlations between functions and structures can be realized only through a comparison of the cytogenetic findings with morphological, physiological, and chemical evidence.

In this article we shall give a brief outline of the techniques and aims of the cytogeneticist, using as an example the chromosome pattern observed in human tumors. Special attention is paid to meningiomas, as the chromosome changes in these tumors are clear and distinctive, and are thus particularly suitable for purposes of demonstration.

2. The Preparation of Human Chromosomes

The chromosomes, carriers of the genetic information of the cell, exist in the non-dividing nucleus in an extremely decondensed form whose finer structure cannot be revealed by light microscopy. In the course of cell division in mammals they contract to form 1–10 μm long structures arranged in a three-dimensional system. This produces considerable overlapping in cell preparations (see Figure 1) and until a few years ago it was impossible to identify and count the individual chromosomes. Until 1956 the chromosome number in man was assumed to be "about 48" [1].

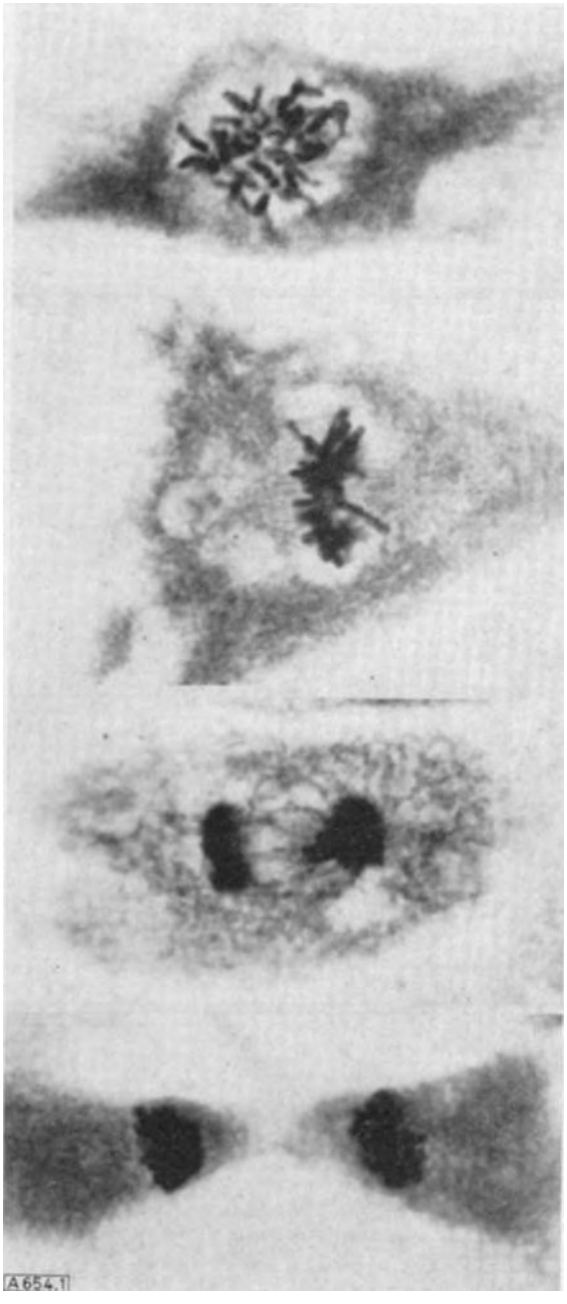

Fig. 1. Division of a brain tumor cell (meningioma) of man. Hematoxylin-Eosin staining, magnification 1200 ×.

The present form of routine chromosome analysis was made possible by three fundamental findings. In 1960, *Nowell* [2] discovered that lymphocytes in the circulating blood, which do not normally divide, undergo

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[1] For references see *G. Heberer*: Handbuch der Humangenetik. Thieme-Verlag, Stuttgart 1968, Vol. I/1, pp. 145ff.

[2] *P. C. Nowell*, Cancer Res. *20*, 462 (1960).

transformation into lymphoblasts and divide after the addition of an extract from *Phaseolus vulgaris*. (This finding is of no importance in the investigation of tumor cells, since such cells undergo spontaneous division.) An important technical improvement was the pretreatment of the cells with a hypotonic solution. This produces a swelling of the cells, resulting in improved separation of the chromosomes [3]. The third fundamental advance is based on the treatment of cells with colchicine derivatives. It has permitted the number of human chromosomes to be definitely established as 46 [4, 5].

Colchicine has several effects: one is that the spindle apparatus (see Section 4), to which the chromosomes are fixed, is destroyed, so that the chromosomes have a better chance to spread out. Furthermore, the chromosomes contract more, acquire clearer outlines, and can be more easily identified under the microscope. The cytostatic effect of colchicine is also very advantageous: on blocking of the cell division, more mitotic cells accumulate and are available for analysis. (For further particulars of the preparation of chromosomes see [6–8].)

The modern cytogeneticist works with cell suspensions or monolayer tissue cultures, in contrast to the section preparations formerly used. Air drying of the cells after hypotonic treatment further improves the spreading out of the chromosomes. This is followed by fixation in the usual way (*e.g.* with acetic acid/alcohol or formalin) and staining with a stain as specific as possible for chromatin structures (*e.g.* Feulgen or Orcein). In cells prepared in this way the chromosomes lie mainly in one optical plane, so that photography and further analysis are substantially facilitated (Figure 2). Most of the methods of preparation employed are modifications of the method developed by *Moorhead et al.* [9].

Fig. 2. Normal human metaphase chromosomes. Orcein staining, magnification 1300 ×.

3. The Preparation and Culture of Tumor Tissues

Preparation of cells is preceded by treatment of the tissue in a manner that varies according to the respective tissue and to the aim of the investigation. Three methods of preparing tissues are used in the cytogenetic study of human tumors: 1) direct preparation; 2) short-time culture; 3) long-time culture of biopsy material.

The direct preparation method is the most reliable for ensuring that the chromosome sets are representative of the tumor sampled. This procedure is particularly suitable for malignant tumors which at any moment contain a relatively high percentage of dividing cells. In the sudden change from body temperature to ambient temperature the cell metabolism and the continuation of initiated cell divisions are slowed down considerably; in addition, no more cells start the process of division. For analysis the tissue is comminuted mechanically and is then subjected to enzyme treatment (*e.g.* with trypsin) to achieve maximum possible conversion of the tissue into a cell suspension. The chromosomes are prepared as described in Section 2.

However, the number of dividing cells is often insufficient for evaluation. In such cases the cell suspension is incubated for some hours in a culture medium, consisting of an isotonic salt solution enriched with supplements whose necessity for the growth of the tissue in question is determined empirically. Besides amino acids, vitamins, trace elements, *etc.*, the addition of 10–30% of homologous or heterologous serum is recommended in many cases. By addition of a small amount of Colcemid (deacetylmethylcolchicine, 0.1 to 1.0 μg per ml of medium, for 2–16 hours) the cells beginning to divide during this period are collected. The chromosomes are prepared in the same way as described above (Section 2).

Prolonged culture of the tumor biopsy material presents both advantages and disadvantages in chromosome analysis. In this method an attempt is made to culture the tumor *in vitro* for a longer period of time. Either small pieces of the tumor are placed in a glass vessel in a plasma clot (a coagulated mass of plasma and homologous embryo extract, generally chicken plasma and chick embryo extract), which is covered with a layer of nutrient medium, or a cell suspension is allowed to establish itself on the bottom of the vessel. In the first case the tumor grows out radially around the original particle, which is both anchored by the clot and nourished by it, and in the second case a uniform sheet of cells is produced. In both techniques the nutrient medium is renewed regularly once or twice a week, and is maintained at a uniform physiological

[3] *T. C. Hsu*, J. Heredity *43*, 167 (1952).

[4] *J. Tjio* and *H. Levan*, Hereditas *42*, 1 (1956).

[5] *C. E. Ford* and *J. L. Hamerton*, Nature (London) *178*, 1020 (1956).

[6] *J. J. Yunis*: Human Chromosome Methodology. Academic Press, New York 1965.

[7] *R. Turpin* and *J. Lejeune*: Les Chromosomes Humains. Gauthier-Villars, Paris 1965.

[8] *R. A. Pfeiffer*: Karyotyp und Phänotyp der autosomalen Chromosomenaberrationen des Menschen. G. Fischer-Verlag, Stuttgart 1968.

[9] *P. S. Moorhead, P. C. Nowell, W. J. Mellman, D. M. Battips*, and *D. A. Hungerford*, Exper. Cell Res. *20*, 613 (1960).

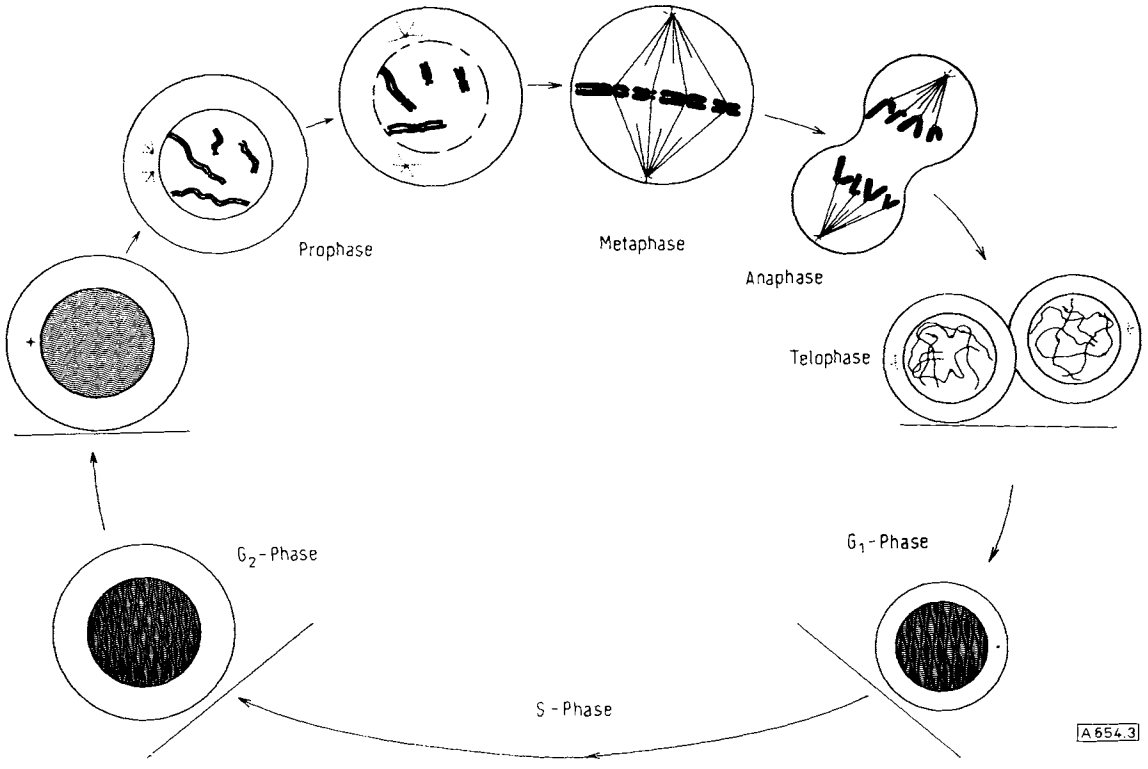

Fig. 3. Schematic representation of a normal cell division cycle. Top: mitosis. Bottom: interphase. For details see text.

pH. When the cells have multiplied sufficiently, they are freed from the bottom of the flask by enzyme treatment. One part is used for chromosome analysis, and the other can be cultured again (subculture).

The advantage of this method is that chromosome analysis can be repeated as often as desired; the disadvantage is that on more prolonged culture a selection or evolution of certain cell types can occur, so that the chromosome sets found do not necessarily correspond to those of the original tumor.

As the chromosomal aberrations of human tumors will be demonstrated in the following section on brain tumors, some particulars of their culture may be mentioned. We used particle cultures (in accordance with the third method), in which the chromosomes of the primary cultures could be analyzed even after a few days. Culture of the tumor particles was performed on cover slips, which were placed in test-tubes filled with the culture medium. The tubes were slowly rotated to ensure oxygen saturation for the tissue [10]. The chromosomes were prepared directly on the cover slips, without preliminary removal of the cells. In this way the cell sheet was preserved, and almost all the cell division figures present were available for study [11].

4. Cell Division and Possible Abnormalities

Under normal conditions the body cells always reproduce in the same way. Figure 3 gives a schematic representation of the cell cycle. In the prophase the thread-like chromatin structures condense to form "chromosomes" with two genetically identical chromatids. During the next stage, the metaphase, the chromosomes contract further and arrange themselves in the "equatorial plate", a disk-shaped structure in the central plane of the cell. The nuclear membrane has disappeared. Each chromosome is stretched between two spindle fibers which end in the centrioles. In the anaphase the two chromatids of each chromosome separate at the centromere, the point of spindle-fiber attachment, and migrate by the progressive shortening of the spindle fibers to their respective poles. In the telophase a new nuclear membrane is formed around the halved chromosome sets, and the chromosomes again disappear by despiralization.

The following G_1 phase (from "growth") is a period of high metabolic activity without observable changes in the cell morphology. Most of the body cells are found in this phase. It can last for days, even months and years, as long as the cell is not preparing to divide. In the latter case the S phase (from "synthesis") begins, during which the nucleus doubles its DNA content (*e.g.* the DNA content of each chromatid) as can be measured cytophotometrically. During this phase the basic structure of the chromosome, a DNA strand wound in a double helix, is doubled. This synthesis phase lasts on average 6–8 hours.

The following, G_2 phase is a short period of high metabolic activity, generally lasting less than an hour, during which the nucleus prepares for its subsequent division. In the following prophase each chromosome again consists of two chromatids instead of one. Mitotic division occurs in this way in all body cells; on average it takes about an hour. In tumor cells the G_1 phase is greatly shortened, and in certain circum-

[10] *G. Kersting*: Die Gewebezüchtung menschlicher Hirngeschwülste. Springer, Berlin 1961.

[11] *J. Lejeune, R. Turpin*, and *M. Gautier*, Rev. franc. Études clin. biol. *5*, 406 (1960).

stances amounts to but a few hours. In these cells reproduction has apparently become an end in itself, the interphase being limited to the minimum time necessary to provide the structures and energy required for further division.

Defects in division can also occur in normal mitosis and lead to numerical and structural changes in the nucleus, but the number of such pathologically altered cells remains relatively small. In tumor cells, on the other hand, they occur in especially high numbers (see Section 6).

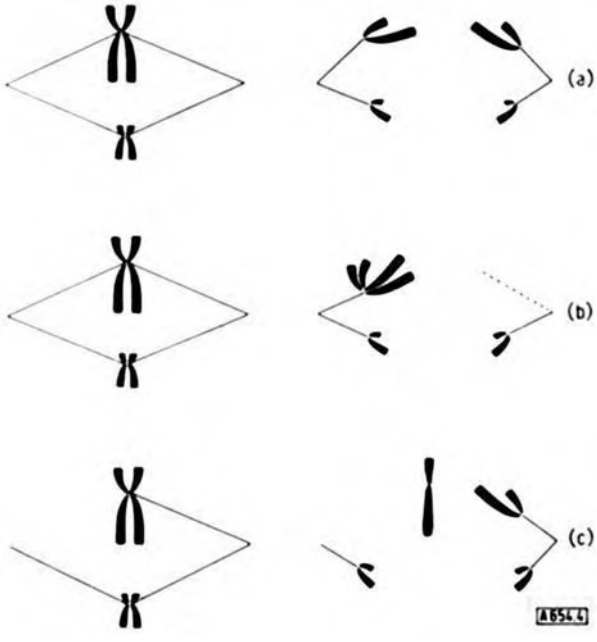

Fig. 4. Mechanism of the most common types of chromosome aberrations.

Left row: arrangement of the chromosomes in the metaphase plate. Right row: separation in the anaphase. (a) normal division, (b) non-disjunction, (c) anaphase lag.

Fig. 4 shows the mechanism of numerical chromosome aberrations. As a result of the non-separation of a centromere, both chromatids can migrate to one daughter cell, so that the chromosome concerned is doubled in one daughter cell and absent in the other (non-disjunction). The second possibility is the absence of the spindle fiber on one side of a chromosome, so that one chromatid does not move to its corresponding pole. It can either move to the other side or remain where it is and finish in either one of the daughter cells according to chance (lag). As a result of the absence of the spindle fiber attachment the affected chromosome is quickly lost.

Another common aberration of the chromosome set is its multiplication (polyploidy). This is one of the fundamental defects of cell division in tumors. Here the doubling process of the chromosomes takes place several times in succession, without any mitosis occurring in the meantime (endo-reduplication). The process is first recognizable in the next cell division, in which the chromosomes mostly appear arranged in double pairs (Figure 5).

Another possibility is that the chromosomes begin to contract as if in prophase, but owing to the absence of spindle fiber formation they soon again lose the condensed form and begin a new cell cycle without preceding division (endomitosis). Here too doubled chromosome sets are found in the next cell division but the paired arrangement of the chromosomes is generally missing (Figure 6). Besides these numerical chromosome aberrations, structural anomalies also play an essential role

Fig. 5. Tetraploid chromosome set after endoreplication (see text). The homologous chromosomes are arranged in pairs.

Fig. 6. Tetraploid chromosome set after endomitosis, a special form of endoreplication (see text). The chromosomes are arranged randomly.

in tumors. Figure 7 shows the commonest structural chromosome aberrations and their formation (for details see legend). The possible origins of these structural aberrations are discussed in Section 6.

5. The Morphology of Human Chromosomes

In considering human chromosomes prepared under standardized conditions, we shall first mention the various shapes of these chromosomes (see Figure 2).

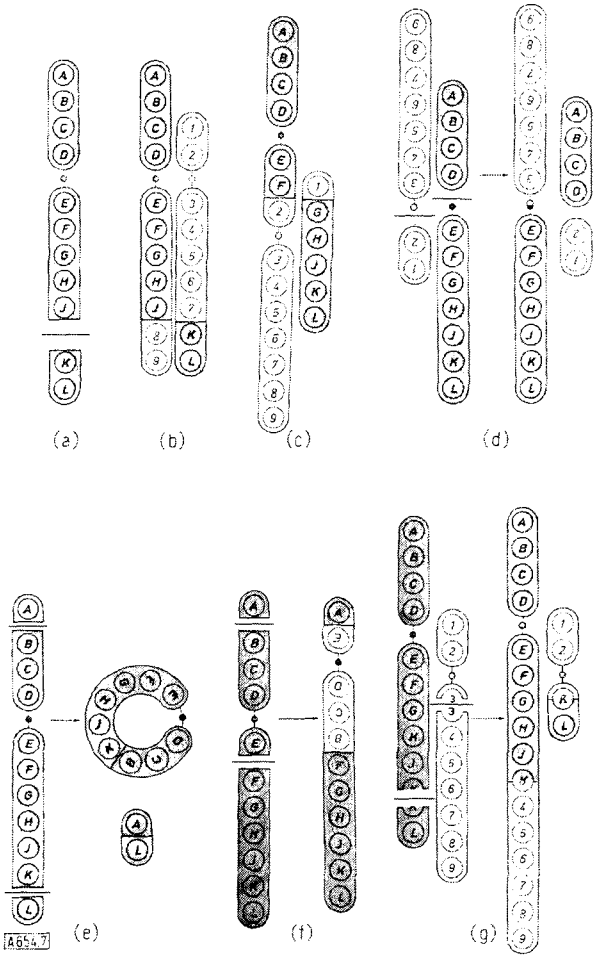

Fig. 7. Schematic representation of the most common structural chromosome aberrations. (a) Break. (b) Reciprocal translocation, generally combined with a change in the shape of both partners; a translocation involving fragments of similar size is not recognizable morphologically. (c) Formation of a dicentric chromosome by translocation. The two recombined fragments (1/GHJKL) become lost as they contain no centromere (—•— or —o—). (d) Central fusion after break of both partners in the immediate neighborhood of the centromere; the chromosome formed from the remainder of the two chromosome arms often becomes lost because of its missing or incomplete centromere. (e) Formation of a ring chromosome after a break at each end of the chromosome. The two fragments can recombine, but will in any case be lost. (f) Pericentric inversion, *i.e.* a double break as in (e); the middle piece is set in again, but in an inverted form (shown white in the figure). (g) Telomeric or tandem fusion. In this one chromosome is broken at the end of the arm and the other near the centromere. During recombination the almost complete arm of the second chromosome becomes attached to the first. The process takes place in marker chromosomes having one short and one excessively long arm.

Independently of the differences in size, three main types can be distinguished: 1. mediocentric chromosomes (the centromere, the point of spindle fiber attachment, occurs approximately in the middle); 2. submediocentric chromosomes (the centromere lies between the middle and the end); 3. subtelocentric or acrocentric chromosomes (the centromer is in the immediate vicinity of the end of the chromosome). A classification of human chromosomes according to size and shape was suggested in 1960 in the "Denver nomenclature" [12], and was then revised and improved in London in 1964 [13] and in Chicago in 1966 [14].

[12] Human Chromosome Study Group: Proposed Standard System of Nomenclature of Human Mitotic Chromosomes. Lancet *i*, 1063 (1960).

Figure 8 gives a schematic representation of the normal human chromosome set. Figure 9 shows the arrangement of a normal female chromosome set obtained under standard conditions of preparation (karyogram).

The autosome pairs (chromosomes with purely somatic information) are numbered from 1 to 22; the gonosomes (sex chromosomes, which besides containing information for the normal development of sex also carry somatic genes) are not numbered. In addition to the numbers the letters A–G are frequently employed; this is *Pätau*'s classification (1960) [15],

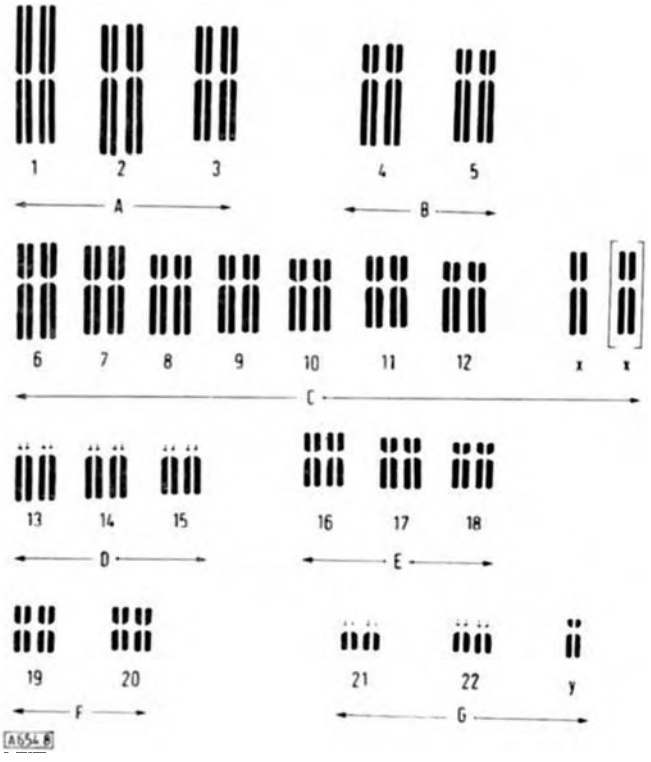

Fig. 8. Schematic representation of the normal human set of chromosomes, in order of decreasing size and morphological characteristics (Denver classification).

Fig. 9. Normal female chromosome set arranged according to the Denver classification (karyogram).

[13] The London Conference on the Normal Human Karyotype. Cytogenetics *2*, 264 (1963).

[14] Chicago Conference: Standardization in Human Cytogenetics. Birth Defects. Orig. Article Series II, 2 (1966), issued by the National Foundation – March of Dimes.

[15] *K. Pätau*, Amer. J. hum. Genetics *12*, 250 (1960).

which places special emphasis on the chromosome shape. Its use is especially recommended for the chromosome groups C, D, F, and G, in which it is often impossible to determine the order of the chromosome pairs within the group. This identification, as well as the allocation of the respective pairs (whose partners derive from the father's and the mother's side), is often greatly facilitated by the use of autoradiography. For this purpose, use is made of the fact that during the S phase the chromosomes follow a certain sequence in their reduplication by labeling them with radioactive thymidine. Figure 10 shows such a labeling pattern of metaphase chromosomes [16].

Fig. 10. Metaphase chromosomes labeled with tritiated thymidine. At the moment of fixation the chromosomes show different labeling patterns, with, however, a general agreement between homologous partners. Upper figure: Microphotographic representation of the metaphase chromosomes. Lower figure: Demonstration of the uptake of radioactive thymidine by covering the slide with a photoemulsion. The arrows indicate the position of the chromosome pair A_1.

6. Chromosome Changes in Human Tumors

The human tumors studied most intensively with regard to their chromosomes are the leukemias, probably because blood or bone marrow are readily accessible without an operation, and because repeated examinations are possible. In one type of leukemia, chronic myeloic leukemia, a definite and reproducible chromosome aberration is demonstrable: the "Philadelphia" chromosome, a deleted chromosome of the G-group [17] (see Figure 11).

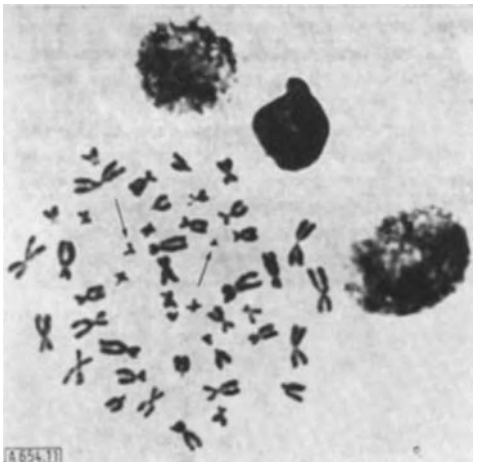

Fig. 11. Metaphase chromosomes in chronic myeloic leukemia. The arrows show the Ph^1-chromosome and its homologous partner [17a].

The importance of this finding lies in its regularity and in the fact that the chromosome is found only in pathologically altered cells. From this one can conclude that the Philadelphia chromosome is not a congenital defect. Such structurally abnormal but typical and recognizable chromosomes are called "marker" chromosomes in cytogenetics.

A similar, defined chromosome aberration, in the sense of a marker chromosome, occurs in Waldenströms macroglobulinemia [18]. In the mosaic form (hence not in all cells) there appears an additional 47th chromosome, which generally has the size of chromosome No. 2 and the shape of chromosome No. 5. This is also a pathological cell strain, which is demonstrable in the blood, but, just as with leukemia, is not a "tumor" in the strict sense.

Such marker chromosomes have also been described in most solid tumors of man, though they are seldom the only pathological finding in the tumor chromosomes. In most cases there are considerable numerical deviations, generally consisting in a moderate to considerable increase in the chromosome numbers between the diploid (46) and tetraploid (92) chromosome sets. Analysis is made more difficult in most cases by the fact that the chromosome changes are not the same in all tumor cells. The number of chromosomes varies from cell to cell, so that only a "modal number" can be given which again can differ from case to case. A great number of chromosome breaks and all types of recombinations given in Figure 7 can also occur.

As an example, reference will be made to HeLa cells, a permanent cell line, derived originally from a carcinoma of the cervix and used today throughout the world for genetic and biochemical studies. The chromosome number and the morphology of these cells can vary considerably from laboratory to laboratory. However, the establishment of such a permanent cell line, which derives from a tumor and is reproducible in subcultures for as long as required, is an exception. Normally, the capacity of cells for division and growth *in vitro* is limited. After an average of 50 subcultures (about $1-1^1/_2$ years) the reproduction capacity of the cultures usually diminishes and the cells die. This occurs not only with cultures

[16] *W. Schmid*, see [6], pp. 91ff.

[17] *P. C. Nowell* and *D. A. Hungerford*, J. nat. Cancer Inst. *25*, 85 (1960).

[17a] We are grateful to Dr. *F. Back*, Institut für Hämatologie GSF, Assoziation Euratom, München, for this photograph.

[18] *C. Bottura*, *J. Ferrari*, and *A. A. Veiga*, Lancet *i*, 1170 (1961).

of tumor origin but also with fibroblast cultures from normal human connective tissue. That further cultivation is no longer feasible is indicated in normal and so far euploid cultures (*i.e.* cultures with a normal diploid set of chromosomes) by increasing polyploidization and the beginning of structural chromosome aberrations.

Up to the present the chromosome sets of about 200 malignant human primary tumors have been described [e.g. 19–23]. The results are unsatisfactory for the above reasons. It is impossible to find a typical combination of chromosomal changes for a particular tumor, *e.g.* cancer of the stomach. A similar lack of agreement exists between different kinds of tumors.

The occasionally expressed presumption that the chromosome E_{16} increases to a substantially greater extent in tumor tissue than the other chromosomes should also be treated with reserve. Deletion of the long arm of chromosomes of the C-group are a common finding in tumors and can lead to chromosomes morphologically indistinguishable from chromosome No. 16. As only two chromosomes of this type are normally present, a considerable increase can easily be simulated in this way, without the relative decrease in the numerous chromosomes of the C-group being noticed. A similar finding, *i.e.* the relative decrease in chromosomes of the G-group, has been discussed by several authors [24–27] on the basis of the material reported in the literature (see Section 7).

In our studies on brain tumors we looked for chromosome changes in relatively benign and slow growing tumors. In this we paid special attention to meningiomas, tumors that do not originate from the brain but from the meninges, forming a histologically particularly uniform system. As a rule they grow only by displacing the surrounding tissue, without infiltrative and metastasizing growth like malignant tumors.

We have demonstrated the loss of a chromosome of the G-group [28] as the basic change in meningiomas. This can occur as the only finding. Furthermore, this loss is sometimes demonstrable as a mosaic pattern together with cells having a completely normal chromosome complement, and in some tumors only normal cells could be found. (Perhaps in this small group a cell line with a missing G chromosome simply could not be detected.) Some tumors in our series of over 30 cytogenetically investigated meningiomas showed more severe histological abnormalities; in this group, besides the G-chromosome, 1–5 other chromosomes were missing (Figs. 12 and 13). However, each chromosome set was uniform and characteristic for the tumor concerned. No great variations from cell to cell, such as those described for malignant tumors, were found in any of the samples investigated by us.

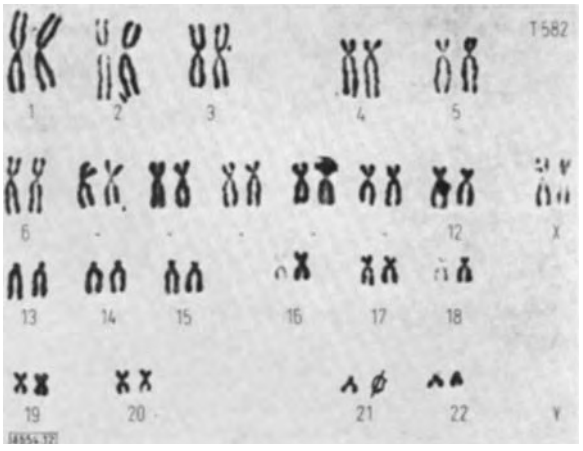

Fig. 12. Karyogram of a meningioma cell. Loss of a chromosome of the G-group (uniform cell strain in the whole tumor).

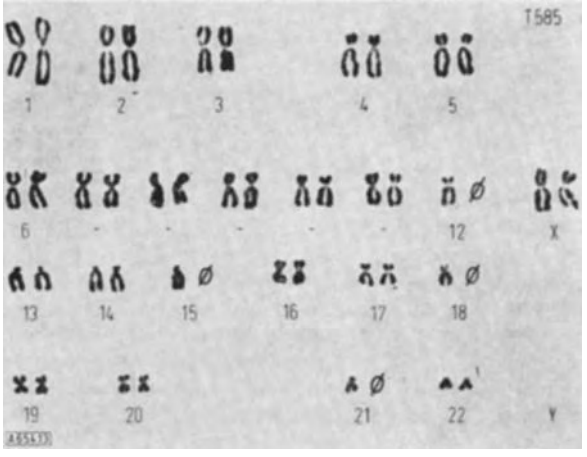

Fig. 13. Karyogram of a meningioma cell. Loss of a chromosome of the G-group and three other chromosomes of different groups (uniform cell strain in the whole tumor).

In some tumors, but even here in only a few cells, there was a doubling of the set of chromosomes and small structural changes, such as are shown in Figure 7. These variations are summarized in Figures 14 and 15.

However, it should be emphasized once more that the structural aberrations described in the benign meningiomas examined by us are rare and of limited importance compared to the constant numerical aberrations. Two chromosomes of the G-group are also missing in the endoreplicated cell shown in Figure 5. We assume that the loss of the G-chromosome was the primary event and the doubling of the chromosome set was the secondary event, possibly occurring *in vitro*.

It is rather unlikely that the chromosome aberrations found by us were influenced by the formation of clones during the period of cultivation. It has been possible to show in over a thousand brain tumors cultured at the Neuropathologisches Institut of Bonn University and at our Institute, that the medium used by us is especially suitable for the propagation of the primary structure of these tumors, though in a two-dimensional system. Neither an overgrowth of connective tissue cells nor further dedifferentiation of nuclear structures has been observed. Comparison with cultures of the same tumors in a typical nutrient medium for fibroblasts was very informative (McCoy 5 A). The cultures grew more slowly, the morphology of the cell sheets was clearly changed, and chromosome analysis showed almost entirely normal chro-

[19] *T. Ishihara, Y. Kikuchi*, and *A. A. Sandberg*, J. nat. Cancer Inst. *30*, 1303 (1963).

[20] *S. Makino, M. S. Sasaki*, and *A. Tonomura*, J. nat. Cancer Inst. *32*, 741 (1964).

[21] *A. A. Sandberg, T. Ishihara, T. Miwa*, and *T. S. Hauschka*, Cancer Res. *21*, 678 (1961).

[22] *A. J. Spriggs*, Brit. J. Radiol. *37*, 210 (1964).

[23] *H. J. Lubs* and *J. H. Salmon*, J. Neurosurg. *22*, 160 (1965).

[24] *H. van Steenis*, Nature (London) *209*, 819 (1966).

[25] *J. W. I. M. Simons*, Nature (London) *209*, 818 (1966).

[26] *N. S. Kiseleva*, Lancet *i*, 616 (1964).

[27] *A. Levan*, Hereditas *55*, 28 (1966).

[28] *K. D. Zang* and *H. Singer*, Nature (London) *216*, 84 (1967).

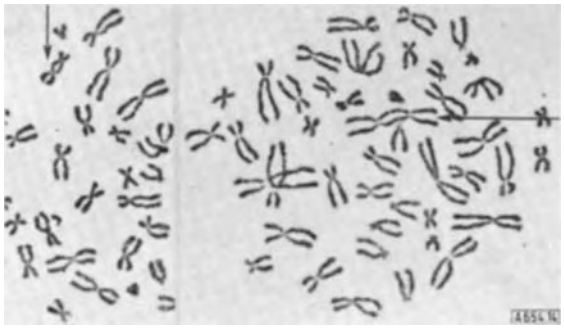

Fig. 14. Dicentric chromosomes in a meningioma.

Fig. 15. Ring chromosomes and multiradial recombination figures in a meningioma.

mosome sets [29]. This example shows the danger of a selective propagation of the connective tissue of a tumor by using an inappropriate technique, and of subsequent interpretation of the observed normal chromosome sets as evidence that the tumor in question is benign. On the other hand, we find in the culture of glioblastomas, the true carcinoma of the brain, the same abundance of numerical and structural chromosome changes as described in other malignant tumors [29].

7. The Relationship between Chromosome Aberrations and Tumor Formation

In his theory of cancer, *Boveri* in 1914 [30] was the first to propose a relationship between chromosome aberrations and tumor formation. The chromosome aberrations found in human tumors in the last ten years have established his theory. Three possible types of relationship are discussed today: 1. It has been suggested that tumors are caused by chromosome changes, as chromosome changes have been demonstrated in many tumors and in the remainder the morphological changes were of such an order that they could not be detected by light microscopy. 2. The chromosome changes are not the primary cause of tumor formation, but the result of it. They can be present or lacking, and vary in most tumors from sample to sample. 3. Morphological chromosome changes can be one of the possible ways in which tumors arise; conversion of normal into tumor tissue (neoplastic transformation) can, however, also occur in another way, without morphological chromosome changes being observable.

[29] *K. D. Zang*, unpublished.

[30] *T. Boveri*: Zur Frage der Entwicklung maligner Tumoren. Fischer-Verlag, Jena 1914.

A common feature of these three at first apparently contradictory views is that today it is no longer possible to maintain the argument that tumors occur without changes in the genetic structure of the cells. Consequently, chromosome changes in the widest sense must also be present. But these changes need not necessarily be detectable microscopically.

It must, however, be left an open question whether the chromosome aberrations found are the (constant) visible expression of these genetic changes, or whether they can be interpreted only as an expression of uncontrolled cell multiplication [31]. On this point even the appearance of marker chromosomes gives no clear information; for the present it only indicates a unicellular and not a multicellular origin of a particular tumor cell population [32].

In chronic myeloic leukemia the deletion of the long arm of a G-chromosome occurs, resulting in a loss of about 40% of the chromosomal DNA. In meningiomas a whole chromosome of this group is missing, and in many malignant tumors with a great increase in the number of chromosomes there seems to be a relative decrease in the chromosomes of the G-group. Consequently, it can be postulated that there is a relationship between this stereotype chromosome aberration and the tumor formation. This hypothesis does not reject other possibilities. It cannot be denied that during the development of (malignant) tumors the chromosome set becomes increasingly abnormal, and that there is no specific correlation between this and the malignity. Thus, in the late stages of chronic myeloic leukemia there is found, apart from the Philadelphia chromosome, an abundance of numerical and structural aberrations. It should rather be supposed that in growing tumors those cells multiply preferentially whose chromosome sets have a genetic constitution promoting their metabolism and reproductive capacity under the respective *in vivo* or *in vitro* conditions. It may well be argued that, as a result of several deletions and translocations, cells with morphologically and numerically different chromosome sets are genetically identical. We are merely attempting, on the basis of our findings, to support the hypothesis that the loss of G-chromosome material could trigger off uncontrolled cell multiplication (see Section 7.1.).

7.1. Chromosome Changes and Tumor Formation due to Exogenous Effects

There are essentially three groups of exogenous factors which are known to induce tumors: 1. ionizing radiation; 2. oncogenic viruses; 3. mutagenic chemicals. It is also known that all these factors can cause chromosome aberration. Using human cells, *Koprowski et al.* [33] established for the first time in 1962 that chromosome aberrations can be caused by the SV40 virus in tissue culture. These aberrations began with the loss

[31] *K. Bayreuther*, Nature (London) *186*, 6 (1960).

[32] *C. E. Ford, J. C. Hamerton*, and *R. H. Mole*, J. cellular comparat. Physiol. *52*, 235 (1958).

[33] *H. Koprowski, J. A. Pontén, F. Jensen, R. G. Radvin, P. S. Moorhead*, and *E. Saksela*, J. cellular comparat. Physiol. *59*, 281 (1962).

of chromosomes of the G-group. Considerable variations in the chromosome number and all the described structural changes, as observed in the chromosome sets of malignant tumors, arose on further culture. These findings have been confirmed repeatedly, and have been found in the meantime also in tissue cultures infected with Rous sarcoma virus, polyoma virus, and adenovirus type 12. All these viruses can cause tumors *in vivo* in animals. On the other hand, however, non-oncogenic viruses, *e.g.* the measles virus, also have the capacity to cause chromosome breaks [34].

Fig. 16. Chromatid breaks and recombination figures in the chromosomes of a peripheral lymphocyte after cyclophosphamide therapy [34a].

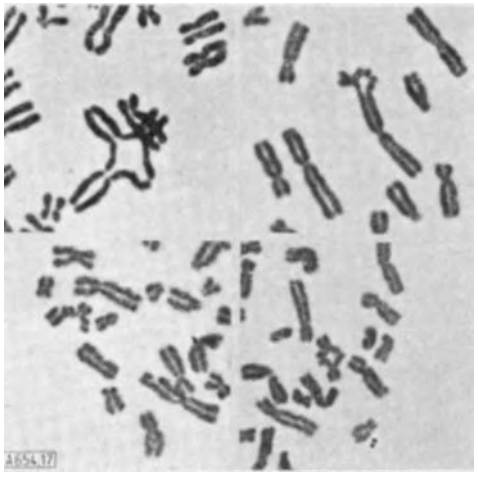

Fig. 17. Chromosome breaks and multiradial recombination figures in chromosomes of peripheral lymphocytes after radium and X-ray therapy [34a].

It is also known that ionizing radiation can cause chromosome changes *in vivo* and *in vitro* (see Figure 16) and that tumors can be induced by X-rays. An interesting example is the case described by *Engel* [35] in which a chronic myeloic leukemia with the typical Philadelphia chromosome occured in a patient several years after X-ray treatment for a bronchial carcinoma.

A finding familiar to the chemist is the production of tumors by the application of mutagenic chemicals. With most substances the induced transformation of the cells is associated with a change in the chromosomes. The effects of urethane [36] and mustard gas [37] in inducing chromosome changes were the first described. Since that time it has been discovered that many alkylating agents have the capacity to cause chromosome aberrations (cf. Fig. 16), and the same occurs with many purine and pyrimidine derivatives [38]. Most DNA-base analogs have a mutagenic effect; it is assumed that they act directly on the DNA of the cell nucleus and alter the chromosome structure. Thus, for example, the effect of urethane can be partly counteracted by thymine [39]. Other chemicals, such as caffeine and colchicine, as well as some other cytostatics, do not affect the DNA but alter or impede the function of the spindle fibers [38]. Considerable chromosome aberrations are also produced in this way.

There is a great similarity between the visible effects of all the chemical, radiological, and viral agents capable of inducing both tumors and chromosome aberrations; primarily, there are disturbances in chromosome disjunction, and, furthermore, chromosome breaks occur. Apparently these exogenous agents have definite and constant predilection sites for the induction of breaks. The broken ends of chromosomes have a predisposition to recombination, *i.e.* to combine with other sites where breaks have taken place, so that numerous recombinations are possible after the simultaneous occurrence of breaks in several chromosomes in the same cell cycle. Thus cell strains differing in chromosome morphology but genetically identical can be produced.

7.2. Chromosome Changes and Tumor Formation due to Endogenous Factors

There is some evidence for the assumption that endogenous as well as the described exogenous factors can play a part in tumor formation and in the increase in chromosome changes.

As an example, we may recall the existence of "tumor families", in which tumors occur over the course of several generations; the tumors are generally malignant, and can show similar or different localization and morphology [39,40]. Such families are said to have a "predisposing factor", but no more definite etiological and pathogenic information can be given.

A correlation has also been found between chromosome anomalies and immunological diseases. Many autoimmune diseases and tumors have been associated, *e.g.* pernicious anemia with carcinoma of the stomach, as well as Hashimoto's thyroiditis with cancer of the

[34] *W. W. Nichols*, Hereditas *50*, 53 (1963).

[34a] We are grateful to Dr. *M. Bauchinger*, Strahlenbiologisches Institut der Universität München, for this photograph.

[35] *E. Engel*, Lancet *ii*, 291 (1965).

[36] *F. Oehlkers*, Z. Vererbungsl. *81*, 313 (1943).

[37] *C. Auerbach*, Proc. Roy. Soc. Edinburgh, Sect. B *62*, 284 (1947).

[38] For references, see *E. Grundmann*: Allgemeine Cytologie. Thieme, Stuttgart 1964.

[39] *O. v. Verschuer*: Handbuch der Humangenetik. Thieme, Stuttgart 1964, Vol. III/1, pp. 671 ff.

[40] *P. C. Koller*, Europ. J. Cancer *3*, 279 (1967).

thyroid gland [41]. On the other hand, mothers having demonstrable thyroid antibodies (Hashimoto's thyroiditis) have children with chromosome anomalies, especially children with a G-trisomy (Down's syndrome), more commonly than healthy mothers. In addition, patients with numerical or structural chromosome anomalies are more inclined to develop malignant tumors than the general population [42].

Chromosome aberrations can be caused *in vitro* in primary normal fibroblast cultures if an extract of genetically foreign lymphocytes is added. It has not yet been made clear whether a classical immune mechanism is involved, or something else [43]. Chromosome changes also arise in normal tissue cultures after activation of lysosomal enzymes [44]; a tumor-inducing factor could, for example, produce a breakdown of lysosomes, whose released enzymes could cause chromosome breaks to recombine in a way that leads to the formation of tumor cells.

We must assume that the majority of the possible morphological chromosome changes are not consistent with cell life. Many findings indicate that immunological mechanisms can lead to chromosome changes. For this reason it can be argued that such immune reactions have a kind of self-protection function, in which the "abnormal" cells are eliminated through an alteration of the chromosome structure. A possible defect in this self-protection system could be that not all cells undergo lethal chromosomal damage and some become so changed that, on the contrary, they exhibit uncontrolled growth [41,45].

[41] For references see *Ph. J. Fialkow*, Blood *30*, 388 (1967).

[42] *R. W. Miller*, New England J. Med. *87*, 275 (1966).

[43] *Ph. J. Fialkow* and *S. M. Gartler*, Nature (London) *211*, 713 (1966).

[44] *A. C. Allison* and *G. R. Patton*, Nature (London) *207*, 1170 (1965).

[45] *K. H. Bauer*: Das Krebsproblem. Springer, Berlin 1963.

8. Outlook

Human chromosomes are very unsuitable for the investigation of many questions in genetics, especially biochemical genetics, mainly because of their small size. On the other hand, some of the difficulties could be eliminated by greater cooperation in morphological, virological, and biochemical research. Thus, there is a possibility of fractionating dividing cells and concentrating the chromosomes [46]. The separation of chromosomes or chromosome groups by physical methods could yield further information on chromosome structure. An "*in vitro* system" of concentrated chromosomes of defined morphology could reveal the functional differences between individual chromosomes. On the cytogenetic side, experiments are already being undertaken to culture strains with defined chromosome aberrations. Biochemical methods can be used to try to find structural or functional differences between these cells and normal cells. Already, for example, a series of observations indicate that in chronic myeloic leukemia the activity of the alkaline leukocyte phosphatase is decreased, whereas in patients with Down's syndrome it is increased.

The goal of drawing up a gene map of the human chromosomes is still far in the future, and will probably never be attained on the same scale as in the case of the giant chromosomes from the salivary gland of *Drosophila melanogaster*, but it is not completely hopeless; for instance, a large number of genes can already be localized on the human X-chromosome, and their sequence and approximate distance apart can be determined.

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Translated by Express Translation Service, London

[46] *J. Mendelsohn*, *D. Moore*, and *N. Salzman*, J. molecular. Biol. *32*, 101 (1968).

Element and Compound. On the Scientific History of Two Fundamental Chemical Concepts[**]

BY E. STRÖKER[*]

A wish is often expressed that any purely factual account be completed by an historical dimension, where not only a science's past, like a venerable arsenal of the factual knowledge possessed in earlier times, but also the thought-structures which led to such knowledge in the first place, should be called to memory. These thought-structures, however, never belong exclusively to the past; they still find themselves as a precipitate in contemporary scientific methods – a sediment in present-day concepts.

In the following article we do not wish to compile a mere inventory of what was regarded at different times as element and as compound, but rather to examine a few, typical, clearly definable thought-structures, which have become what they now are through the changing usage of the concepts of "element" and of "compound" in the course of the history of chemistry. The alchemistic doctrines of

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elements shall not be examined at all, and the concepts of "element" and "compound" will be considered only insofar as the history of their development has been significant for chemical science.

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These two concepts recall a very distant past. It is commonly known that the earliest reflections on nature are to be found in the Ionian philosophy of the Vth century B.C. Just one hundred years later we find the first "doctrine of elements", which was to play an important role in chemistry right down to the Renaissance.

Fragments of a poem "On Nature" by the author of this doctrine, Empedocles, a follower of the old Pythagoreans, are still extant. In his poem, Empedocles raises the question of the *rhizomata*, of the "roots" of all things. He conceived them as four divinities (that there should be four may be explained on the basis of the Orphic-Pythagoric tradition, which regarded the number four as sacred): fire, earth, air, and water. Empedocles supposes that all that exists is composed of these. Things share in them in different ways, and this is the reason why things are different. Their composition may vary. Also the qualitative changes, the coming-to-be and the passing-away of things, are based on the mixture and exchange of such particles. Each of the four "roots" is in itself unchangeable in mode and in quantity, and is not subject to growth or decrease. It is likely that Empedocles also conceived the idea of continuous exchange of fire, water, earth, and air as an exchange of small particles, imperceptible because of their smallness, so that all obvious quantitative as well as qualitative changes are ultimately based on the motion of such particles.

To be sure, the present-day chemist cannot expect to do anything on the basis of this Empedoclean doctrine of elements, which is still tangibly captive of the archaic-mythical *Weltanschauung*. But let us bring out the posing of the question from which this doctrine originated, in order to see how its significance went far beyond just the material content of its own statements.

With the advent of Ionian natural philosophy a way of thinking came into being, which would be of decisive significance for the whole of Western science. Confronting the world, man asked of it as a whole – what it was. He was not satisfied, however, with the mere evidence of things and sought a deeper understanding about what lasts as permanent behind their change, about what their *hypokeimenon* – that which "underlies" all coming-to-be and all passing away – may be. And it was peculiar to this earliest philosophical thinking, that it regarded no longer demons but *material* principles as being involved in the foundation of the world. By assuming four such principles, which should explain the plurality and changeableness of sensible phenomena, Empedocles establishes himself and his doctrine within a much older tradition of thought. He may be regarded, however, as the advocate of the first doctrine of elements; the concept of the material element originates from him. Though the designation *stoicheion* was introduced later by Aristotle, the four "roots" of all things, as Empedocles conceives them, are already properly *stoichaia*, or elements – in the specific sense, at least, and as understood not only by the Greeks in their later classical doctrine of nature but also by chemists up to the time of Robert Boyle. This means that from the era of Empedocles on *elements* are *basic materials*, insofar as all material is composed of them, *i.e.* all natural things originate from them. The elements themselves, on the other hand, are unoriginated, unchangeable, indestructible; their total quantity in the universe must be regarded as constant.

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We shall not concern ourselves here with an examination of the reasons which later led to the peculiar revision of this doctrine of elements by Leucippus and Democritus. The most far-reaching aspect of their philosophy of nature was that in it the qualitative difference of the elements was annulled, *i.e.* all material qualities were reduced to purely mechanical processes of motion of the corpuscles of a single matter. All Democritean particles were of the same kind, distinguished from one another only in shape and magnitude. They were also thought to be unchangeable, unoriginated, imperishable, of finite magnitude, and yet indivisible – *átoma*. The concept of *atom* was used from then on to denote the smallest, reputedly (mechanically) indivisible particles of matter.

It has been necessary to briefly recall the Democritean atomism, even though it not only failed to foster the development of the previous doctrine of elements but also actually did away with the very notion of element. In so doing, however, this atomism was to be a constant and determining factor in the later discussion on the nature of matter.

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Democritus' sharpest opponent, Aristotle, was the successful continuator of this discussion but nowhere in the history of chemistry does he find adequate appreciation; only the accusation of having fallen back into the old doctrine of the four elements is leveled against him. We are fully justified, then, in stressing Aristotle's role as author of a doctrine, which permanently influenced subsequent chemical thinking. Problems of matter and of material change found their honored place in the Aristotelian philosophy. The first precise determination and elaboration of the concept of matter – *hyle* – was done by Aristotle.

For Aristotle, however, matter is always qualitatively determined matter. The assumption of a matter deprived of quality, whose *átoma* are merely differently formed and only mechanically moved and ordered – the Democritean corpuscular kinetic pattern of change – is, according to Aristotle, wholly irreconcilable with that of experienced reality. Aristotle's main argument against Democritus presupposes quite def-

initely the acceptance of the tangible world. No aggregation of atoms but qualitative manifoldness and fullness, not only mechanical motion but also development and change, coming-to-be and passing away – this is what such a world exhibits.

Significantly, however, it is with this particular set of problems that Aristotle runs into difficulties in his criticism of Democritus. He was the first to see clearly the distinction between a *mixture* and what was later to be termed a chemical *compound*. The Greek word *mixis* explicitly denotes a chemical compound as opposed to a mixture, for which the term *synthesis* is used [1].

According to Aristotle, it is precisely here in the interpretation of *mixis* – of the compound, therefore – that atomism fails, since it does not succeed in explaining the amazing effect of *henosis*, of the "becoming one" of different material elements in the entirely new kind of matter of the *mixis*: for the qualities of a *mixis* are not the summation of the peculiarities of the original materials but are wholly new and of a different kind. Hence, Aristotle assumes that in the *mixis* the original materials could not have remained unchanged, even in their smallest particles, since otherwise the compound would be nothing but a macroscopic illusion and actually only a mixture of the atoms of the original materials.

Aristotle is well aware, on the other hand, that the original substances which go into the making of a compound – that is in the *mixis* – can be retrieved; therefore, these substances can neither be lost nor destroyed. The possibility of decomposing a compound into its component parts would seem to involve precisely the opposite of what is suggested by the new quality of the compound – no sooner is the problem of the *mixis* seen and formulated with clarity, than it leads to an aporia.

Briefly, Aristotle attempted to overcome this difficulty as follows: it must be granted that in the *mixis* an entirely new matter has arisen from the original materials; nevertheless, the components are present *dynamei*, "potentially", also in the compound. In the compound the components are no longer what they were as individuals; it is likely that they have undergone an intrinsic change. It is also true, however, that the elements do not perish in the compound, since it is always possible to retrieve them by analysis of the compound itself.

For the first time, some very significant questions are raised, questions which have concerned chemists ever since. It would no doubt be an error to regard Aristotle as a chemist in order to easily dismiss him as an amateur. The Aristotelian doctrine of *mixis* must be regarded explicitly as a philosophical discussion of principles. In other words, the doctrine must be considered here in its true context as an aim at clarifying not chemical *facts* but rather those concepts without which we would find it impossible to state with precision questions about such facts. The problem is not, "what is matter and how is a *mixis* made from it", but, how is one to think of this *mixis* as existent *tout court*.

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On the other hand, however, the question whether a *mixis* can be understood as matter which "consists of" other materials, is a later differentiation of the Aristotelian problem. Aristotle develops his discussion on principles wholly within the framework of ordinary language. In ordinary language, however, it is taken for granted that a compound owes its *ex*istence to the same materials of which it *con*sists. (The present-day chemist still says, for instance, that hydrochloric acid "consists of" oxygen and chlorine, and finds this way of expressing himself meaningful throughout.)

Aristotle established a way of questioning and reasoning, which was used in, and strongly influenced, discussions on the composition and structure of matter until late in the XVIIth century. Such discussion was carried on – though not without frequent interruptions owing to the dominance of alchemy – in the main in two clearly separate philosophical camps, without first being related to chemical experience.

On the one hand, the old Democritean doctrine was revived in the philosophy of the Stoics and found its continuation in the so-called philosophical atomism. According to its fundamental concept, however, atomism could never have solved the Aristotelian problem, viz.: how to interpret the formation of chemical compounds from the elements and the possibility of analyzing the former into the latter. Atomism was even incapable of distinguishing between these two categories of matter.

On the other hand, this distinction, clearly formulated for the first time by Aristotle, became the cause of a heated controversy in the Aristotelian camp on the problem of the divisibility of matter. The appeal to Democritus' non-qualitative atoms of a single matter did not at first contribute to its solution. There seemed to be also a qualitative difference between the smallest chemical particles of a given matter and those of another. This assumption of the existence of the specific smallest particles of a given matter – of the *minima naturalia* – played an important role throughout the Middle Ages, since it constituted the background on which was based the question of the nature and the fate of the *minima naturalia* of the elements when the latter form a *mixis*. In the *minima naturalia* of the Aristotelian tradition we may easily recognize the conceptual forerunners of the molecules of modern-day chemistry. It is also easy to see how the distinction between atom and molecule became possible only in the realm of the doctrine of *minima*; it found no place in ancient atomism.

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Two reasons justify our turning our attention to Robert Boyle who, in the middle of the XVIIth century, dealt thoroughly with the traditional doctrines of elements and finally developed an entirely new conception of the *chemical element*. At last chemistry was

[1] *Aristotle*, De generatione et corruptione, 328a 1–13.

established as an *empirical science*. Further, in a remarkable attempt to derive a compromise between the doctrines of atomism and of the *minima naturalia*, Boyle was the first to successfully resolve the conflicting ideas surrounding the precise conceptual interpretation of the notion of a *chemical compound*.

Let us first consider this latter attempt of Boyles to establish a compromise between the two doctrines – an attempt which was based in part on important preliminary work done by Sennert and Gassendi. On the one hand, the atoms conceived by the atomists were considered, at that time, to be too little "chemical", in their qualitative indistinction, to be accepted as ultimate building-stones of the material world. On the other hand, the few basic principles of this doctrine – magnitude, form, and motion – did prove their usefulness in a mechanistic conception, which in the physics of the time was scoring one success after the other. From this standpoint one can understand Boyle's attempt to reduce once more all chemical qualities to mechanical principles, and yet to take into account that Democritus' heaps of atoms apparently were of no use to the chemist. For the elementary materials, then, Boyle introduced the notion of texture – of an atomical pattern, as it were – to be determined exclusively on the basis of the geometrical and topological properties of the smallest Democritean particles. Chemical compounds could be explained then as the coming together of several textures and their re-organization into a structure through the motion of particles – as the heterogeneous particles taking part in the formation of a definite pattern [2].

This resulted in a doctrine that was a peculiar mixture of atomism and that of *minima naturalia*. On the one hand, it recognized the right of the doctrine of *minima naturalia* to stress the specificity of material particles; on the other hand, it tried to *explain* this specificity in terms of the corpuscles, and of their texture and structure. Though the explanation was mechanistic, it was able to overcome to a certain extent the determined opposition which such explanation had encountered up to that time. The Democritean notion of mere aggregates of corpuscles was superseded here by the notion of *structure* – in place of the disordered aggregate the organization of particles into *structures* was now envisaged. The concept of structure, introduced by Boyle and so eminently important for chemistry, first silenced the centuries-old controversy on the union of elements in chemical compounds.

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Of no lesser importance, however, was Boyle's new conception of an element [3]. This notion, which different traditions had made obscure, is discussed by Boyle for the first time within the framework of empirical research. *Experiments* at last should decide whether the materials which were hitherto considered "elements" are indeed such and not actually compounds. As elements they had to exhibit themselves as "perfectly homogeneous and simple", not composed of other materials or of one another. And why should there be only four elements? Indeed no reason had yet been put forward which could have excluded the possibility of a large number of elements.

The fundamental change in methodical outlook, which Robert Boyle's considerations brought about, can only be fully appreciated, as it were, against the background of tradition. The older doctrines viewed the elements only from the standpoint of their being *in* all *other* materials, as basic materials; the question of the existence of elements arose only in connection with "compounds". Boyle, on the contrary, asked what sort of materials the elements were *in themselves* and *among other* materials. By taking only *chemical simplicity* into account and regarding it as the only chemically essential determination, and further by accepting the possibility of a large, *still indeterminate multiplicity of elements*, Boyle opened up entirely new fields of chemical research. He forcefully confronted chemistry with its proper aim, viz.: to enquire into the multiplicity of materials in order to differentiate between elements and compounds of such elements.

Boyle's new concept of elements was bound to raise questions, on whose answer alone would depend how and in what sense other materials could be envisaged as being composed of elements. It had to be experimentally established which of the materials could be further analyzed, and whether, and if so how often, this process could be repeated. These questions show how stimulating Boyle's ideas were for analytical chemistry – it is not by chance that this name originated from him.

Can it be convincingly established, however, whether a material is simple or compound? The chemist, apparently, would never be able to decide with absolute certainty whether the products obtained by an analysis are really the ultimately simple chemical materials or whether new analytical methods would show that they are still compounds.

Consequently, Boyle did not venture to actually identify any materials as elements. The objection voiced against him on this account fails to duly appreciate these considerations and overstates a rather widespread interpretation of Boyle's views on the elements.

Boyle is often regarded as the author of the "analytical definition" of elements. In such definition the notion of element is explicitly determined in relation to the status of the analytical methods used for its discovery. The definition accordingly refuses to speak of elements "as such". It is easy to see, however, that this interpretation is anachronistic; it is also easy to see how effortlessly it slipped into the history of science. It is one thing to think of a chemical element as a material which in itself *is* simple and cannot be further analyzed chemically, but quite another thing to define an element as a material which *cannot* be further analyzed by experimental methods current at the time.

[2] The Works of the Honourable R. Boyle, 1772 (repr. Hildesheim, 1964–66), Vol. I, p. 493f.; Vol. III, pp. 17f., 49f.

[3] Ref. [2], Vol. I, pp. 495f., 530f., 562.

The statement that "there are chemical elements" does not mean the same thing in both cases. In the first case we are confronted with a metaphysical statement about a quality regarded as pertaining to the material world. Boyle had this in mind when he asserted that "nature makes use of elements". Only in the second case, however, where the existence of chemical elements is tied to their experimental demonstrability, does it correspond to an analytical definition. Boyle did indeed clear the way for it, but it was Lavoisier who first formulated it explicitly.

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In the latter half of the XVIIIth century, a number of epoch-making accomplishments in chemistry are connected with the name of Lavoisier. This seems to substantiate the opinion of those who identify Lavoisier with the climax of a Copernican revolution in chemical thinking. He was responsible for the first systematic application and use of quantitative methods, which led to the confutation of phlogistics and to the grounding of the modern doctrine of oxidation. Among other things, however, this brought about also a decisive reform of the basic views on elements and compounds – and this in a twofold way.

For one thing, the above-mentioned analytical definition of elements aquired significance. Seizing upon Boyle's insight that one could not be sure about the elementary nature of any material if its chemical analysis did not take place, Lavoisier gave it a methodically decisive interpretation, which constituted a turning-point in chemistry's scientific consciousness. Lavoisier purged Boyle's concept of element of all metaphysical implications and directed this concept exclusively on the expediency of the analytical experiment. Certain materials are chemically determined as elements, insofar and so long as there is no way of further analyzing them. They are elements "*pour nous, à notre égard*". The question whether nature itself has produced elements as such lies beyond the ken of chemical science [4].

If one is now to consider that for chemistry elements are not only *basic materials* as a definite class of materials of which other materials are composed, but also basic materials in a wider sense – that is, that the notion of element as such is also the foundation of the kind and structure of our *knowledge* of all remaining materials – then it is clear that Lavoisier's analytical definition means much more than the prudent reserve and self-criticism of its author would lead one to believe. It was an expression of a state of things, whose main significance could be grasped only by the later theoretically advanced chemical science, viz.: that all its statements could not refer ultimately to elements as something simply given in nature but to fundamental hypotheses on the nature of the elements. Most of these hypotheses have brilliantly stood the test of time.

The second result of Lavoisier's reform – much more tangible for positive research than the first – was his interpretation of the processes of oxidation and of reduction, which led to the objective determination of several elements and compounds [5]. Substances which in earlier times were considered as chemically simple as, for instance, water and calcareous metals, now proved to be further decomposable compounds. And conversely, materials which phlogistonists had held to be compounds now had to be considered elements, *e.g.*, sulfur, phosphorus, hydrogen, oxygen, and particularly the metals. What Lavoisier accomplished with this transformation of views on elements and compounds can be measured only in the light of chemistry's later development – it was the start of an entirely new orientation of material systematics.

The first chemical terminology, developed in 1787 by Lavoisier in association with G. de Morveau, Berthollet, and Fourcroy, was firmly constructed on the principle of the new distinction between element and compound. That this terminology has proved itself useful up to the present day, if not in detail still in the essentials of its systematics, is a clear sign of the level of chemical knowledge attained through Lavoisier's work. It was the beginning of a chemical technical language, of whose significance hardly anybody is still aware, since it has long been taken for granted that each science has its own technical terms.

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At the same time, however, this terminology plainly reflects the limits of XVIIIth century chemistry, especially with regard to the element-compound problem. It was not by chance that it went no further than a terminology; all efforts to construct a symbolism, in fact, failed. It still lacked the theoretical foundation which was to be layed down for the first time during the XIXth century. Through his quantitative research on metal-ion precipitates, neutralization, and metathesis, Richter, who was practically unknown in his own day, managed for the first time to give the concept of chemical equivalence a clearly defined meaning and to lay down the foundations of stoichiometry. Lastly, Dalton's atomic theory furnished the basis for the clarification of Richter's stoichiometric results and for a first glimpse into the quantitative composition of compounds. Dalton was the first to recognize the significance of atomic weight in chemical research. From then on the relative atomic weight became the essential characteristic of an element [6].

Though the weights determined by Dalton have today only an historical interest, his view must be regarded as one of the most decisive turning points for XIXth century chemistry. With it, in fact, not only was the way open for a precise study of the chemical proportions for individual compounds, and thus for precise quantitative knowledge on the structure of the material world and its laws, but Dalton's insight also served as a basis for the construction of a set of char-

[4] Oeuvres de Lavoisier, Paris (1862), Vol. I, p. 4.

[5] Ref. [4], Vol. II, pp. 225–233, 623–655.

[6] *J. Dalton*, A New System of Chemical Philosophy. London 1808; German translation by *Fr. Wolff*, Berlin 1812, Vol. I, p. 237.

acteristic symbols, with few and very simple syntactical rules for their application, so that one could speak of a language of signs and formulas in the full meaning of the term. Berzelius developed the symbolic language further, and it was soon supplemented by structural formulas. In its present form, this language is not only a means of information but belongs so inalienably as an essential methodical tool to modern chemistry, that the latter would be simply unthinkable without it. Furthermore, the elegance of this chemical sign-language lies in its ability to illustrate the basic structure of chemical thinking in the simplest terms – the basic distinction between element and compound; any systematics with which the chemist attempts to bestow order and clarity on the fullness and multiformity of the material world is finally oriented on this distinction.

Thanks to Daltonian chemistry's forceful stand on the importance of atomic weight, a third important factor comes into play in this connection. Far from simply remaining a characteristic number for each element, it served as a means of investigating the possibility of *relationships* between different elements. This led in the 1870's to the drawing up of the periodic system of elements, which constituted the basic structure for all further systematization of matter. The atomic weight – or better, the atomic mass – later lost its fundamental significance for this system and had to be replaced by the nuclear charge of the atom. It still remains, however, an historically essential fact that atomic weight offered only one aspect – the most important among several, however – to at least attempt to systematize the elements, an ever greater number of which was being discovered.

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Timidly begun in 1817 with Döbereiner's doctrine of triads, carried on in the fifties about just as promisingly by Pettenkofer and Dumas, half a century was to pass before the periodic system of the elements was established. About 1865 Newlands spoke of a "law of octaves", which he believed he had found in his drawing up of the elements in horizontal series (according to increasing atomic mass) and in vertical series (according to alleged chemical analogy of the elements) [7]. At the beginning this theory was regarded as something of a game and not taken very seriously. However, the fundamental idea of *periodicity*, led later to Meyer's and Mendeléeff's periodic system of the elements – a system that has proved of immense value for science up to our own day [8].

The historical details of this discovery, its testing and verification, and lastly its subsequent completion and correction [9] will not be dealt with here. The pertinent question arises, however, what this system of the elements has meant for chemistry. For the present-day chemist it may have long ago become a triviality; the historian of science, however, may point out how little this system can be taken for granted. For what does it imply to say not only that chemistry has a system, as indeed do some other sciences, but that this system is (i) a system of the chemical *elements*, and (ii) is determined by a *periodic law*?

That chemistry's fundamental norm lies in a system of elements is a statement of fact which for a long time has been a banality for the present-day chemist. However, several centuries were required for this statement of fact to attain clear scientific identity from the obscurity of a host of confused ideas. The final outcome then, was that the chemist must understand the whole of his object of research only in terms of an element or as a combination of elements and nothing else, so that to the chemist, the question of *how* a chemical substance is *constituted* is, therefore, equivalent to the question about its *composition* of elements.

In order to illustrate the meaning of the periodicity of this system, let us again refer to Boyle. It is difficult for us to appreciate the magnitude of the result he achieved and its effects on the history of science. By breaking the chains of the old doctrine of the four elements, Boyle confronted chemistry for the first time with the possibility of an unlimited multiplicity of elements and with the prospect of a series of continued discoveries of elements. Though the establishment of the periodic system did not actually limit Boyle's indeterminate multiplicity of elements, the latter was strictly regulated according to the principles of the system. The fact that up to that time every discovery of an element had been more or less accidental or, at any rate, could be directed by no possible forecast, caused also its chemical properties to appear more or less arbitrary. Through its unequivocal place-disposition the periodic system therefore directed the searching and regulated the expectations of the finding of new elements and their possibilities of forming compounds.

Its uniqueness consists precisely in the periodicity of this system of elements. In the periodic recurrence of a few basic properties, and in the regulated declension of all other chemical and physical properties of the elements, lies, in the final analysis, the normative and real system-generating impulse of chemical science as a whole. For although the periodicity of the system is unable in principle to limit the number of elements, it does in fact radically exclude the arbitrariness of unendingly "new" and forever "other" elements. It seems to be an idle question to inquire whether chemistry could at all be possible as a science if it were not based on a two-dimensional order of elements but only on a one-dimensional series of "totally different" elements. At least it would not be so systematic as it actually is.

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On the threshold of the XXth century, chemistry could afford less than ever to rest confidently on its own laurels. New kinds of experiences not only urged it

[7] *J. A. R. Newlands*, On the Discovery of the Periodic Law. London 1884.

[8] *L. Meyer*, Die modernen Theorien der Chemie und ihre Bedeutung für die chemische Mechanik. Breslau 1864; 5th Edit. 1884. *D. Mendeléeff*, Die Grundlagen der Chemie. Petersburg 1869; German translation Petersburg 1891, p. 666f.

[9] See *E. Ströker*, Denkwege der Chemie. Freiburg-München 1967, p. 189f.

beyond the already inquired but also compelled it to radically revise its basic assumptions. The discovery of radioactive elements that disintegrate spontaneously, and the discovery of cathode rays and of their corpuscular nature posed peremptorily the problem of the *structure of the atom*. The old notion of the unchangeability and indivisibility of the atom – and with it of the elements – had finally died.

The gradual recognition of the mysterious language of atomic spectra as a code on the subtler structure of matter, culminating in Bohr's concept of atomic structure in 1913, marked the beginning of a new era, and of a new understanding of all that was contained in the age-old question on the elements and their compounds. Modern atomic physics has given us the tools for a deeper understanding of the hitherto enigmatic order of the elements in the periodic system, and of their existence and reactivity. "Atomic shell" "atomic nucleus", and electron "shell-structure" furnished the first important concepts for the explanation of what was traditionally called the "properties" and the "qualities" of the elements. Finally, the Pauli principle also provided a solution to the enigma of the periodic law, which Mendeléeff had already sought to resolve by ever renewed and unsuccessful attempts. The wonderful ground-plan of the periodic system could now be reconstructed, and one could at last rationalize the hitherto hidden order of the chemical elements.

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Surely, also the chemically most important property of the elements, viz.: the ability to enter into combination *tout court*, posed new and difficult theoretical problems. Bohr's theory of the atom still lacked the adequate means to explain the mechanism of chemical composition. It is well known that only with the help of wave mechanics has it become possible to tackle the theoretical problems which arose from the extensive experimental work of molecular physics. Because of the endless difficulties which stand in the way of a complete wave-mechanical explanation of chemical bonding for all possible molecules, it is legitimate to doubt whether one can speak strictly of a *theory* of chemical bonding. Nevertheless, wave mechanics must be regarded today as the basis of any explanation of chemical bonding.

To be sure, the exemplary mathematical exactness of this basis can blind no one to the fact that with it the world of matter has become for us something very strange. Elements and compounds which, according to a long-cherished view, the world still consists of, could indeed be fully explained in the conditions of their existence. But the natural scientist's ageless search for something permanent and unchangeable in the material world cannot reach its goal. It has to yield in our day to the knowledge of the essential changeability, impermanence, and destructibility of the old matter.

In conclusion, it should not be overlooked that this knowledge has finally reconciled an ancient contradiction which lasted until modern times and whose earliest rudimentary expression can be seen in the Democritean-Aristotelian controversy. The latest developments of chemistry have carried it beyond the ancient aporetic and have basically mediated the two positions. Still based as mechanics on "atomistic" foundations, it has dissociated itself nevertheless from the Democritean conception and is now to be thought of in terms of *structures* and such structures are to be considered *dynamically*. The ancient quest of Aristotle has thus been satisfied – his *mixis*, starting point of all future problems regarding the concepts of "element" and "compound", can be interpreted without contradiction in present-day research.

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COMMUNICATIONS

High-melting Aromatic Compounds as Stationary Phases in Gas Chromatography

By *F. A. Holdinghausen, D. Freitag, W. Ried,* and *I. Halász* [*]

Dedicated to Professor K. Winnacker on the occasion of his 65th birthday.

When used as stationary phases [1,2], solid organic substances combine advantages of gas-solid and distribution chromatography. Whereas the organic compounds used previously were not particularly stable to heat, our experiments were conducted with high-melting aromatic compounds.

We built our own gas-chromatographic apparatus [3], which contained a flame ionization detector with an appropriate rapid pen recorder and a flow-programming unit [4].

We obtained a stationary phase by mixing a solution of rubrene (5,6,11,12-tetraphenylnaphthacene, m.p. ~330 °C) in benzene with glass beads and evaporating the solvent under an IR lamp [5]. The rubrene cannot then be rubbed off the carrier. The stationary phase consists of 1 wt-% of rubrene

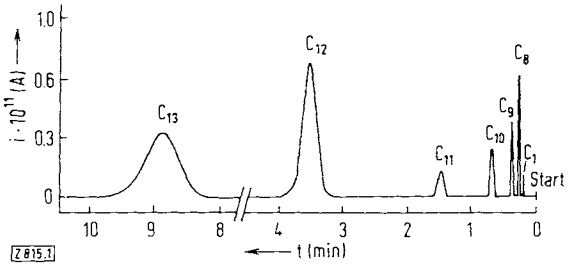

Fig. 1. Separation of C_8- to C_{13}-normal paraffins on solid-coated glass beads. Stationary phase: 1 % of rubrene on glass beads; 50 mg of rubrene per meter of column. Internal diameter of column 2.3 mm; sieve fraction 0.10–0.12 mm. Carrier gas N_2. Δp = 3.0 atm; u = 20 cm/sec. Quantity of sample 5 µg. Ordinate: ionic current of the flame ionization detector.

and 99 wt-% of glass beads. This ratio enables the desired low temperature to be used in the analysis. Figure 1 shows the separation of C_8- to C_{13}-*n*-paraffins at 54 °C. Methane was added to the sample in order to mark the passage time of an inert substance. Not only is the analysis temperature low and the rate of separation high, but also it is noteworthy that the later bands remain symmetrical even at high capacity ratios ($k' = 50$).

A considerable disadvantage of this column is the oxygen-sensitivity of the rubrene. If the traces of oxygen in commercial nitrogen carrier gas are not removed, the life of the column is only a few weeks.

Interesting separations can be carried out on graphitized carbon black [2,6,7]. As well as many advantages, this stationary phase has two disadvantages: the carbon black pellets have not sufficient mechanical strength, and high analysis temperatures are necessary.

To overcome these disadvantages, pelleted graphitized carbon black [**] was covered with 1 wt-% of 2′, 3′, 5′, 6′, 2‴, 3‴, 5‴, 6‴-octaphenyl-*p*-quinquephenyl [8] (m.p. ~470 °C). For this operation a solution of the compound in boiling tetralin was mixed with the carbon black and the solvent was evaporated in a vacuum. The product does not become dusty, neither when the column is filled nor in the flow-programmed gas-chromatographic analysis. The favorable relative retentions of individual components on carbon black are retained with this low coverage [7], the bands are substantially symmetrical, and the analysis temperature can be selected to be somewhat lower. The vapor pressure of this stationary phase is less than 10^{-4} torr at 300 °C; thus the column does not "bleed" and has a long life and an impeccable base line. Figure 2 shows the separation of the ethyl esters of four

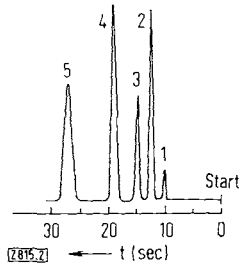

Fig. 2. Separation of fatty acid ethyl esters on graphitized carbon black coated with 1% of octaphenylquinquephenyl. 1: Methane. 2: Ethyl acetate. 3: Ethyl propionate. 4: Ethyl butyrate. 5: Ethyl valerate. Length of column 1 m; internal diameter 2 mm; sieve fraction 0.20–0.25 mm. Carrier gas N_2. $p_i = 2.4$ atm; $p_o = 1.6$ atm; $\bar{u} = 10$ cm/sec. Amount of sample 5 µg.

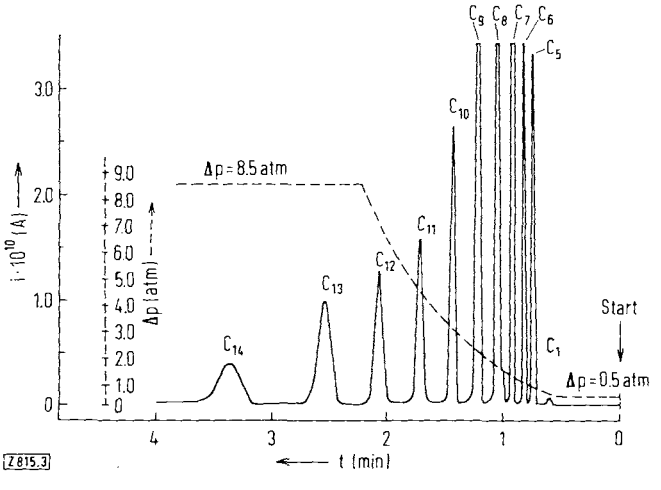

Fig. 3. Flow-programmed separation of C_5- to C_{14}-normal paraffins. Stationary phase as in Fig. 2. $T = 320$ °C. Length of column 2 m; internal diameter 2.3 mm; sieve fraction 0.20–0.25 mm. Carrier gas N_2. Amount of sample 50 µg. Ordinate: see Fig. 1.

fatty acids at 300 °C within 30 sec. In the separation of methyl esters of higher fatty acids under the same conditions the bands remain symmetrical even at extraordinarily high capacity ratios ($k' = 215$).

Figure 3 shows the flow-programmed separation of the C_5- to C_{14}-normal paraffins on the same stationary phase. The broken line shows the decrease in pressure in the column as a function of time – it increases almost exponentially from C_1 to C_{12}.

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[**] Degussa, Frankfurt/Main, Type CK-3, graphitized at Siemens-Plania-Werke AG., Meitingen bei Augsburg, Germany.

[1] *C. G. Scott* in *M. van Swaay*: Gas Chromatography 1962, Hamburg. Butterworths, London 1962, p. 36 and 176; *H. Kelker*, Z. Elektrochem. Ber., Bunsenges. physik. Chem. *67*, 698 (1963); *S. Dal Nogare*, Analytic. Chem. *37*, 1450 (1965).

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[7] *W. Schneider*, *H. Bruderreck*, and *I. Halász*, Analytic. Chem. *36*, 1533 (1964).

[8] *W. Ried* and *K. H. Bönnighausen*, Chem. Ber. *93*, 1769 (1960).

Ligand Reorganization in the Trigonal Bipyramid

By *J. D. Dunitz* and *V. Prelog* [*]

In a recent paper *Muetterties* [1] has discussed the interconvertibility of isomers [A (1,2,3,4,5)] with trigonal bipyramidal geometry through the process: trigonal bipyramid → square pyramid → trigonal bipyramid [2]. Irrespective of whether the square pyramid is regarded as corresponding to a transition state or to an intermediate, the process can be regarded (Fig. 1) as one in which the angle between a pair of apical ligands (1,2) decreases from 180° to 120°, while the angle between a pair of equatorial ligands (3,4) increases from 120° to 180°. At some stage in this process the angle between 1 and 2 must equal the angle between 3 and 4 to give the square pyramidal geometry.

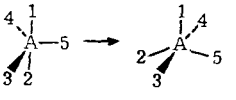

Fig. 1

The problem of keeping track of the various interconversion paths between the ten possible diastereomeric pairs of enantiomers may at first sight appear somewhat intricate; for example, it is not immediately obvious how to convert a given diastereomer into its enantiomer, an interconversion for which at least five steps are necessary [1]. In view of the current interest in problems of this kind, *e.g.* in phosphorus chemistry [1,3,4], we wish to draw attention to the usefulness of simple graph theory in dealing with them. We assume, with *Muetterties*, that the result of each interconversion step

depends at most on the result of the immediately preceding interconversion and not on any earlier interconversion. This implies that, starting from any given state of the system, the possible results of any sequence of interconversions can be represented by a Markov chain[5] or, alternatively, by the corresponding tree diagram[5]. In particular, all such interconversion paths leading from one stereoisomer to another are represented by a Petersen graph, a bridgeless regular graph of degree 3 that is constructed as follows[6]: Each of the ten couples (1,2), (1,3), ... (4,5) that can be formed from five elements is assigned to a vertex, and the vertices are then connected by edges if and only if the corresponding couples contain no elements in common (Fig. 2).

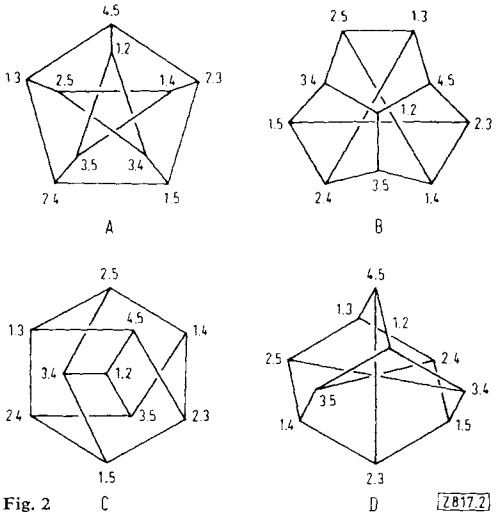

Fig. 2

The ten diastereomeric pairs of enantiomers obtainable by permutation of five different ligands in a trigonal bipyramidal arrangement may be specified by the two ligands in the apical positions (1,2), (1,3), ... (4,5) in each case. If each diastereomer is now associated with one of the vertices of a Petersen graph, the fifteen edges each represent possible interconversion steps. Any sequence of interconversions is thus associated with a corresponding path between vertices of the graph. For any such path the chirality of the resulting diastereomer depends on the chirality of the diastereomer associated with the origin of the path and on the parity of the path (whether the number of edges traversed is even or odd). In particular, a cyclic path leads back to the original enantiomer if the number of interconversion steps is even, and to the opposite enantiomer if the number is odd. From Fig. 2 it follows that a cyclic path leading to inversion of the original diastereomer must contain at least five interconversion steps. The probability that a sequence of five random steps leads back to the origin is easily seen to be $3\times 2\times 2\times 1\times 1/3^5$ or 4/81.

Various stereochemical restrictions (*e.g.* two ligands linked so that they cannot simultaneously occupy apical positions, one ligand constrained to occupy an equatorial position) can be introduced by appropriate modifications of the graph (*e.g.* all paths passing through a given vertex or through a given sub-set of vertices may be regarded as forbidden).

In Fig. 2 we have shown in addition to the usual representations A, B, and C of the Petersen graph another representation D that may have some mnemonic value for chemists. In this new representation the ten couples (1,2), (1,3), ... (4,5) are associated with the ten vertices of an adamantane skeleton in which the six secondary atoms are linked by the three diagonals of the corresponding octahedron. Notice that all cyclic paths that run exclusively along the adamantane skeleton contain an even number of edges and hence lead back to the original enantiomer; cyclic paths that contain an odd number of edges must include an odd number of diagonals.

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[1] *E. L. Muetterties*, Inorg. Chem. *6*, 635 (1967).

[2] This process has sometimes been called "pseudo-rotation", a term that has been also used in a quite different context (see *J. E. Kilpatrick*, *K. S. Pitzer*, and *R. Spitzer*, J. Amer. chem. Soc. *69*, 2483 (1947)).

[3] *M. J. Gallagher* and *I. D. Jenkins* in *E. L. Eliel* and *N. L. Allinger*: Topics in Stereochemistry, Vol. 3, Interscience, New York 1968 (in press).

[4] *F. H. Westheimer*, Accounts Chem. Res. *1*, 70 (1968).

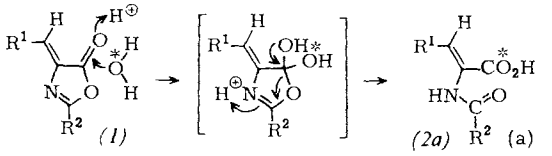
[5] See, for example, *S. Lipschutz*, Finite Mathematics. Schaum Publishing Co., New York 1966.

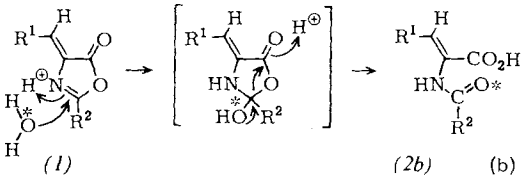
[6] *D. König*: Theorie der endlichen und unendlichen Graphen, Akademische Verlagsgesellschaft Leipzig 1936, reprinted by Chelsea Publishing Company, New York, p. 194.

Course of Acid Hydrolysis of 4-Alkylidene- and 4-Arylalkylideneoxazol-5-ones

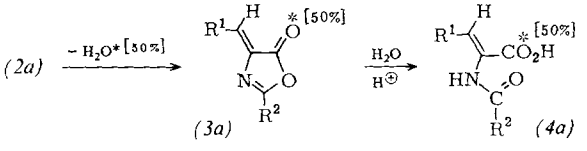
By *W. Steglich*, *V. Austel*, and *A. Prox*[*]

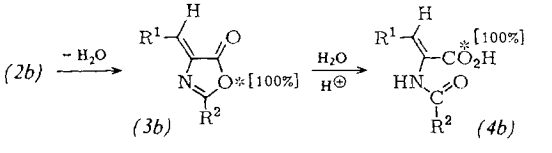
In principle, water can add to the C=O or to the C=N double bond on acid hydrolysis of 4-alkylidene- and 4-arylalkylideneoxazol-5-ones *(1)* to 2-acylaminoacrylic acids *(2)*.





If $H_2{}^{18}O$ is used, the carboxyl group of the 2-acylaminoacrylic acid *(2a)* is labeled by route (a), but the acyl group becomes labeled by route (b). The position of the label can be easily determined, namely, by recyclizing the 2-acylaminoacrylic acids *(2)* by trifluoroacetic anhydride to the oxazolones *(3)* and opening these to 2-acylaminoacrylic acids *(4)* by $H_2{}^{16}O/H^+$.





On cyclization, the acid *(2a)* loses 50 % of its ^{18}O, but *(2b)* does not lose any. Opening of *(3a)* by $H_2{}^{16}O$ according to route (a) yields *(4a)*, which in contrast to *(2a)* contains only 50 % of the ^{18}O in the carboxyl group. However, *(2b)* gives *(4b)* by mechanism (b), without loss of ^{18}O. In the conversion of *(2b)* into *(4b)* the label of the acyl group migrates to the carboxyl group.

For mass-spectrometric comparison of the ^{18}O content of the acids *(2)* and *(4)*, several 4-alkylidene- and 4-arylalkylidene-oxazolones were hydrolyzed to acids *(2)* and these were converted into acids *(4)* as described above. Table 1 records the ^{18}O contents of *(2)* and *(4)*; it shows that there is no loss of ^{18}O in any of the cases studied for conversion of *(2)* into *(4)*, thus proving route (b) to be correct. An additional proof is provided by the mass-spectrometric fragmentation, which shows that all the ^{18}O of *(2)* occurs in the acyl group, whereas in *(4)* it is all in the carboxyl group.

Table 1. Mass-spectrometrically determined content of ^{18}O-labeled 2-acylaminoacrylic acids *(2)* and *(4)* [a].

(1)		*(2)*	*(4)*
R^1	R^2	content of ^{18}O-*(2)* (%)	content of ^{18}O-*(4)* (%)
H	CH_3	56	56
CH_3	CF_3	54	55
C_6H_5	CH_3	56	55
C_6H_5	C_6H_5	14.5 [b]	

[a] The oxazolone *(1)* (0.5 mmole) in CF_3CO_2H (0.7 ml) was treated with 61 % $H_2{}^{18}O$ (0.04 ml) and kept for 3 h at room temperature or, where $R^1 = R^2 = C_6H_5$, for 1.5 h at 90 °C (bomb tube). After removal of CF_3CO_2H by distillation under vacuum the radioactivity of the product *(2)* was determined by a MS 9 (AEI) mass spectrometer at 20 eV. For conversion into *(4)*, the product *(2)* (0.5 mmole) was set aside in trifluoroacetic anhydride (1 ml) for 15 min; the solution was then evaporated under vacuum and *(3)* was treated as above with $H_2{}^{16}O$.

[b] Owing to slow hydrolysis the $H_2{}^{18}O$ was diluted by exchange with CF_3CO_2H. The isotope ratio of the benzoyl ion (13.5 % *m/e* 107) shows that the ^{18}O is in the benzoyl group.

A 1,4-addition of water is excluded by the hydrolysis of 4-ethylidene-2-trifluoromethyloxazol-5-one by D_2O/CF_3CO_2D, since the NMR spectrum shows that no deuterium is incorporated into the 3-position of the resulting 2-(trifluoroacetamido)crotonic acid. H_2S[1] and HN_3[2] also add to C-2.

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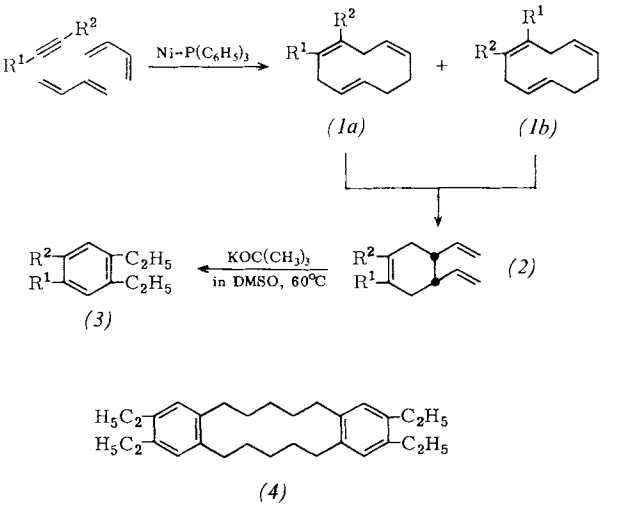
Preparation of Tri- and Tetra-substituted Aromatic Compounds

By *P. Heimbach* and *R. Schimpf*[*]

4,5-Disubstituted *cis,cis,trans*-1,4,7-cyclodecatrienes *(1a)* and *(1b)* can be prepared from 1,3-butadiene and disubstituted alkynes in high yield on use of a nickel catalyst bearing triphenylphosphine as ligand[1]. If monosubstituted alkynes are used, the corresponding ten-membered rings are obtained in yields of only 40–70 % calculated on the alkyne used. The cyclodecatrienes *(1a)* and *(1b)* are valuable for further syntheses, and so are the 1,2-disubstituted *cis*-4,5-divinylcyclohexenes *(2)* that can be obtained from them by stereospecific valence isomerization[2,3]. Isomerization of compounds *(2)*, by, *e.g.*, potassium *tert*-butoxide in dimethyl sulfoxide[4], affords on complete conversion almost quantitative yields of aromatic compounds of the durene type, such as *(3)*, which are difficultly accessible by other methods.

IR and NMR spectra are in accord with the structures assigned. Product *(3a)* can be oxidized to pyromellitic acid. Product *(3d)* is obtained in almost quantitative yield on complete conversion of 1,2,4-trivinylcyclohexane, which is



Cpd.	R^1	R^2	B.p. (°C/torr) (m.p. (°C))	n_D^{20}	n_D^{20} (lit.)
(3a)	CH_3	CH_3	106/14	1.5080	1.5095 [5]
(3b)	C_2H_5	CH_3	111/13	1.5060	
(3c)	$-(CH_2)_{10}-$		(31.5–32)		
(3d)	C_2H_5	H	93/12	1.5010	1.5009 [6]
(4)			(149–150)		

formed by thermal isomerization of 1,5,9-cyclododecatriene[1].

The isomerization of trivinylcyclohexane occurs also with lithium in ethylenediamine or sodium in *o*-chlorotoluene[6], but yields are only 61 % at 90 % conversion. We have also used substituted 1,3-dienes in place of butadiene for the synthesis of *(3)*.

Experimental:

Compound *(2)* (0.15 mole) is heated with potassium *tert*-butoxide (15 mmole) and dimethyl sulfoxide (35 ml) at 60 °C for 4 to 24 h (reaction course followed *e.g. via* the refractive index). All volatile components are then removed at 10^{-4} torr and condensed. DMSO is extracted from the condensate with water and the residue *(3)* is dried. Conversion and yield: 98–100 %.

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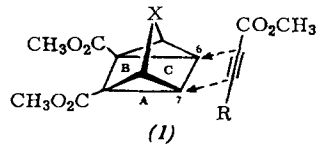
Cycloadditions to Derivatives of 3-Azaquadricyclane (Bishomopyrrole)[1]

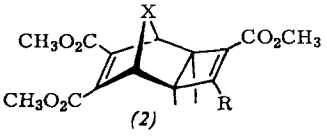
By *H. Prinzbach, R. Fuchs, R. Kitzing*, and *H. Achenbach*[*]

Isocyclic tetracyclo[3.2.0.$0^{2,7}$.$0^{4,6}$]heptane derivatives *(1)* usually add dienophilic reagents at positions 6 and 7, yielding *exo*-tricyclenes *(2)* with cleavage of the cyclopropane link-

ages A [2]. In contrast, the bridge oxygen atom of the 3-oxa systems *(3)* directs the same dienophiles to positions 2 and 4, whereby bonds B are broken with formation of compounds *(4)* [3].

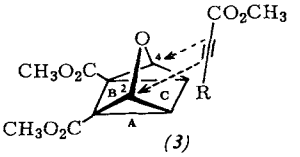


(1)

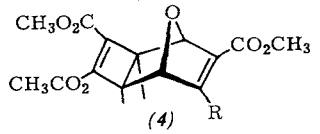


(2)

X = CH_2, $C(CH_3)_2$, $C{=}C(CH_3)_2$, $C{=}C(C_6H_5)_2$, $C{=}CHC_6H_5$, $C{=}O$

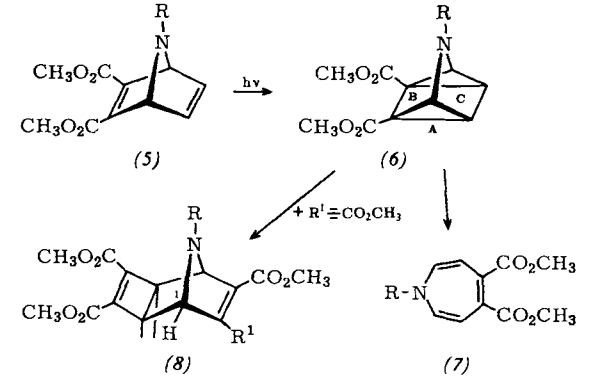


(3)



(4)

Like *(1)* and *(3)*, 3-azaquadricyclanes *(6)* [4] (accessible from pyrroles by way of *(5)* [5,6]) also have diene properties. However, valence isomerization requires only slight thermal activation, leading to the azepines *(7)*, so that good results in the addition reactions are obtained only on use of very reactive reagents. Dimethyl acetylenedicarboxylate or methyl propiolate and *(6a)* to *(6d)* give 50–70% yields of the adducts *(8a)* to *(8d)*.

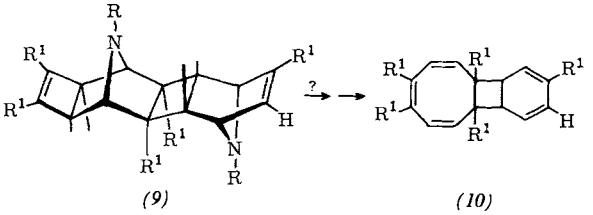


(5) *(6)* *(8)* *(7)*

(a), R = $SO_2C_6H_4CH_3$, R^1 = CO_2CH_3
(b), R = $SO_2C_6H_4CH_3$, R^1 = H
(c), R = $COCH_3$, R^1 = CO_2CH_3
(d), R = $COCH_3$, R^1 = H

For this purpose, the compound *(6)* is kept for 24 to 48 h at −15 to −30 °C in a 10- to 20-fold excess of the dienophile. The azepine *(7)* formed can be separated cleanly by chromatography. *(8a)–(8d)* are isolated by crystallization from CH_2Cl_2.

The structures *(8)* are proved by elemental analysis, mass spectra, UV, IR, and, in particular, NMR data (Table 1). The parallelism of *(1)* and *(3)* observed for course of pyrolysis and direction of addition [5] is thus valid also for the aza skeleton *(6)*. In batches containing equimolar amounts of *(6)* and dimethyl acetylenedicarboxylate or methyl propiolate the products *(8)* can compete as dienophile; *e.g. (8b)* and *(6a)* give a product that for spectroscopic reasons (Table 1) is assigned structure *(9)*. We are testing whether the [8.4.1.1^{4,7}.0^{2,9}.0^{3,8}.0^{11,14}]hexadeca-5,12-diene derivatives *(9)*, which are thus readily accessible, can provide a route to C_{14} compounds of type *(10)* by elimination of both aza bridges.



(9) *(10)*

R = $SO_2C_6H_4CH_3$, R^1 = CO_2CH_3

Table 1. 9-Azatricyclo[4.2.1.0^{2,5}]nonadienes *(8)* and pentamethyl 15,16-ditosyl-15,16-diazahexacyclo[8.4.1.1^{4,7}.0^{2,9}.0^{3,8}.0^{11,14}]hexadeca-5,12-dien-2,5,9,12,13-pentacarboxylate (9).

Cpd.	m.p. (°C)	UV [a] λ_{max} (nm) (ε)	Molecular ion at *m/e*	NMR [b] (τ, TMS = 10)
(8a)	151	225 (23400)	505	2.36 (2,D,*J*=8 Hz), 2.72 (2,D,*J*=8 Hz), 5.16 (2,S), 6.17 (6,S), 6.25 (6,S), 7.04 (2,S), 7.60 (3,S)
(8b)	187	223 (20700)	447	2.45 (2,D,*J*=8 Hz), 2.74 (2,D,*J*=8 Hz), 3.24 (1,D,*J*=2.2 Hz), 5.12 (1,S), 5.30 (1,D,*J*=2.2 Hz), 6.14 (6,S), 6.31 (3,S), 7.21 (2,S), 7.62 (3,S)
(8c)	137	210 (18600)	393	4.60 (*ca.* 1,S), 5.00 (*ca.* 1,S), 6.18 (12,S), 6.94 (2,br.S), 8.08 (3,S)
(8d)	116–118	210 (17500)	335	2.77(*ca.*0.7;D;*J*=2.6 Hz), 2.82(*ca.* 0.3;D;*J*=2.6 Hz), 4.62 (*ca.* 0.3; S), 4.81(*ca.*0.7;D;*J*=2.6Hz), 5.02 (*ca.* 0.7; S), 5.23(*ca.*0.3; D;*J*=2.6 Hz) 6.14–6.20 (9,br.S), 7.15 (2,S), 8.10 (*ca.* 2.1,S), 8.12 (*ca.* 0.9,S)
(9)	287–290 (decomp.)	230 (28200)	811	2.3–3.1 (8,M), 3.86 (1,D), 4.9–5.7 (4,M), 6.18–6.35 (15), 6.69 (2,S), 7.60 (3,S), 7.68 (3,S), 8.22 (2,br.S)

[a] In ethanol. [b] In $CDCl_3$ (*ca.* 36 °C).

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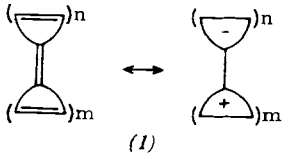
11,12,13,14-Tetraphenyl-3,8-methanopentahendecafulvalene [1]

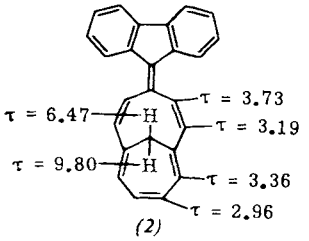
By *H. Prinzbach* and *L. Knothe* [*]

Cyclic, cross-conjugated compounds *(1)* containing two potentially "aromatic" partial systems ($m = 1, 3, 5..$; $n = 2, 4..$) are very readily polarizable, equally reactive towards electrophiles and nucleophiles (also radical reagents), and correspondingly unstable [2]. So far, none of the parent compounds *(1)* has been isolated; only *(1b)* has been prepared [3] in very dilute solution.



(1)

(a), n = 2, m = 1
(b), n = 2, m = 3
(c), n = 2, m = 5



(2)

We have now obtained the non-annelated, phenyl-substituted compound *(4)* by a method similar to that used [4] for compound *(2)*, which was the first stable derivative of the $6\pi - 10\pi$ series *(1c)*. When 9.6 mmoles of lithium tetraphenylcyclopentadienide was treated with 8.3 mmoles of compound *(3)* [5] in 100 ml of tetrahydrofuran at −30 °C a very complex mixture was formed. This was not separated but was oxidized with 20 mmoles of chloranil in boiling carbon tetrachloride, the oxidation products being separated on a silica gel column. One of the brownish-red zones afforded hydrocarbon *(4)*, m.p. 229–232 °C (yield 3–4%), which crystallizes from carbon tetrachloride as thin reddish-brown needles. The structure *(4)* was proved by elemental analysis, mass spectrum [6], IR and particularly UV and NMR data.

m/e: 522 (M^+, 100%), 523 (46%), 524 (9%), 315 (5%), 261 (M^{2+}, 3%), 121 (6%), 119 (20%), 117 (20%), 82 (5%), 38 (6%), 36 (19%), 28 (10%).

IR (KBr): ν = 1595, 1515, 1492, 1437, 1246, 1214 cm^{-1}.

UV: λ_{max}(cyclohexane) = 439 (ε = 22200), 349 (24400), 256 nm (42200).

λ_{max}(nitromethane) = 445 (ε = 18900), 371 nm (12100).

The presence of the symmetry plane in *(4)* is shown by the NMR spectrum (Fig. 1) which contains a multiplet due to 20 phenyl protons, the A_2B_2 system for H (4), H (5), H (6), and H (7), the AB quartet for H (1), H (2) and H (9), H (10), and the AX quartet for H (17a) and H (17b); the coupling constants agree with those for *(2)*, but the chemical shifts show clearly the anisotropic influence of the phenyl groups.

As was to be expected, the signals of H (1), H (2), H (9), H (10), and H (17a) show a marked diamagnetic shift. On the other hand the protons H (4), H (5), H (6), H (7), and H (17b), which are further removed from the phenyl groups, resonate at about the same frequencies as in *(2)* and are clearly only slightly more deshielded than are the corresponding protons in the tropylidene [τ H (2,5) = 3.88; τ H (3,4) = 3.45; $CDCl_3$]. The resulting alternation in the π-electron density distribution in *(4)* is evident from the coupling constants J_{12}, which at 12 Hz indicate the high bond order of a largely localized olefinic C=C double bond [7]. The value of

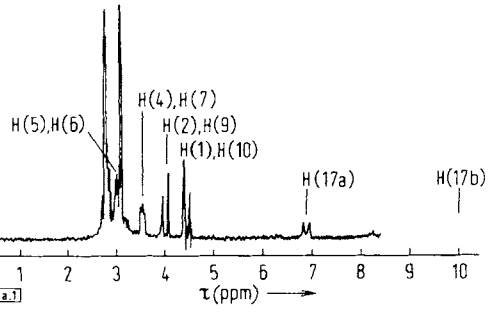
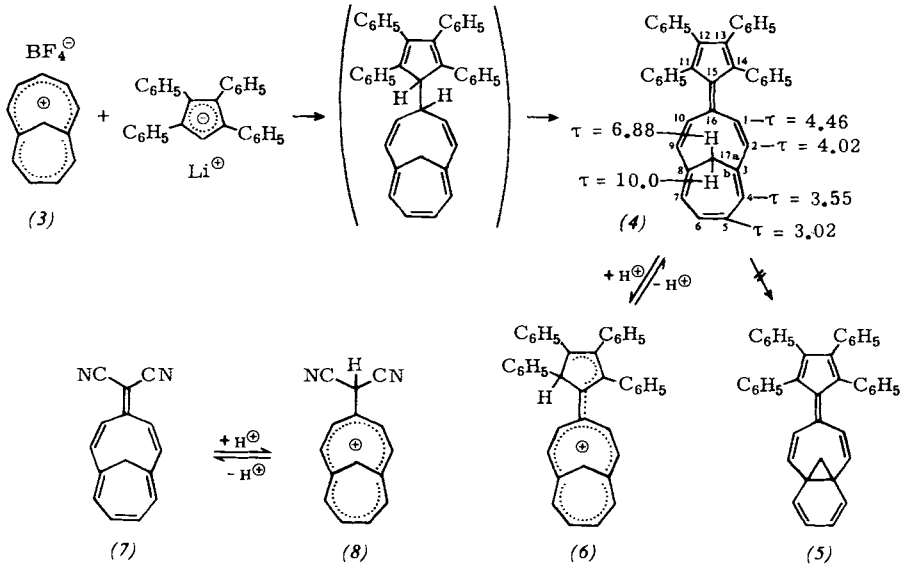


Fig. 1. NMR spectrum (100 MHz) of *(4)* in $CDCl_3$. A doublet having J = 11.0 Hz occurs at τ = 10.0.

J_{17a17b} (11 Hz) excludes the valence-isomeric form *(5)* [8]. In contrast to *(2)*, however, but like the analogous calicene [9] and sesquifulvalene derivative [10], compound *(4)* is protonated in CF_3CO_2H or in perchloric acid/ethanol [**]. UV and NMR measurements prove that electrophilic attack by the proton occurs mainly, if not exclusively, at position 11, yielding ion *(6)*, with the positive charge also delocalized over the aryl-substituted five-membered ring and the charge



(3) *(4)* *(7)* *(8)* *(6)* *(5)*

deficit in the eleven-membered ring correspondingly diminished. When compared with the π-π^* excitation of the unsubstituted cation *(3)*[11] (λ_{max} = 423 nm; ε = 4000; 60% sulfuric acid) or the conjugate acid *(8)* of dicyanohendecafulvene *(7)* (λ_{max} = 426 nm; perchloric acid/ethanol[**][12]), the transition of longest wavelength for *(6)* (λ_{max} = 610 nm, ε = 24400; perchloric acid/ethanol[**]) is greatly shifted towards longer wavelengths. The τ values of the protons of the eleven-membered ring in *(6)* (multiplet between τ = 1.6 and 2.1; CF_3CO_2H) are, on the average, about 0.85 ppm units greater than the τ values of *(3)*.

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An X-Ray Study of Non-stabilized Ylids

By *J. C. J. Bart*[*]

No X-ray crystallographic work on the air-sensitive, non-stabilized phosphonium ylids (Wittig reagents) has hitherto been reported. Alkylenetriphenylphosphoranes, which may be pictured as

$$(C_6H_5)_3P{=}CR_2 \leftrightarrow (C_6H_5)_3\overset{\oplus}{P}-\overset{\ominus}{C}R_2$$

afforded the following crystallographic data[1]:

$(C_6H_5)_3PCH_2$ *(1)* (yellow): a = 18.455, b = 9.614, c = 18.103 Å; β = 106°56′.

Space group $P2_1/c$, with 2 molecules per asymmetric unit.

$(C_6H_5)_3PC(CH_3)_2$ *(2)* (red): a = 19.201, b = 11.289, c = 16.950 Å; α = 89°36′, β = 70°55′, γ = 88°44′.

Space group $A\,1$ or $A\,\bar{1}$, Z = 8, V = 3471.3 Å^3; d (calc) = 1.165 g/cc.

A three-dimensional structure analysis of *(1)* has now been completed. The atomic positions were determined by Patterson and Fourier methods and refined by a least-squares procedure with 2586 linear diffractometer data. The hydrogen atoms were located by difference maps; final R-factor 0.064. No significant differences were found between the two independent molecules in the asymmetric unit. The average length of the bond formally written as P=C is 1.661 Å (estimated standard deviation 0.008 Å). This is considerably less than the single bond distance (~ 1.85 Å) in tertiary phosphines and significantly shorter than that in the stabilized ylids $Ph_3P{=}CXY$ for which structural data are available[2]. Similar phosphorus-carbon lengths were found only in $Ph_3P{=}C{=}C{=}X$ (X = O,S)[3]; the nature of the P=C bond is not yet clear in these compounds. The value of 1.661 Å is close to that obtained according to *Pauling*[4] by summation of the double bond radii of P and C (1.665 Å) and indicates π-bonding character[5].

Other studies give evidence for a polar formulation ($\overset{\oplus}{P}$-$\overset{\ominus}{C}$) of *(1)*. *Lüttke* and *Wilhelm*[6] estimate a bond order of 1.3 for the phosphorus-methylene bond from IR data. The near identity of the ^{31}P–NMR chemical shifts[7] in *(1)* and in $[(C_6H_5)_3P^{\oplus}CH_3]Br^{\ominus}$ suggests little delocalization of the electron-density at the carbanion. The observed short $P{=}CH_2$ distance would evidence overlap of the empty d-orbital of P with the CH_2 p-orbital and consequent stabilization of the carbanion. If it is assumed that the phosphorus d-orbitals are of suitable size and energy for effective bonding[5,8], then the overlap with the CH_2 p-orbital is close to the carbon atom, thus giving polarity to the bond. The methylene carbon atom is sp^2 hybridized. The overlap of a sp^3-hybrid orbital and a d-orbital of P is clearly less efficient than that between a p- and a d-orbital.

The P–C (phenyl) bond lengths are close to the average 1.823 Å, which is slightly longer than the average of similar bonds in most other quadruply connected phosphorus compounds[2,3]. Phosphorus has a distorted tetrahedral coordination in *(1)* with C(phenyl)-P-C(methylene) angles ranging between 111.4° and 115.0° (average 113.5°) and C(phenyl)-P-C-(phenyl) angles between 102.8° and 107.4° (average 105.0°). The latter value is slightly larger than that found in $P(C_6H_5)_3$ (103.0°)[9]. The phenyl groups have unequal rotations around the P–C bonds and adopt a paddle-wheel arrangement. Despite the presence of two molecules in general positions in the asymmetric unit and the polar nature of the $P{=}CH_2$ group, no dimerization or strong molecular interaction is observed in the solid. The molecules are packed by ordinary van der Waals forces. The arrangement of the molecules in the crystal structure is pseudo $P2_1/a$.

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[1] Substances *(1)* and *(2)* were prepared in a salt-free state by Drs. *M. Schlosser* and *K. F. Christmann* of Heidelberg University.

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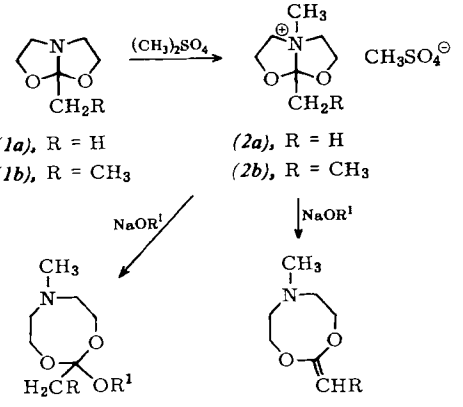
Synthesis of 1,3-Dioxa-6-azacyclooctanes from 4,6-Dioxa-1-azabicyclo[3.3.0]octanes

By *R. Feinauer* [*]

On reaction with carboxylic acids or anhydrides[1], phenols, or secondary amines[2], 4,6-dioxa-1-azabicyclo[3.3.0]octanes *(1)* yield carboxamides by ring fission. The reaction with aliphatic aldehydes[3] leads to 3-acyloxyalkyl-2-alkyloxazolidines.

We have converted compounds *(1)* into 1,3-dioxa-6-azacyclooctanes *(3)* and *(4)* by methylation with dimethyl sulfate and treatment of the methylation products *(2)* with Na alkoxide.



(1a), R = H; *(1b)*, R = CH_3 — *(2a)*, R = H; *(2b)*, R = CH_3

(3a), R = H, R^1 = CH_3; *(3b)*, R = CH_3, R^1 = CH_3; *(3c)*, R = H, R^1 = C_2H_5; *(3d)*, R = CH_3, R^1 = C_2H_5 — *(4a)*, R = H; *(4b)*, R = CH_3

Starting material	Yield (%)		B.p. (°C/torr)		n_D^{20}	
	(3)	*(4)*	*(3)*	*(4)*	*(3)*	*(4)*
(2a)	*(3a)*, 38	*(4a)*, < 5	57/3	—	1.4546	—
(2a)	*(3c)*, 20	*(4a)*, < 5	50/1	—	1.4490	—
(2b)	*(3b)*, 42	*(4b)*, 5	66/2	54/2	1.4556	1.4780
(2b)	*(3d)*, 10	*(4b)*, 37	70/2	54/2	1.4522	1.4780

1-Methyl-5-alkyl-4,6-dioxa-1-azoniabicyclo[3.3.0]octane methosulfate (2):

Dimethyl sulfate (0.4 mole) was added with cooling and stirring to a solution of *(1a)* or *(1b)* in CH_2Cl_2 (200 ml) at such a rate that the internal temperature did not exceed 30 °C. After 30 minutes' stirring, the vessel was placed in ice. The colorless crystals of *(2a)* or *(2b)* that separated were filtered off, washed with CH_2Cl_2, and dried in a desiccator. *(2a)*, yield 79%, m.p. 100–101 °C. *(2b)*, yield 82%, m.p. 112 to 113 °C.

2-Alkoxy-2-alkyl- (3) and 2-alkylidene-6-methyl-1,3-dioxa-6-azacyclooctane (4):

The methosulfate *(2)* (0.4 mole) was dissolved in methanol or ethanol (100 ml), and to it was added at 60 °C with stirring a solution of Na (0.4 mole) in the corresponding alcohol (150 ml); the whole was then kept at 60 °C for a further 2 h. After cooling the solution was filtered from precipitated $NaCH_3SO_4$, the excess of alcohol was distilled off through a column, and the residue was distilled and fractionated through a rotating band column under vacuum. The properties of the compounds *(3)* and *(4)* obtained are summarized in the Table.

Reaction of *(2a)* with methoxide or ethoxide gives mainly *(3a)* or *(3c)*, respectively; *(4a)* could only be detected in traces spectroscopically, presumably because of its lower stability. With Na methoxide *(2b)* gives mainly *(3b)* but with Na ethoxide gives mainly *(4b)*. *(3b)* could not be converted thermally into *(4b)*. This indicates that addition of the alkoxide anion and elimination of a proton compete in formation of *(3)* or *(4)* from *(2)* and alkoxide. The products *(3)* and *(4)* are colorless liquids; their structures are proved by elemental analyses, determination of molecular weights, and IR, NMR, and mass spectra.

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Fixation of Molecular Nitrogen on Nickel(0)

By *P. W. Jolly* and *K. Jonas* [*]

Since 1965 several complexes of transition metals (Ru[1], Os[2], Co[3], and Ir[4]) have been found that contain nitrogen as ligand. We now report a nitrogen-nickel(0) complex in which two nickel atoms are bound to one nitrogen molecule. If nickel acetylacetonate is treated with trimethylaluminum in the presence of tricyclohexylphosphine and nitrogen at −30 to +20 °C, a yield of *ca.* 40% of bis[bis(tricyclohexylphosphine)nickel]dinitrogen is obtained as dark red crystals.

$$2\ Ni(acac)_2 + 4\ (C_6H_{11})_3P + 4\ Al(CH_3)_3 + N_2 \rightarrow N_2[Ni(P(C_6H_{11})_3)_2]_2 + 4\ (CH_3)_2Al(acac) + 4\ CH_3\cdot$$

The nitrogen molecule can easily be replaced by other ligands, such as olefins, phosphines, or CO. When ethylene or the isomers of 1,5,9-cyclododecatriene are used, known bis(tricyclohexylphosphine)nickel-olefin complexes[5] are obtained and exactly $^1/_2$ mole of N_2 is liberated per g-atom of Ni.

Cryoscopic determination of the molecular weight in benzene and the IR spectra show that the complex *(1)* in the dark red solution presumably exists as an equilibrium mixture of *(2)* and *(3)*.

$$\underset{(1)}{N_2[Ni(P(C_6H_{11})_3)_2]_2} \rightleftharpoons \underset{(2)}{N_2{\cdot}Ni(P(C_6H_{11})_3)_2} + \underset{(3)}{Ni(P(C_6H_{11})_3)_2}$$

$$(1) \xrightleftharpoons[N_2]{Ar} 2\ (3)$$

The band at 2028 cm^{-1} is probably to be ascribed to the NN stretching vibration; it disappears if argon is passed through the solution, which then becomes yellow and gives a freezing-point depression indicating that the equilibrium has been shifted entirely towards the right. The yellow solution absorbs nitrogen with red coloration, and the starting system is reformed (mol. wt. and band at 2028 cm^{-1}).

(1) presumably has the structure:

$$[C_6H_{11})_3P]_2Ni : N \equiv N : Ni[P(C_6H_{11})_3]_2$$

X-ray structure analysis is in progress[6] (cell data: $P2_{1/n}$, a = 21.83 Å, b = 16.54 Å, c = 21.24 Å, β = 102.7°, Z = 4, d (X-ray) = 1.12, d (pycn.) = 1.13).

Experimental:

A solution of $Al(CH_3)_3$ (2.2 ml) in toluene (5 ml) is added dropwise and slowly to a solution of $Ni(acac)_2$ (5 g, approx. 20 mmole) and tricyclohexylphosphine (12 g, approx. 40 mmole) in toluene (50 ml) at −20 °C with stirring and passage of nitrogen. The reaction mixture is allowed to warm to room temperature and stirred for a further 10 h. Red crystals

are precipitated, which are sucked off, washed with ether, and dried. The compound can be recrystallized from toluene under nitrogen.

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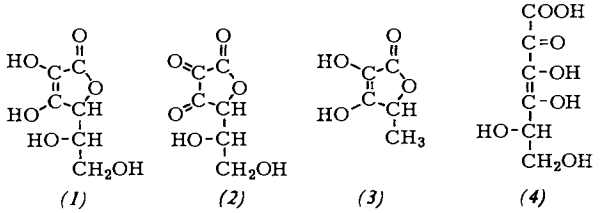
Constitution and Synthesis of an *aci*-Reductone Formed on Non-oxidative Degradation of Dehydroascorbic Acid[**]

By *K. Wisser*, *W. Heimann*, and *E. Mögel*[*]

On two-electron oxidation L(+)-ascorbic acid *(1)* (vitamin C) is converted into L(+)-dehydroascorbic acid *(2)*, which can be reduced back to *(1) in vivo* and *in vitro*. The dehydro acid *(2)* decomposes non-oxidatively and non-enzymically to products that are of interest in food chemistry because they cause discoloration and changes in taste.

CO_2, oxalic acid, threonic acid, furfuryl alcohol, L-xylosone (?), ethylglyoxal, and 2-keto-3-deoxy-L-pentono-γ-lactone (5-hydroxymethyltetrahydro-2,3-furandione) have been detected as degradation products[1–5]. Little is reliably known about the course of the degradation. A strongly reducing compound arising on degradation of *(2)* has been formulated as *(3)*[1] but also as *(4)*[3].

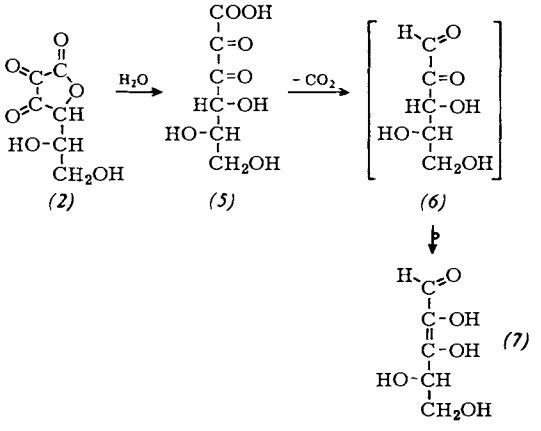


(1) *(2)* *(3)* *(4)*

Developing a thin-layer chromatogram of an aqueous solution of *(2)* obtained on silica gel or aluminum oxide at room temperature affords many zones that obviously arise from products formed by catalytic decomposition of *(2)* on silica gel or aluminum oxide but have been held by most authors to represent the initial stage of the degradation of *(2)*. 2,3-Diketogulonic acid *(5)* (R_F = 0.1) is obtained after about 1 h at room temperature on thin-layer chromatography on cellulose with butanol/glacial acetic acid/water (4:1:1); after some weeks a new substance of R_F = 0.8 appears which is strongly reducing analogous to *(1)*. This second zone appears homogeneous in several eluants and on two-dimensional thin-layer chromatography.

On use of 1-^{14}C-labeled *(2)* autoradiography of the chromatogram shows that the new compound no longer contains C-1; apparently the acid *(5)* is decarboxylated slowly even at room temperature. Polarography of the eluted zone indicates an enediol grouping and an aldehyde group activated by conjugation. K_{diss} for sulfite addition was determined, also polarographically, as 1.1×10^{-3}. The IR spectrum contains a sharp absorption band at 1700 cm^{-1}; compounds of tetronediol type, such as *(1)*, *(3)*, 3,4-dihydroxy-2,5-dihydrofuranone, and the corresponding deuterated compounds, however, show two sharp bands, one between 1630 and 1665 cm^{-1} and the other between 1737 and 1754 cm^{-1}. At pH 5 the compound gave a UV band with λ_{max} = 291 nm, similar to that of triosereductone (λ_{max} = 288 nm).

From these results it is concluded that decomposition of *(2)* leads by way of *(5)* and *(6)* to *(7)*; and this has been prepared also from L-arabinose by way of the osazone and osone[6,7].



(2) *(5)* *(6)* *(7)*

Enolization of the arabosone to give *(7)* occurs analogously to the proton-catalyzed isomerization of hydroxypyruvaldehyde to triosereductone[8].

The L-2,3,4,5-tetrahydroxy-2-pentenal prepared from L-arabinose is chromatographically, polarographically, and UV- and IR-spectroscopically identical with the non-oxidative degradation product of *(2)*.

Substance *(7)*, which was obtained in mg quantities, is a yellow syrup and decomposes slowly at room temperature with browning. We suggest that it be called L-pentosereductone or erythroreductone.

The *aci*-reductone formed on warming *(2)* in dilute sulfuric acid is not compound *(3)* as previously postulated[1]; authentic *(3)* has different UV and IR spectra. The product isolated by the procedure of reference[1] is mainly an as yet unidentified reducing compound plus a smaller amount of *(7)*.

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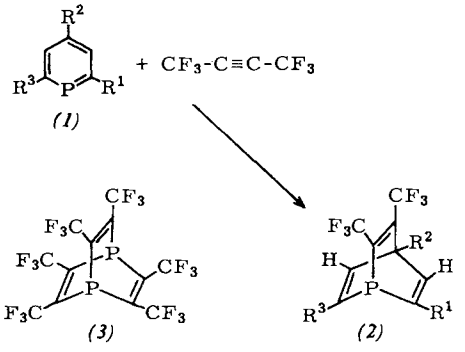
Substituted 1-Phosphabarrelenes (1-Phospha[2.2.2]octa-2,5,7-trienes)[1]

By *G. Märkl* and *F. Lieb*[*]

2,4,6-Trisubstituted phosphorins *(1)*[2] have only slight diene reactivity. 2,4,6-Triphenylphosphorin *(1a)*, $R^1 = R^2 = R^3 = C_6H_5$, for example, reacts neither with diethyl acetylenedicarboxylate nor with maleic anhydride; with tetracyanoethylene only a charge-transfer band at 450 nm is to be observed[3].

However, the highly reactive dienophile hexafluoro-2-butyne reacts with 2,4,6-triaryl- or 2,4,6-trialkyl-substituted phosphorins even at 100 °C, whereas the analogous reaction with aromatic hydrocarbons such as benzene and durene[4,5] requires about 200 °C.

In accord with the mode of reaction observed for durene[4], cycloaddition of hexafluorobutyne to the phosphorins *(1)* occurs exclusively in the 1,4-position, yielding the substituted 1-phosphabarrelenes *(2)* described in the Table.



	$R^1 = R^3$	R^2	M.p. (°C)	Yield (%)	UV-Spectrum λ_{max}, nm (ε) [a]	IR-Spectrum $\nu_{C=C}$ (cm^{-1})
(2a)	C_6H_5	C_6H_5	189	53	291 (7600); 226 (27600)	1589 (m); 1633 (m)
(2b)	$C(CH_3)_3$	CH_3	92–93	89	286 (520); 247 (630); 218 (1280)	1600 (m); 1650 (w)
(2c)	CH_3	C_6H_5	105–106	41	292 [b] (450); 248 [b] (1260); 220 (3450)	1594 (m); 1651 (w)

[a] In ethanol. [b] Shoulder.

The molecular weight of *(2a)*, determined osmometrically in $CHCl_3$, was 474.5 (calc. 486.4).

NMR spectra of *(2)* in $CDCl_3$: *(2a)*: aromatic protons (15 H), τ = 2.12–2.88 (m); ring protons (2H), τ = 2.0 (d), $^3J_{P-H}$ = 7 Hz. *(2b)*: $(CH_3)_3C-$ (18H), τ = 8.86 (s); CH_3- (3H), τ = 8.0 (q), $^5J_{F-H}$ = 2.7 Hz; ring protons (2H), τ = 3.39 (d); $^3J_{P-H}$ = 7 Hz. *(2c)*: aromatic protons and ring protons (7H), τ = 2.22–2.83 (m); CH_3- (6H), τ = 7.92 (doublet of doublets), $^3J_{P-H}$ = 14 Hz, $^4J_{H-H}$ = 2 Hz.

The ^1H–NMR spectra confirm the symmetrical structure of *(2)*. The protons in the hetero ring system are at lower field than those in the known homoannular barrelenes[1,4-6]. The ^{31}P resonance (H_3PO_4 as external standard) for *(2a)* amounts to + 65 ppm (in benzene) and by comparison with that of *(1a)* (−178 ppm[2]) confirms the presence of a tertiary phosphine[7]. The UV spectra do not permit an unambiguous opinion about p_π- and d_π–p_π-orbital interactions.

The formation of *(2)* from phosphabenzene derivatives makes it probable that the 1,4-diphosphabarrelene derivative *(3)* formed, according to *Krespan*[8], on reaction of hexafluorobutyne with red phosphorus arises from tetrakis(trifluoromethyl)-1,4-diphosphabenzene (which has not yet been isolated).

6,7-Di-tert-butyl-4-methyl-2,3-bis(trifluoromethyl)-1-phosphabarrelene (2b):

2,6-Di-*tert*-butyl-4-methylphosphorin (m.p. 54–55 °C; 2.5 mmoles, 0.56 g) was dissolved in anhydrous methylcyclohexane (12 ml). Hexafluoro-2-butyne (*ca.* 10 mmoles, 1.6–1.7 g) was condensed into the solution which was then heated for 48 h at 100 °C. After cooling, the solvent was removed. The residue crystallized when rubbed (yield 0.85 g; m.p. 88–90 °C; recrystallization from ethanol/water).

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A Synthesis of Pyrrole Derivatives

By *P. Rosenmund* and *K. Grübel*[*]

We describe here a synthesis of alkyl-substituted pyrroles in acceptable yield from starting materials that are technically readily accessible and thus cheap.

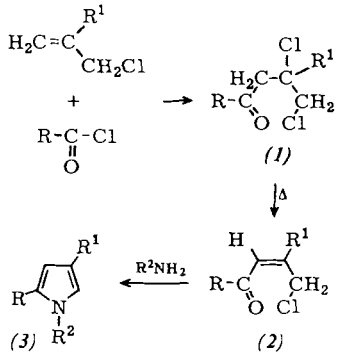
Addition of acid chlorides to alkenes under Friedel-Crafts conditions is known. We have allowed complexes of acid chlorides with $AlCl_3$ to react with allyl or methallyl chloride, this technique being, we believe, new. We thus obtained almost homogeneous addition products in 80 to 90 % yield. These are mainly the β,γ-dichloro ketones *(1)* that are formed in accord with the Markownikoff rule; the products cannot be distilled entirely without decomposition even under the mildest conditions. They eliminate 1 molar equivalent of HCl, *e.g.*, when warmed gently with dicyclohexylethylamine, being converted into the pungent α,β-unsaturated ketones *(2)*.

For preparation of the pyrrole derivatives, the crude product *(1)* was heated with an excess of an amine R^2NH_2 in methanol for several hours at 150–200 °C (autoclave). Substituted pyrroles *(3)* (see Table) corresponding to the starting materials resulted; they could also be obtained from *(2)* and the amine.

The route by which the pyrroles are formed is not yet clear. If the reaction is carried out below 100 °C a substance is obtained that is volatile in steam, begins to boil at 75 to 80 °C and explodes violently after a few ml have passed over. It is possible that an aziridine is present.

2-Methylpyrrole (3a):

1.1 moles of anhydrous aluminum chloride is added to 3 moles of acetyl chloride with good stirring and cooling to −5 °C. The mixture is cooled to −10 °C and 1 mole of allyl chloride is added at such a rate that the temperature does not



Compound	R	R^1	R^2	Yield (%)	B.p. (°C/torr) M.p. (°C)
(3a)	CH_3	H	H	39	147/760
(3b)	$CH_3(CH_2)_2$	H	H	30 [a]	75/13
(3c)	C_6H_5	H	H	24 [a]	129
(3d)	CH_3	CH_3	H	36	67/13
(3e)	CH_3	H	C_2H_5	33	157/760
(3f)	CH_3	CH_3	CH_3	42	48/13

[a] Instead of 3 moles of acid chloride per mole of allyl chloride, 1.2 moles of acid chloride + 200 ml of CH_2Cl_2 may be used.

rise above −5 °C (heat of reaction!); the whole is then stirred for about 1/4 h, and hydrolyzed by dropwise addition to a violently agitated mixture of ice and water. After decomposition of the acetyl chloride the liquid is extracted several times with methylene chloride, and the organic phase is washed with $NaHCO_3$ solution, dried, and kept *in vacuo* in a rotating evaporator at room temperature until the weight remains constant. There remain 85 to 90 % of the addition product, calculated on 4,5-dichloro-2-pentanone *(1)*, R = CH_3, R^1 = H.

The dichloro ketone is added without further purification to a ten-fold amount of methanol and a ten-fold molar amount of ammonia in an autoclave and kept there for 4 h at 170 to 190 °C. Methanol is then removed from the autoclave contents by distillation through a column and the residue is distilled in steam. Extraction with ether gives 0.39 mole of 2-methylpyrrole, b.p. 147 °C.

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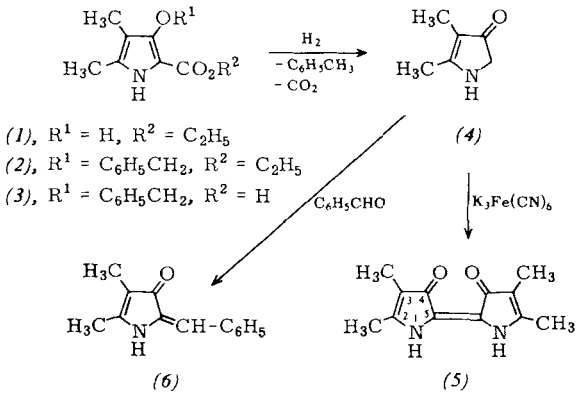
Tetramethylpyrrole-indigo

By *H. Bauer* [*]

Continuing studies of colored oxidation products from β-hydroxypyrrole derivatives [1] we have synthesized an alkyl-substituted β-hydroxypyrrole *(4)* containing a free α-position, oxidation of which to an indigoid dye *(5)* [2] led to the conjugated system that is smaller than any other to date. Pyrrole-indigo compounds have hitherto been confined to the 2,2'-diphenyl [3], 3,3'-bis(ethoxycarbonyl)-2,2'-dimethyl [4], and 2,2'-bis(methoxycarbonyl) compound [5].

2,2',3,3'-Tetramethyl-5,5'-bipyrrolinylidene-4,4'-dione (tetramethylpyrrole-indigo) *(5)* is obtained as follows: Ethyl 3-hydroxy-4,5-dimethyl-2-pyrrolecarboxylate *(1)* [6] is converted by benzyl chloride in acetone/K_2CO_3 (9–10 h under reflux) into the benzyloxy compound *(2)*, whence saponification with 2 N NaOH/CH_3OH affords the carboxylic acid *(3)*. On hydrogenolytic debenzylation with PdO/H_2 in ethanol simultaneous decarboxylation occurs, giving the hydroxypyrrole *(4)*. According to the NMR spectrum in D_6–DMSO [(τ = 2.63 (1 H); τ = 6.42 (2 H), d; τ = 7.95 (3 H),



s; τ = 8.48 (3 H), s] this exists as the ketone; its condensation with benzaldehyde affords 5-benzylidene-2,3-dimethyl-4-pyrrolinone *(6)* [orange prisms from ethanol/water; m.p. 195–198 °C; IR spectrum (in KBr), 3250, 3045, 3010, 2915, 2855, 1673, 1650, 1560 cm^{-1}; UV spectrum (in CH_3OH), λ_{max} = 313 nm (log ε = 4.28), 428 (3.81)]. $K_3Fe(CN)_6$ in aqueous ethanol oxidizes *(4)* to *(5)*, which separates as reddish-brown needles (recrystallizes from nitrobenzene, pyridine, or DMF; sublimes at 200 °C in a high vacuum; does not melt below 340 °C; sparingly soluble in the usual solvents).

IR (KBr): 3250, 2910, 2850, 1628, 1560, 1550, 1537 cm^{-1}. UV ($CHCl_3$): λ_{max} = 315 nm (log ε = 4.07), 528 (3.85). NMR (CF_3COOH): τ = 0.1 (1 H); τ = 7.48 (3 H); τ = 8.03 (3 H). Mass spectrum: molecular ion at *m/e* = 218.

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S-Thioacylation of the Sulfinate Anion: Preparation and Properties of Some Sulfonylformamides, -thioformamides, and -formamidines

By *A. Senning, O. Nørgaard Sørensen*, and *Ch. Jacobsen* [*]

Although treatment of metal sulfinates with acid chlorides is known to give mixed anhydrides by *O*-acylation [1], we have observed that thioacylation with *N,N*-dimethylthiocarbamoyl chloride takes place at the sulfur atom.

$$R{-}SO_2^{\ominus} + (CH_3)_2N{-}CS{-}Cl \rightarrow R{-}SO_2{-}CS{-}N(CH_3)_2 + Cl^{\ominus}$$
(1)

The *N,N*-dimethylsulfonylthioformamides *(1)* (see Table 1) are yellow crystalline compounds whose IR spectra contain the expected sulfonyl bands [which together with the stability of the compounds towards hydrolytic influences and their comparatively high melting points rules out the alternative structure, *i.e.* the isomeric mixed anhydrides $R{-}SO{-}O{-}CS{-}N(CH_3)_2$] and whose *N*-methyl groups are non-equivalent in nuclear resonance spectroscopy at room temperature. Pyrolysis of *(1a)* at 200 °C affords diphenyl sulfide and tetramethylurea in a reaction whose mechanism is not yet understood.

Oxidation of *(1)* with ozone or *m*-chloroperbenzoic acid in chloroform at 0 °C leads to colorless sulfonylformamides *(2)*, which are the first authentic compounds containing an

$$\underset{(1)}{R\text{-}SO_2\text{-}CS\text{-}N(CH_3)_2} + O_3 \rightarrow \underset{(2)}{R\text{-}SO_2\text{-}CO\text{-}N(CH_3)_2} + SO_2$$

α-oxosulfonyl grouping[2]. The IR spectra of the sulfonylformamides *(2)* (see Table 1) contain the expected CO and SO_2 bands and the NMR spectra at room temperature again show non-equivalence of the *N*-methyl groups.

A quasi-Wittig reaction[3] of *(1)* with *N*-sulfinyl-*p*-toluenesulfonamide leads to colorless sulfonylformamidines *(3)*.

$$\underset{(1)}{R\text{-}SO_2\text{-}CS\text{-}N(CH_3)_2} + (p)\text{-}CH_3\text{-}C_6H_4\text{-}SO_2\text{-}N{=}S{=}O \rightarrow$$

$$R\text{-}SO_2\text{-}\underset{\underset{N\text{-}SO_2\text{-}C_6H_4\text{-}CH_3\text{-}(p)}{\|}}{C}\text{-}N(CH_3)_2 + [S_2O]$$

$$\underset{(3)}{}$$

The IR spectra of the sulfonylformamidines *(3)* (see Table 1) contain the expected C=N and SO_2 bands. In *(3)* the *N*-methyl groups are equivalent in the NMR spectrum at room temperature, in contrast to those in *(1)* and *(2)*.

Table 1. Compounds *(1)*–*(3)* prepared.

	R	M.p. (°C)	Yield (%)	νSO_2 (cm^{-1}) (in KBr)	νCO or $\nu C{=}N$ (cm^{-1}) (in KBr)
(1a)	C_6H_5	119–120	67	1130, 1285	–
(1b)	*p*-CH_3-C_6H_4	144–145	55	1130, 1290	–
(1c)	*p*-Cl-C_6H_4	150–151	64	1130, 1290	–
(2a)	C_6H_5	102–103	36	1140, 1287	1680
(2b)	*p*-CH_3-C_6H_4	79–80	37	1143, 1296	1680
(2c)	*p*-Cl-C_6H_4	104–105	46	1143, 1290	1680
(3a)	C_6H_5	134–135.5	45	1135, 1265, 1297	1620
(3b)	*p*-CH_3-C_6H_4	178–179	55	1140, 1290, 1300	1625
(3c)	*p*-Cl-C_6H_4	146–148	50	1143, 1287, 1310	1630

Experimental:

Synthesis of *(1)*: *N,N*-Dimethylthiocarbamoyl chloride (0.15 mole), sodium sulfinate (0.15 mole), benzene (200 ml), and water (200 ml) are refluxed for 3 h. After drying and evaporation the benzene layer affords crude *(1)*, which is recrystallized from methanol/acetone (9:1).

Synthesis of *(2)*: A stream of O_3/O_2 (6% O_3) is passed through a solution of *(1)* (0.03 mole) in chloroform (200 ml) at 0 °C. When the solution is saturated with O_3, it is evaporated and the crude *(2)* recrystallized from absolute ethanol. The compounds decompose upon prolonged standing.

Synthesis of *(3)*: A mixture of *(1)*, (0.04 mole), *N*-sulfinyl-*p*-toluenesulfonamide (0.04 mole), and dry benzene (200 ml) is refluxed until evolution of SO_2 ceases. The solution is shaken with 2 N NaOH and with water, dried, and evaporated. The residue, *(3)*, is recrystallized from absolute ethanol.

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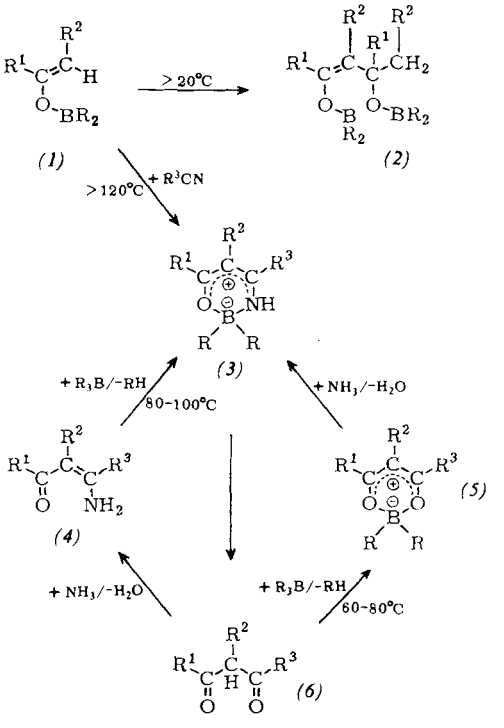
Addition of Substituted Vinyloxyboranes to Nitriles

By *R. Köster* and *W. Fenzl*[*]

Substituted vinyloxyboranes of type *(1)* undergo dimerization to *(2)* even at room temperature, whereas compounds $R_2B\text{-}O\text{-}CH{=}CR^2_2$ and $R_2B\text{-}O\text{-}CR^1{=}CR^2_2$ are stable compounds that can mostly be distilled without decomposition[1]. As expected, reaction of *(1)* with nitriles affords the heterocyclic compounds *(3)* (cf. Table 1) which have a resonance-stabilized π-system, are usually yellow to orange, and are stable to heat and hydrolysis. Their structure is proved mainly by ^1H-NMR and mass spectra [($R = C_2H_5$) main fragment: M-ethyl]. Compound *(3d)* [obtained from *(4d)*] and a few aryl derivatives were previously known[2]. We have now prepared *(3d)* from *(6d)* by way of *(4d)* and *(5d)*[2a].



Addition of *(1)* to nitriles yields *(3)* rapidly at temperatures above 120 °C. *(1)* is best prepared (variants A–F) in presence of a nitrile and not isolated.

Substituted vinyloxyboranes *(1)* are formed alongside ethane from triethylborane and a carbonyl compound with the partial structure $-CH_2CO-$ (variant A). Ketones afford *(1)* in *ca.* 90% yield, but aldehydes give yields of only about 40%. Alkoxydiethylboranes are formed simultaneously with loss of ethylene[3,4]. No appreciable quantity of *(1)* or *(3)* (*ca.* 7%) is obtained from ketones and tripropyl- or higher trialkyl-boranes. Because of the almost quantitative enolysis the aldehydes CHR^2_2CHO and triphenyl- or tribenzyl-borane give the thermally stable alkenyloxydiorganoboranes $R_2BOCH{=}CR^2_2$.

Compounds *(1)* can also be obtained, like vinyloxymetal compounds[5], by 1,4-addition of triethylborane to methyl vinyl ketone[6] (variant B) or acrolein[7] (variant C).

Compounds *(1)* are also formed from enolizable aldehydes or ketones with methoxy- (variant D) or diethylaminodialkylboranes (variant E), also by addition of, *e.g.*, chlorodiethylborane to enolizable aldehydes or ketones followed by loss of HCl (variant F). Alkenyloxyboranes are in general also accessible by oxidation of alkenylboranes with trimethylamine oxide[8]. The yields of *(3)* obtained on addition of nitriles to compounds *(1)* obtained by variants A, B, D, or E are appreciably higher than are obtained by working with variants C and F.

The route *(1)* → *(3)* permits greater variation (formation of a new C skeleton) than does route *(6)* → *(4)* → *(3)*. In spite of the C skeleton provided in *(6)*, the route *(6)* → *(4)* → *(3)* is not necessarily available: it is known that only the isomers *(4)* with R^1 = aryl and R^3 = alkyl, and not those with R^1 = alkyl and R^3 = aryl, are accessible from NH_3 and *(6)* (R^1, R^3 = alkyl and aryl). If R^1 and R^3 are similar, *e.g.*, two alkyl groups, then the route *(6)* → *(3)* by way of *(4)* as well as by way of *(5)* affords inseparable mixtures of the two isomers.

Table 1. 2,2-Diethyl-2,3-dihydro-2*H*-1,3,2-oxazaborines *(3)*.

Cpd.	R^1	R^2	R^3	B.p. (°C/torr)	Yield of *(3)* (%)	Prepn. of *(1)*, variant
(3a)	C_6H_5	H	C_6H_5	168–169/0.13 [a]	70 (34)	A (E)
(3b)	CH_3	H	C_6H_5	94–96/0.09	10	A
(3c)	C_6H_5	H	CH_3	108–112/0.12 [b]	10	A
(3d)	CH_3	H	CH_3	101–103/10	10	A
(3e)	$-(CH_2)_3-$		C_6H_5	109–113/10^{-4} [c]	88	A
(3f)	$-(CH_2)_4-$		C_6H_5	138/0.13	80	A
(3g)	CH_3	C_3H_7	C_2H_5	98/0.2	37	B
(3h)	CH_3	C_3H_7	C_6H_5	114–116/0.13	57	B
(3i)	C_6H_5	H	C_2H_5	119–121/0.3	19	E
(3j)	C_6H_5	CH_3	C_6H_5	124–126/10^{-4}	66 (19)	A (E)

[a] M.p. = 83–85 °C; [b] M.p. = 61–63 °C; [c] M.p. = 48–49 °C.

2,2-Diethyl-2,3-dihydro-4,6-diphenyl-2H-1,3,2-oxazaborine (3a) by way of (1a) according to variant A:

Triethylborane (49 g, 0.5 mole), acetophenone (60 g, 0.5 mole), and benzonitrile (103 g) are shaken in a 500-ml autoclave at 160 °C for 5 h. 10.1 l (at S.T.P.) of gas (C_2H_6 84.2 %, C_2H_4 12.8 %, H_2 3.0 %) are then released; the residual 196 g of reddish-brown liquid, when distilled in a vacuum, gives 82 g of forerun (by-products and excess of benzonitrile) and 108 g (70 %) of the orange compound *(3a)*, which solidifies. After recrystallization from hexane this melts at 83–85 °C. ^1H–NMR spectrum (CCl_4): [τ = 2.13 m, 2.54 m], 3.68 s, broad, 4.05 s, [9.12 m, 9.48 m] in the proportions [2:(3 + 5)]:1:1:10.

2,2-Diethyl-2,3-dihydro-6-methyl-4-phenyl-5-propyl-2H-1,3,2-oxazaborine (3h) by way of (1h) according to variant B:

To 0.1–0.2 mole of benzonitrile at 140 °C are added 1 ml of triethylborane and then, slowly, equivalent amounts (each 0.1 mole), separately, of methyl vinyl ketone and triethylborane. The temperature of the mixture must not fall below 120 °C. The mixture is then heated for 3–4 h at 145 °C and on distillation in a vacuum affords a forerun (up to 57 °C/10 torr) followed by 15.4 g (57 %) of orange-yellow *(3h)* (slight residue). If the nitrile and triethylborane are first mixed, the yield of *(3h)* falls to *ca.* 24 %.

Our methods permit the preparation of compounds, some of which have been very difficultly accessible. Of the condensations of nitriles with ketones in the presence of various catalysts, as previously known, only the route from *(1)* by way of *(3)* (after hydrolysis) led to *(6)*. Acylation of ketones with carboxylic anhydrides in the presence of BF_3 [9] leads analogously to *(6)* by way of *(5)* (R = F) [10]; it is possible that in this reaction compounds *(1)* with R = F, although not yet isolated, function as intermediates. Addition of alkenyloxyboranes to nitriles [*(1)* → *(3)*] is to be regarded as a new type of Claisen condensation [11]. Similarly, as in aldol condensations [12], a suitable intermediate, here *(1)*, makes the desired syntheses possible.

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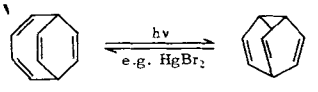
Rearrangements in the Bullvalene System Induced by Heavy-metal Salts

By *H.-P. Löffler* and *G. Schröder* [*]

Bullvalene *(2)* is formed in good yield on irradiation of bicyclo[4.2.2]decatetraene *(1)* with ultraviolet light [1,2]. We now report the reverse reaction, *(2)* → *(1)*, induced by heavy-metal salts.



(1) *(2)*

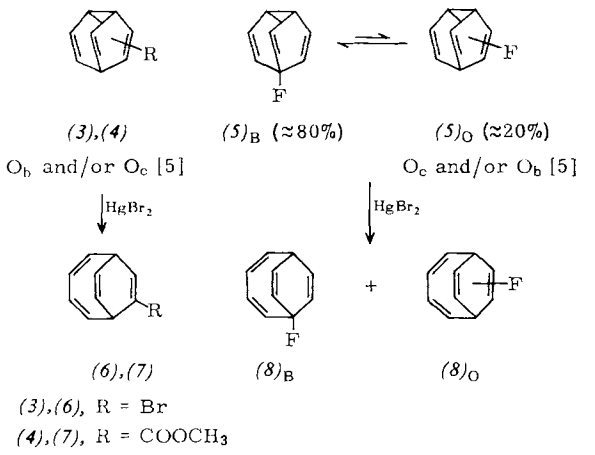
Preparation of (1) from (2):

A mixture of bullvalene *(2)* [3] (5 g), $HgBr_2$ (3 g), and ether (90 ml) is stirred for 24 h at 22 °C. The ether is removed by fractional distillation under slight vacuum and the residue is extracted with pentane; the pentane solution is then concentrated in a fractionating column and the residual concentrate thus obtained is sublimed in a vacuum (yield 4.5 g).

A gas chromatogram (column: 20 % Carbowax on Chromosorb W; 140 °C) indicates that the product is substantially homogeneous (*ca.* 98 %); there are small amounts of bullvalene (0.5 %) and *ca.* 1 % of *cis*-9,10-dihydronaphthalene [**] (identified by comparison of the retention times and IR spectra of the separated components with those of authentic materials [4]). According to the IR, UV, and NMR spectra the main component (m.p. 39–39.5 °C) is unambiguously bicyclo[4.2.2]deca-2,4,7,9-tetraene *(1)* [1,2]. Thus *(1)* can be synthesized readily and in preparatively useful yield from bullvalene by use of $HgBr_2$. The rearrangement has also been brought about so far by HgX_2 where X = Cl, Br, or I, and by $ZnBr_2$ (in CH_3OH, 36 h at 20 °C, 34 % yield) or $SbBr_3$ (in CS_2, 14 h at 0 °C, 12 % yield), these yields being determined gas-chromatographically.

Monosubstituted bullvalenes *(3)*–*(5)* afford monosubstituted bicyclo[4.2.2]decatetraenes *(6)*–*(8)*, in which the position of the substituents in the bicyclic rearrangement product appears to depend on the position isomer that preponderates in the equilibrium mixture of the monosubstituted bullvalene.

Bromo- *(3)* [5], methoxycarbonyl- *(4)* [6], and fluoro-bullvalene *(5)* [7] can be preparatively rearranged in the same way as bullvalene. The pentane extracts of the rearrangement mixtures from *(3)* (in CH_3OH, 24 h at 20 °C) and *(5)* (in



(3),(6), R = Br

(4),(7), R = $COOCH_3$

Table 1. Rearrangements of the monosubstituted bullvalenes (3)–(5).

Cpd.	Product	Yield (%)	λ_{max} (nm) (ε) [a]	^{1}H–NMR [b]
(3)	(6)	84 [c]	256 (3340) 265 (3270) 276 (2240) sh	τ = 4.1 (5H), complex multiplet; τ = 4.6 (2H), symm. 4-line signal [d]; τ = 6.6 (1H), m; τ = 6.9 (1H), m
(4)	(7)	80	257 (3380) 266 (3320) 278 (2320) sh	τ = 3.3 (1H), d (J = 6.5 Hz); τ = 4.2 (6H), m; τ = 6.2, m; τ = 6.33 (together 4H), s; τ = 6.7 (1H), pseudoquartett (J = 6.5 Hz)
(5)B (5)O	(8)B	47 [c]	257 (3600) 266 (3660) 275 (2260) sh	τ = 4.3 (8H), m; τ = 6.8 (1H), m
(5)B (5)O	(8)O	14 [c]	254 (3600) 263 (3680) 272 (2900) sh	τ = 4.3, m; τ = 5.0, pseudoquartet, (together 7H); τ = 6.8 (2H), broad m [e]

[a] In cyclohexane.

[b] Varian A 56/60 A; CCl_4 solution; TMS as internal standard.

[c] Determined by gas chromatography.

[d] Since this signal, due to the protons of the ethylene bridge [1], corresponds to only 2 H, the Br must be on the ethylene bridge.

[e] ^{19}F–NMR: δ = +99.2 ppm (J = 4.8 Hz), pseudodoublet; δ = +99.5 ppm (J = 4.8 Hz), pseudotriplet; δ = +99.8 ppm (J = 4.8 Hz), pseudodoublet. Distance from the middle of the doublets to the middle of the triplet = 20.8 Hz; CCl_3F as external standard.

CH_3OH, 48 h at 20 °C) were concentrated and analyzed gas-chromatographically (for yields see Table 1); the bicyclo-[4.2.2]decatetraene derivatives (6) and (8) were separated by preparative gas chromatography.

Product (7) was obtained by distillation of the concentrated pentane extract from the rearrangement mixture of (4) (in CH_3OH, 40 h at 20 °C) and was obtained pure (m.p. 45 to 45.5 °C) by recrystallization. Compounds (5)–(8) were characterized by their spectra (UV, IR, NMR). It is not possible to tell from the results so far available to which of the three possible positions the olefinic fluorine atom of $(8)_O$ is attached.

The heavy-metal salts are probably involved in the reaction more as complex-formers [8] than as Lewis acids. Bullvalene (2) in ether is unaffected by boron trifluoride-ether even after long contact times.

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[**] Note added in proof: In the presence of $HgBr_2$, (1) rearranges to cis-9,10-dihydronaphthalene after longer reaction times.

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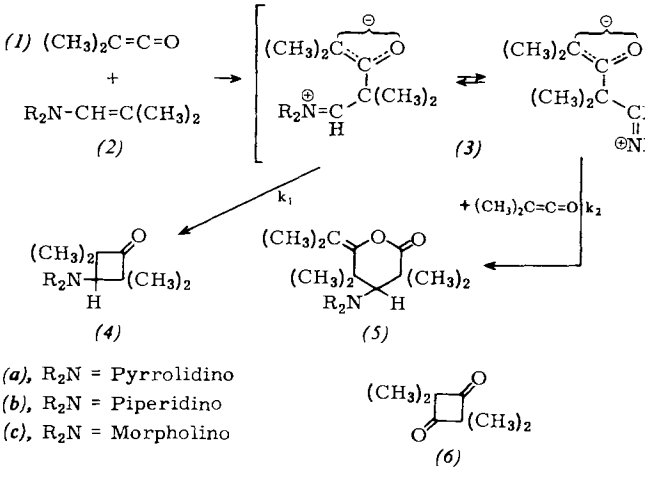
Cyclobutanones from Enamines and Ketenes by Two-stage Addition

By P. Otto, L. A. Feiler, and R. Huisgen [*]

cis-Stereospecificity [1–3] and solvent-dependence of the addition constants [4] provide strong evidence that cycloadditions of ketenes to olefins and vinyl ethers are one-stage multicenter reactions. Exclusive formation of cyclobutanones (and not Diels-Alder adducts) from ketenes and 1,3-dienes points in the same direction [5]. Enamines appear, however, to react by a different mechanism, at least in polar solvents. Here apparently a two-stage process involving a zwitterion [see (3)] occurs.

After treatment of dimethylketene (1) with 1-isobutenylpiperidine (2b) or *N*,*N*-dimethylisobutenylamine in polar solvents, Hasek and Martin [6] isolated the cyclobutanones (4) as well as the 2:1 adducts (5) [7] and 3:1 adducts, the structure of the latter still being unknown.

We have found that the cyclobutanones (4) are unaffected by dimethylketene in acetonitrile over many days. The 2:1 adducts (5) are formed only in presence of 1 equivalent of boron trifluoride-ether in CH_2Cl_2.



We show here that (4) and (5) arise through a common intermediate and propose that this is the zwitterion (3). At low stationary concentration of (1), (3) cyclizes irreversibly to the cyclobutanone (4). As the concentration of (1) is increased, the 1,4-dipolar cycloaddition [8] of (3) to (1) to give (5) increases in importance. The competing reactions

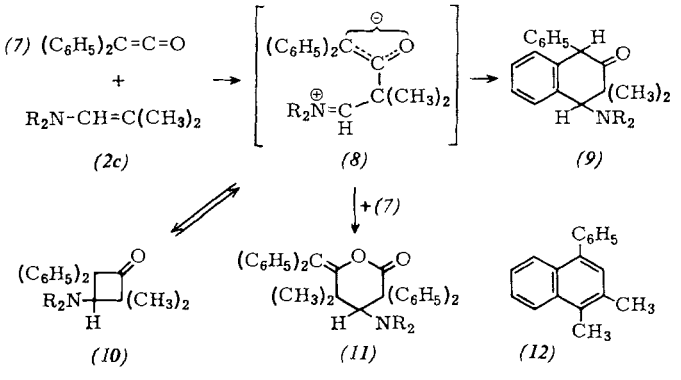
d(4)/d(5) = k_1/k_2(dimethylketene)

rapidly occur after the rate-determining step, namely the formation of *(3)* from *(1)* and *(2)*.

The following experiments (1) and (2) prove the dependence of the ratio *(4)*:*(5)* on the concentration of *(1)* and on the mode of addition. (1) If 11.9 mmoles of dimethylketene *(1)* in 15 ml of acetonitrile were added to a solution of 42.6 mmole of 1-isobutenylpyrrolidine *(2a)* in 35 ml of acetonitrile during 30 min at 20 °C, then dimethyketene *(1)* was consumed so rapidly that the solution became merely pale yellow; distillation in a high vacuum gave 5.7 mmoles of 1:1 adduct *(4a)* and 0.34 mmole of 2:1 adduct *(5a)*, *i.e.*, a ratio of 17:1. (2) However, when 2.6 mmoles of *(2a)* were added all at once to 11.9 mmoles of *(1)* in 15 ml of acetonitrile, then the yellow ketene solution was decolorized only after 10 h; the excess of *(1)* was converted into the dimer *(6)*; working-up in this case yielded 1.26 mmoles of *(4a)* and 0.87 mmole of *(5a)*, *i.e.* a ratio of only 1.4:1.

The enamines *(2b)* and *(2c)* react more slowly with dimethylketene. Decolorization in the process (1) involving an excess of enamine requires 90 min and 10 h, respectively; dependence on the method of mixing was thus less marked. For 1-isobutenylpiperidine the ratios *(3b)*:*(4b)* by procedures (1) and (2) were 2.4:1 and 0.96:1, respectively; and for 4-isobutenylmorpholine *(2c)* the corresponding ratios *(3c)*:*(4c)* were 4.5:1 and 2.2:1, respectively.

We obtained the cyclobutanone *(10)* as main product of the reaction of diphenylketene *(7)* with *(2c)* in *n*-pentane at +5 °C if traces of acid were removed by addition of potassium carbonate. Boiling with methanol, or addition of acid even in the cold, rearranged *(10)* to the *cis-trans*-isomers *(9A)* and *(9B)* of the 2-tetralone. Conversion into 1,2-dimethyl-4-phenylnaphthalene *(12)* and mass spectra[9] confirmed the structures *(9)*, but it has not yet been possible to assign the *cis-trans*-configurations.



R_2N = Morpholino

The hypothesis that conversion of *(10)* into *(9)* also involved the zwitterion *(8)* as intermediate proved correct. The action of an excess of diphenylketene on the cyclobutanone *(10)* afforded the 2:1 adduct *(11)*; chemical and spectroscopic findings agree with the δ-enol-lactone structure *(11)*. Conversion of *(10)* into *(11)* (possible in this case) does not permit a similar proof for *(8)* as intermediate in the cycloaddition as was furnished above for the zwitterion *(3)*.

Enamines that have hydrogen on the β-carbon atom give β-acyl-enamines on reaction with ketenes[10,11]. Presumably also here an intermediate corresponding to *(3)* and *(8)* is responsible, but subsequently undergoes a proton loss.

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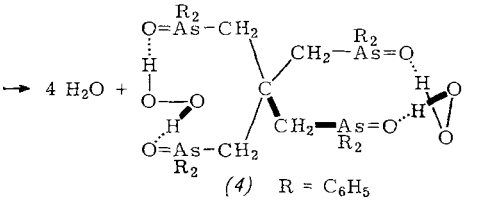
A Spirocyclic 1:2 Adduct of Tetrakis(diphenylarsorylmethyl)methane and Hydrogen Peroxide[1]

By *J. Ellermann* and *D. Schirmacher*[*]

In contrast to tetrakis(diphenylphosphinomethyl)methane[2] *(1)* which yields with H_2O_2 directly tetrakis(diphenylphosphorylmethyl)methane[3] *(2)*, tetrakis(diphenylarsinomethyl)methane[4] *(3)* and H_2O_2 give first a 1:2 tetrakis(diphenylarsorylmethyl)methane-hydrogen peroxide adduct *(4)*, which is converted into tetrakis(diphenylarsorylmethyl)-methane *(5)* with loss of H_2O_2 only when heated under high vacuum.

$C[CH_2P(C_6H_5)_2]_4$ *(1)* $\qquad$ $C[CH_2P(O)(C_6H_5)_2]_4$ *(2)*

$$C[CH_2As(C_6H_5)_2]_4 + 6\ H_2O_2$$
(3)



(4) R = C_6H_5

$$(4) \xrightarrow[\text{High vacuum}]{140^\circ C} C[CH_2As(O)(C_6H_5)_2]_4 + 2\ H_2O_2$$
(5)

The composition and monomeric nature of *(4)* and *(5)* are proved by elemental analyses and osmometric molecular weight determinations in $CHCl_3$. When *(4)* is suspended in dilute H_2SO_4, hydrogen peroxide can be detected by $TiOSO_4$. The structures of *(4)* and *(5)* follow from the IR spectra. These both show, in addition to the absorptions due to *(3)*[4], a broad band for the (As=O) stretching vibration[5] at 895 cm^{-1} (vs) and the expected[6] shifts to higher wave numbers of $\nu_{1,2}(As-C_6H_5)$[4] and $\nu(AsC_3)$[4] by about 10 and 40 cm^{-1}, respectively. The IR spectrum of *(4)* also contains the absorptions of the coordinated hydrogen peroxide, most of which correspond in position to those of crystalline H_2O_2[7] (Table 1) and in respect of the (O–H) stretching vibrations accord very well with those observed for $(C_6H_5)_3AsO \cdot H_2O_2$[8].

Table 1. IR absorption bands of *(4)* and crystalline H_2O_2 [7] (cm^{-1}).

Assignment	*(4)*	(H_2O_2)	Assignment	*(4)*	(H_2O_2)
ν_s (O—H)	3270 sh	3291	δ_{as}(O—O—H)	1388 ms	1380
ν_{as}(O—H)	3170 ms	3208	ν(O—O)	920 mw	880
ν(—O···H—)	2820 m, broad	2732 [a]	ρ_t(O—O—H)	640 mw	635
δ_s(O-O-H)	1403 mw	1404			

[a] (—O···H—) and/or overtones or combination tones of δ_s(O—O—H) and δ_{as}(O—O—H).

From comparison of the long-wave shift of ν_s- and ν_{as}(O—H) with gaseous and liquid H_2O_2 [ν(O—H) at *ca.* 3600 and 3400 cm^{-1}, respectively][9] it follows, in accord with expectations for structure *(4)*, that neither H_2O_2 molecule contains a free OH group and thus that both H_2O_2 are acting as *bidentate* ligands forming strong hydrogen bonds to the oxygen atoms that are bound to arsenic. That their bidentate function is intramolecular follows from the monomeric molecular state of *(4)*. Further, the eleven-membered spirocyclic rings enable the H_2O_2 molecules to retain the energetically favored[10] *trans*-arrangement of the H atoms. The *trans*-arrangement of H atoms is confirmed also by the low intensity of ν(O—O) (small dipole moment of the O—O group). Although the intense broad absorption of the (As=O) stretching vibration occurs in the region of the (O—O) stretching vibrations[11] and it is conceivable that it hides ν(O—O), the assignment of the band at 920 cm^{-1} to ν(O—O) seems nevertheless certain since there is no band at 920 cm^{-1} in *(5)*. The stretching vibration for the (=O···H—) bridges[5] is assigned to the broad band at 2820 cm^{-1}. With few exceptions[6] coordination of (As=O) groups to metals shifts the ν(As=O) absorptions to lower wave numbers; that such a shift is substantially absent for *(4)* may be due to the smaller mass and the smaller electron-acceptor ability of the protons of hydrogen peroxide.

Experimental:

A mixture of compound *(3)* (700 mg, 0.71 mmole) and acetone (50 ml) is treated with 30 % H_2O_2 (1 ml, *ca.* 9 mmoles) with stirring and heating under reflux. It dissolves slowly, leading in about 30 min to a clear colorless solution, which is heated for a further 30 min. Acetone, water, and excess of hydrogen peroxide are then removed under reduced pressure at 15 °C, leaving a colorless oil that crystallizes in a vacuum. This residue is dried for *ca.* 30 min under high vacuum, then dissolved in CH_2Cl_2 (10 ml) and reprecipitated with petroleum ether (50 ml). The then analytically pure product is filtered off, washed four times each with 5 ml of petroleum ether, and dried under high vacuum; it is very readily soluble in CH_2Cl_2 and $CHCl_3$, soluble in acetone and acetonitrile, and almost insoluble in ether, petroleum ether, CS_2 or benzene. Yield 80 %. M.p. from 104 °C with loss of H_2O_2.

If the adduct *(4)* is heated for 5–6 h under high vacuum at 130–140 °C, H_2O_2 distils off and a brownish product is obtained that is dissolved in CH_2Cl_2 (10 ml) and reprecipitated with petroleum ether (25 ml). Compound *(5)* is thus obtained colorless and crystalline; it is filtered off, washed several times with 5 ml of petroleum ether, and dried under high vacuum. M.p. 204–207 °C (decomp.).

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[5] The vibrations of the four As=O groups and the =O···H– bridges, as well as those of the two added H_2O_2 molecules, are only to be observed singly, since the individual As=O groups in *(4)* do not enter into valence or mass coupling with one another. This is in agreement with the predictions of the local symmetry method (cf. *F. A. Cotton*, *A. Liehr*, and *G. Wilkinson*, J. inorg. nuclear Chem. *2*, 141 (1956)).

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CONFERENCE REPORTS

Transport Processes of Noble Gases in Solids, especially Nuclear Fuels

By *K. E. Zimen*[*]

There are solid systems in which noble gases are produced naturally: minerals that contain U, Th, or K from which ^4He, ^{219}Rn, ^{220}Rn, ^{222}Rn, or ^{40}Ar arises in geological times; also meteorites in which some primordial noble gas may be present and in which some cosmogenic noble gas may have arisen by nuclear spallation reactions.

There are also solid systems, and in particular fuels, in which noble gases are formed artificially. The fission products of U or Pu consist to about 30 % of Kr and Xe. Furthermore, noble gases can be incorporated into almost all solid bodies artificially, by nuclear reactions, ion bombardment, nuclear recoil, or entry by diffusion.

Noble gases, whether produced naturally or artificially, are normally present in the solid bodies in atomically disperse form and diffuse out after their formation because of their extremely low solubility. Further, the noble gases can escape owing to recoil during the nuclear transmutation and in certain cases by formation of bubbles, which are moving in temperature gradients. In addition, changes in the solid body – evaporation, recrystallization, and surface reactions – naturally contribute to the loss of noble gas.

Investigation of the behavior and transport of noble gases began with the so-called Hahn emanation method, in which the natural emanations were used for qualitative observation of physical and chemical changes in solids as a function of temperature or time. Today, diffusion coefficients and activation energies of noble gases can be determined quantitatively, and in individual cases the kinetics of diffusion of noble-gas atoms and observation of recoil effects can be used to provide information about fine structure and vacancies in crystalline and amorphous solids – information that cannot be obtained from diffraction methods (X-ray, neutrons), which depend on periodic structure. Of particular importance is the release of fission gases from nuclear fuels because of build-up of pressure in the fuel elements and contamination of the circulating coolant from defective fuel-element cans.

The relevant publications from the Hahn-Meitner-Institut, numbering fourty up to the present, were reviewed.

Lecture at Darmstadt (Germany) on May 28, 1968 [VB 121 IE]
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Study of the Mechanism of Dehydrogenase Reactions by Measurement of the Isotope Effects

By *D. Palm* [*]

Classical kinetic methods for the study of enzyme reactions have recently been extended by methods for selective determination of fast or slow steps in complex reaction sequences.

Slow and irreversible steps can be detected also in enzyme kinetics by differences in the reaction rate of isotopically labeled substrates. This is particularly so for the isotope effects (IE's) of the hydrogen isotopes, for which primary and secondary IE's can be detected [1]. Thus hydrogen transfer in NAD-dependent dehydrogenases is particularly suited for investigation of the empirical and theoretical relation of IE to enzyme-kinetic values.

The primary IE (4.1 to 6.8 at 25 °C) for the substrates [1-T]-ethanol, -1-propanol, and -1-butanol confirm the required rate-determining hydrogen transfer for alcohol dehydrogenase (ADH) from yeast, but an increase in IE with rising temperature also shows a change in the rate-determining step. For the ADH of liver the small secondary IE (1.4 to 1.6 at 25 °C) for the homologous alcohols is in agreement with a rate-determining dissociation of the enzyme-NADH complex, which is independent of the substrate.

The reverse reaction, studied with the stereospecifically labeled [A-4-T]NADH again shows primary IE's of 2 to 5 (depending on the corresponding homologous aldehydes) for yeast enzyme, whereas only a small difference from unity was found for the liver enzyme. The sterically hindered substrate 2-methylcyclohexanone for liver ADH stands out with an IE of 3.6; since 2-[*methyl*-T]methylcyclohexanone reacts 4.5% faster, the site of steric hindrance can be more accurately localized [2].

In the case of lactate dehydrogenase of rabbit muscle the IE of 2.5 for L-[2-T]lactate corresponds to a product of two secondary IE's, which are due to isomerization and dissociation of the enzyme-NADH complex. This interpretation excludes a kinetic influence of ternary complexes. The reverse reaction with [A-4-T]NADH also shows an IE of up to 2.0 that indicates isomerizations, but under the influence of pyruvate inhibition at concentrations $> 1 \times 10^{-3}$ M the IE disappears.

Finally, a mechanism similar to that for yeast ADH can be ascribed to glucose-6-phosphate dehydrogenase and 6-phosphogluconate dehydrogenase.

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Oxidation of Pyrrolic Impurities in Polyamides

By *P. Schlack* [*]

When prepared under not quite perfect conditions, polyamides may contain pyrrole groups formed in side reactions and detectable by Ehrlich's reagent. In nylon 6 (polycaprolactam) pyrroles are observed particularly if 1,11-diaminoundecanone is formed by loss of water and CO_2 from two moles of 6-aminohexanoic acid or if the corresponding anhydro base is formed from ε-caprolactam by loss of water. This ketimine is very sensitive to oxygen and after autoxidation gives an intense pyrrole reaction.

Polycaprolactam fibers ("Perlon") that contain units of this imine show a strong tendency to yellow on fairly long exposure to light in the presence of oxygen or on thermal oxidation. *Rochas* and *Martin* have found that polyamide fibers (nylon 66) may also give a positive pyrrole reaction after photoxidation [1]. They assumed that the pyrroles were formed by reaction of amino end groups in the fiber with α,α'-dioxoadipic acid formed by oxidation of adipyl groups. *Marek* and *Larch* came to the conclusion that it was almost wholly the diamine groups that were involved in pyrrole formation; they held that primary attack by the oxygen was always on the methylene groups next to the amide nitrogen [2].

In studies of the yellowing of polyamide textiles in our Institute, *F. Sommermann* [3] found that pyrroles are also formed on oxidation of N-free olefinic substances such as 3-heptene, oleic acid, methyl linoleate, and squalene in the presence of primary amines or amino acids and also on subsequent addition of such amines. Since sweat contains glycerides of polyunsaturated fatty acids, squalene, ammonium salts, and other nitrogenous bases, pyrroles or their colored oxidation products could be formed on textile substrates even without chemical participation of the fiber substance.

Only the primary amino end groups of the fiber come into question as a nitrogen source for pyrrole formation within the fiber substance. If however, the amino groups are inactivated by acylation, *e.g.* by acetic anhydride [4], then pyrrole can no longer be formed on the fiber unless ammonia or amino groups are newly formed. Autoxidation in light is then also greatly hindered. Most of the amino groups can be blocked under remarkably mild conditions that can be realized in practice, namely, by impregnating the textile goods with solutions of anhydride-forming aromatic polycarboxylic acids, *e.g.* trimellitic acid, then drying them, and heating them for one to two minutes at 170–180 °C by passage through a thermofixing apparatus. The tendency to yellowing is much reduced by this pretreatment.

From the UV spectra of the dyes formed in the fiber by *p*-(dimethylamino)benzaldehyde it can be concluded that both α- and β-methine dyes occur side by side, whereas the dyes formed from unsaturated fatty acid esters and amino acids appear to consist mainly of β-derivatives.

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Aromatic Sigmatropic Rearrangements

By *Hans Schmid* [*]

Aromatic sigmatropic rearrangements are thermal reactions whose transition states can, to a first approximation, be considered as interaction complexes between two pseudoradical halves that have arisen by homolysis of the bond that is attacked. At least one of these halves must be aromatic in nature, *i.e.* its π-system is to be described by aromatic molecular orbitals. A well-known example is the thermal Claisen rearrangement of allyl aryl ethers that occurs with inversion

of the allyl group. The transition state for the sigmatropic-[3,3]-reactions involved (allyl aryl ether $\rightleftarrows$ 2-allyl-3,5-cyclohexadien-1-one $\rightleftarrows$ 4-allyl-2,5-cyclohexadien-1-one) are controlled in accord with the Woodward-Hoffmann rules by suprafacial-suprafacial interaction of the single occupied ψ_2 of the allyl radical and the singly occupied ψ_4 of the phenoxy radical (cf. ref. [1]).

Aryl propargyl ethers behave like allyl aryl ethers. Their thermal ring closure to chromenes, observed by *Iway* and *Ide* [2] does not occur directly, but by a [3,3]-sigmatropic rearrangement, followed by enolization to *o*-allenylphenol which even at about 80 °C undergoes an aromatic [1,5]-hydrogen shift and thereupon an electrocyclization to the chromene [3].

The rearrangement of 3-(1-methyl-2,2,2-trichloroethylidene)-1,4-cyclohexadiene to 1-methyl-4-(2,2,2-trichloroethyl)benzene which occurs at 20–70 °C and was observed by *von Auwers* [4] may also be a suprafacial C,C-[1,5] aromatic sigmatropic reaction that is controlled by the ψ_3 of the tolyl radical and the p-orbital of the $CCl_3^{\bullet}$. However, this would lead to a very strained transition state.

On the basis of the MO diagrams the formation of *o*-(1-vinylallyl)phenol ([3,3]-rearrangement) and of *p*-(2,4-pentadienyl)-phenol ([5,5]-rearrangement) is to be expected in the thermolysis of 2,4-pentadienyl phenyl ether. Experiments with substituted ethers have given the following series: [5,5] > [3,3] $\gg$ ([1,5]?) [5].

Sigmatropic rearrangements in polar systems occur particularly rapidly when the charge is better distributed in the transition state than in the starting materials. In the dienol-benzene rearrangement of 2-allyl-2-methyl-3,5-cyclohexadien-1-ol and 4-allyl-4-methyl-2,5-cyclohexadien-1-ol with *p*-toluenesulfonic acid in ether at −40 °C the products formed, with loss of water, are those expected from the MO diagram (ψ_3 of the tolyl radical, ψ_2 of the allyl radical), namely: *o*-allyltoluene by [1,2]-, *m*-allyltoluene by [3,3]-, and *p*-allyltoluene by [3,4]-rearrangement. It is always the allyl group that migrates, in the first reaction without and in the others necessarily with inversion [1].

The rearrangement of 2- and 4-allylcyclohexadienones to allylated phenols effected by BCl_3 [6] occurs similarly. Competing reactions for the crotyl and dimethylallyl compounds are heterolysis to the phenolic compound and crotyl-cation or dimethylallyl-cation.

Sigmatropic reactions may also play a part in other aromatic rearrangements (*e.g.* the "acid-catalyzed" and the thermal Fischer indole synthesis [7]).

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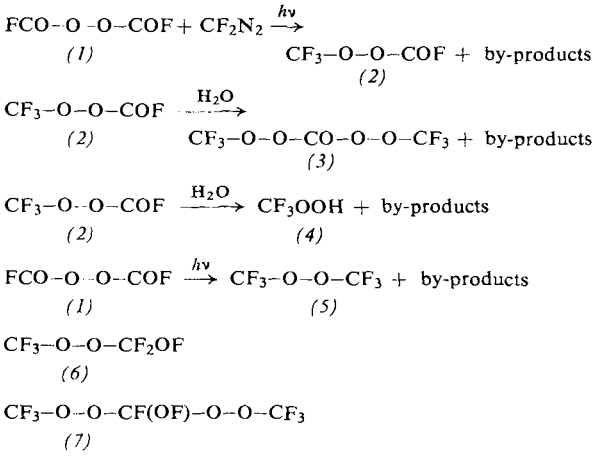
SELECTED ABSTRACTS

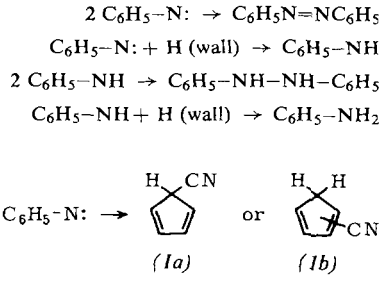
The preparation of α,β-unsaturated ketones by oxidative decarboxylation of γ-oxo carboxylic acids with lead dioxide has been described by *D. V. Hertzler, J. M. Berdahl,* and *E. J. Eisenbraun.* With γ-oxo carboxylic acids having no alkyl or aryl substituents in the α or β positions, the yield does not exceed 40 %; 84 % of ketone was obtained in the most favorable case (3-benzoyl-2-phenylpropionic acid). / J. org. Chemistry *33*, 2008 (1968) / −Kr. [Rd 878 IE]

The new fluorocarbon peroxides *(2)*—*(7)* have been prepared by *R. L. Talbott.* The photolysis of an equimolar mixture of bis(fluoroformyl) peroxide *(1)* and difluorodiazine in a quartz apparatus yields *inter alia* fluoroformyl trifluoromethyl peroxide *(2)*, which is converted by hydrolysis into bistrifluoromethyl bisperoxycarbonate *(3)* or trifluoromethyl hydroperoxide *(4)*, depending on the conditions. Prolonged photolysis of *(1)* leads to bistrifluoromethyl peroxide *(5)*.



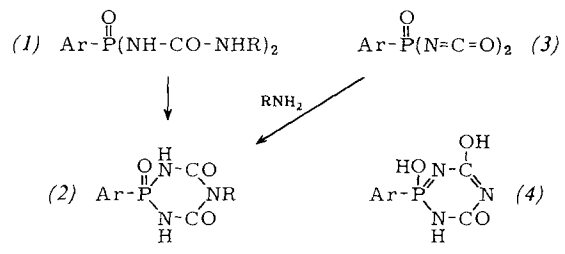
The low-temperature fluorination of *(2)* and *(3)* leads to fluoroxydifluoromethyl trifluoromethyl peroxide *(6)* and fluoroxybis(trifluoromethylperoxy)fluoromethane *(7)*. The new peroxides *(2)*—*(7)* are colorless gases or liquids with high vapor pressures, which are stable for some time at room temperature. / J. org. Chemistry *33*, 2095 (1968) / −Kr. [Rd 879 IE]

The thermal rearrangement of phenylnitrene into cyclopentadienecarbonitrile has been studied by *E. Hedaya, M. E. Kent, D. W. McNeil, F. P. Lossing,* and *T. McAllister.* The mass spectra recorded during the decomposition of phenyl azide could be best explained by the assumption of the following reactions:



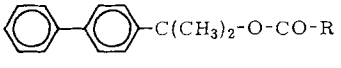
When large quantities were used (flash photolysis in a vacuum), *(1)* could even be chemically characterized. *(1a)* could not be detected. *(1b)*, *i.e.* 1- and/or 2-cyclopentadienecarbonitrile, is evidently present. The rearrangement probably proceeds *via* bicyclo[3.1.0]hex-2-en-6-ylidenenitrene. / Tetrahedron Letters *1968*, 3415 / –Kr. [Rd 881 IE]

4,6-Dioxo-2-arylperhydro-1,3,5,2-triazaphosphorine 2-oxide *(2)* has been prepared by *G. Tomaschewski, Ch. Berseck*, and *G. Hilgetag* by pyrolysis of arylphosphonic diureides *(1)* and by the reaction of arylphosphonic diisocyanates *(3)* with NH_3 or primary amines. The second method is more versatile and gives better yields.



Examples: *(2)* from *(1)*, Ar = C_6H_5, R = H (m.p. 250 °C, yield 20 %), R = CH_3 (236 °C, 75 %); *(2)* from *(3)*, Ar = C_6H_5, R = *n*-C_4H_9 (224–225 °C, 81 %), Ar = *p*-NO_2–C_6H_4, R = CH_3 (220–221 °C, 95 %). The IR spectra of *(2)*, R = H, can be best interpreted by the assumption of tautomerism between *(2)* and *(4)*. / Chem. Ber. *101*, 2037 (1968) / –Kr. [Rd 882 IE]

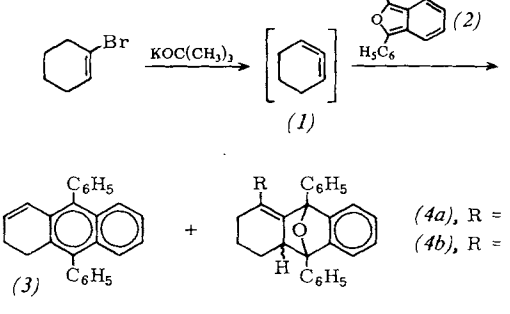
The use of 1-(*p*-biphenylyl)-1-methylethoxycarbonyl groups for the synthesis of peptides has been reported by *P. Sieber* and *B. Iselin*. α-*N*-Protected amino acids are easily obtained from amino acid esters or their salts by reaction with the carbonate *(1)* or the azide *(2)*. The group is cleaved so quickly by dilute acetic acid that even other acid-sensitive protective groups (*e.g.* those derived from *tert*-butanol) are not attacked. The cleavage of this and other aralkyloxycarbonyl groups is a first order reaction; the reaction rates depend on the stability of the corresponding carbonium ions.



(1), R = OC_6H_5 *(2)*, R = N_3

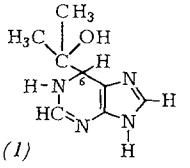
The α-(1-(*p*-biphenylyl)-1-methyl-ethoxycarbonyl) amino acids are suitable for conventional peptide syntheses and syntheses on a solid phase; no steric hindrance is observed. / Helv. chim. Acta *51*, 614, 622 (1968) / –Kr. [Rd 883 IE]

1,2-Cyclohexadiene ***(1)*** has been detected by *G. Wittig* and *P. Fritze* as a short-lived intermediate in the rearrangement of 1-bromocyclohexene with potassium *tert*-butoxide. With 1,3-diphenylbenzo[*c*]furan *(2)*, *(1)* can be intercepted as *(3)* and *(4a)*; in the absence of *(2)*, the dimer octahydrobiphenylene



is formed. In order to be sure that the reaction does not proceed *via* cyclohexyne, 1,2-dibromocyclohexene was used. Under similar conditions, the bromo compound *(4b)* was formed together with 9,10-diphenylanthracene; *(4b)* could only be formed *via* an allene. / Liebigs Ann. Chem. *711*, 82 (1968) / –Kr. [Rd 884 IE]

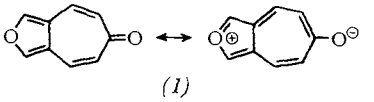
The photochemical addition of alcohols to purines has been observed by *H. Linschitz* and *J. S. Connolly* on irradiation of O_2-free solutions with UV light (2537 Å). The addition of isopropanol to purine gives *(1)*; the addition of ethanol yields two isomeric products, which can be isolated by fractional



(1)

crystallization. The addition can be followed by means of a new band at about 292 nm. Since similar changes in the absorption spectrum were observed on irradiation of ethanolic solutions of heterocyclic compounds, such as pyridine, pyrazine, benzimidazole, benzoxazole, quinoline, isoquinoline, quinoxaline, and phenazine, the reaction appears to be general. / J. Amer. chem. Soc. *90*, 2979 (1968) / –Ma. [Rd 885 IE]

***6H*-Cyclohepta[c]furan-6-one** (furo[3,4-*d*]tropone), a new heterocyclic system *(1)*, has been synthesized by *M. J. Cook* and *E. J. Forbes*, (i) from 3,4-furandicarbaldehyde by condensation with acetone in ethanol/10 % NaOH (38 % yield),



(1)

and (ii) from the dialdehyde by condensation with the diethyl ester of acetonedicarboxylic acid, hydrolysis, and decarboxylation with 0.5 % HCl (7 % yield). *(1)*, m.p. 140 °C, forms carbonyl derivatives and takes up deuterium on dissolution in D_2SO_4. The aromatic character of *(1)* is much weaker than that of tropone, and comparable to that of benzo[*d*]tropone. / Tetrahedron *24*, 4501 (1968) / –Ma. [Rd 886 IE]

Tetramethylsilane (TMS) cannot be used indiscriminately as an internal standard in NMR spectroscopy in solution, according to *P. Laszlo, A. Speert, R. Ottinger*, and *J. Reisse*. It is normally assumed that TMS does not react with the solvent, and that the van der Waals contribution of the solvent to the chemical shift is the same for TMS as for the substance whose spectrum is being recorded. When this assumption was checked for a group of solvents having aromatic character, such as pyridine, nitrobenzene, benzaldehyde, benzonitrile, and aniline, it was found that they form "complexes" with TMS (and with the tetramethyl derivatives of germanium, tin, and lead) with apparent heats of formation of 1–2 kcal/mole; this corresponds to additional chemical shifts of 0.10–0.15 ppm. Neopentane, cyclohexane, and 2,2,4,4-tetramethylpentane are suggested as replacements for TMS in such solvents. / J. chem. Physics *48*, 1732 (1968) / –Hz. [Rd 888 IE]

The vapor pressures and melting points of XeF_2 and XeF_4 have been measured by *F. Schreiner, G. N. McDonald*, and *C. L. Chernick*. The vapor pressure between 273 and 388 °K can be represented for XeF_2 by the equation

$\log P = -3057.67/T - 1.23521 \log T + 13.969736$

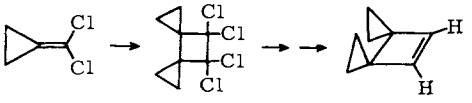
and for XeF_4 by

$\log P = -3226.21/T - 0.43434 \log T + 12.301738$

XeF_2 has the higher vapor pressure over the entire temperature range studied. The triple points were determined as discontinuities in the heating and cooling curves; they occur at 402.18 °K for XeF_2 and at 390.25 °K for XeF_4. The enthalpies of sublimation at 330 °K calculated from the vapor pressure equations are 55.2 ± 0.8 kJ/mole for XeF_2 and 60.6 ± 1.0 kJ/mole for XeF_4. The standard entropy for XeF_4 vapor at 298.15 °K was calculated from the vapor pressure and the specific heats, and was found to be 305.2 $J \cdot deg^{-1} \cdot mole^{-1}$; an entropy of 122.8 $J \cdot deg^{-1} \cdot mole^{-1}$ is given for solid XeF_2 at 330 °K. / J. physic. Chem. *72*, 1162 (1968) / –Hz.

[Rd 889 IE]

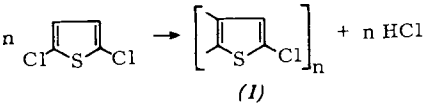
Dispiro[2.0.2.2]oct-7-ene, which is of theoretical interest, was synthesized by *W. R. Dobier jun., D. Lomas,* and *P. Tarrant.* Decomposition of Na trichloroacetate in the presence of allene gives 2,1-dichloro-2-methylenecyclopropane (20% yield), which on heating to 215 °C gives a quantitative yield of 1-(dichloromethylene)cyclopropane *(1)*. On prolonged heating at temperatures above 120 °C, the latter changes into



(1) *(2)* *(3)*

7,7,8,8-tetrachlorodispiro[2.0.2.2]octane *(2)* (100%). Zn in ethanol converts *(2)* into 7,8-dichlorodispiro[2.0.2.2]oct-7-ene (85%), the reduction of which with Na/THF/*tert*-butanol gives dispiro[2.0.2.2]oct-7-ene *(3)* (80%). The compound is thermally stable up to 300 °C. / J. Amer. chem. Soc. *90*, 3594 (1968) / –Ma. [Rd 893 IE]

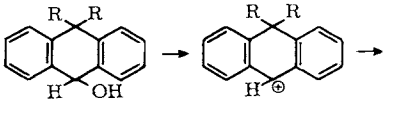
A new type of polymerization was observed by *P. Kovacic* and *J. S. Ramsey* in the reaction of 2,5-dichlorothiophene with $AlCl_3$ and $CuCl_2$ (molar ratios 1:4:2) in CS_2 at 12–29 °C. A brown polymeric powder was obtained, m.p. about 115 to 150 °C (yield 93%). The reaction apparently proceeds according to:



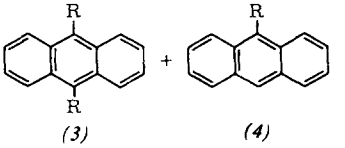
(1)

The structure *(1)* is adopted on the basis of NMR and IR spectra. Distillation of *(1)* gives the dimeric yellow $C_8H_3Cl_3S_2$; chromatography of the ether-soluble fraction of *(1)* gives the yellow tetrameric $C_{16}H_6Cl_4S_4$, m.p. 197–199 °C. Hitherto, polythienylene compounds bonded in the 2,3-positions have been unknown. The reaction is a nuclear linkage by elimination of HCl, and is presumably a cationic polymerization. / Chem. Commun. *1968*, 802 / –Ma. [Rd 894 IE]

A trans-annular rearrangement of 9,10-dihydroanthracene derivatives has been reported by *A. L. J. Beckwith, W. B. Renfrow, A. Renfrow,* and *J. K. Teuber.* Thus, for example *(1a)* rearranges on heating in acetic acid (12 hours) into 9,10-dibenzylanthracene *(3a)* and to *(4a)* in yields of 60% and 19% respectively. Analogously, 58% of *(3b)* and 23% of *(4b)* are formed from *(1b)*. On the other hand, diallylanthranol *(1c)*



(1) *(2)*



(3) *(4)*

(a), R = C_6H_5-CH_2
(b), R = *p*-Cl-C_6H_4-CH_2
(c), R = CH_2=CH-CH_2

is converted exclusively into *(3c)* (86% yield). The reaction proceeds *via* the carbonium ion *(2)* which undergoes aromatization – presumably intramolecularly. / Tetrahedron Letters *1968*, 3463 / –Kr. [Rd 904 IE]

BOOK REVIEWS

Handbuch der Lebensmittelchemie (Manual of Food Chemistry). Vol. II/2: Analysis of Foodstuffs. Compiled by *L. Acker et al.* Springer-Verlag, Berlin-Heidelberg-New York 1967. 1st Edit., xxxii, 1552 pages, 162 illustrations, bound, DM 389.– / $97.25.

28 specialists from Germany and abroad have collaborated in producing this manual [*], which is divided into 26 sections under individual headings. Such a comprehensive book is equally valuable as a reference work and for the study of food chemistry. It will prove invaluable to food chemists, food technologists, biologists, medical workers, engineers, and advanced students.

The authors provide a clear introduction to each method, followed by a detailed explanation of how to carry out the investigation, incorporating many well chosen examples. Great emphasis is placed on the interpretation of analytical data. By engaging leading experts in the individual fields it was possible to draw on their accumulated broad experience of the methods. The publisher and editor are to be specially congratulated on coordinating the lay-out of the items, which is exemplary.

Particular attention has been paid to impurities and preservatives, the treatment of which covers approximately 700 pages, nearly half of the volume. This highlights the importance of the field and indicates the direction toward which food chemistry will have to be increasingly oriented. It is very gratifying that the authors have taken the trouble to cover thoroughly both home and foreign literature and to include books as well as journals in the references.

This beautifully printed and produced volume provides an indispensable source of readily available information for every laboratory dealing with the testing and investigation of foodstuffs, and fills a long-standing gap in the German literature in this special field. *P. F. Pelshenke* [NB 737 IE]

[*] Cf. Angew. Chem. *79*, 195 (1967); Angew. Chem. internat. Edit. *6*, 189 (1967).

The Organic Compounds of Magnesium, Beryllium, Calcium, Strontium, and Barium. By *S. T. Ioffe* and *A. N. Nesmeyanov* (Vol. 2 of the series "Methods of Elemento-Organic Chemistry"). North-Holland Publishing Company, Amsterdam 1967. 1st Edit., x, 735 pp., many illustrations, bound, Dfl. 100.00.

The book is divided into two parts which differ in their size and treatment. The first part (650 pages) contains 18 chapters describing the reactions of Grignard reagents with various classes of organic compounds, as well as the preparation, analysis, and structure of Grignard compounds. This part is evidently based on the three-volume handbook on organomagnesium compounds (1950) by the same authors, which has been condensed and brought up to date by the inclusion of additional material. The second part presents a much more detailed discussion of the organic compounds of beryllium (27 pages), calcium, strontium, and barium (18 pages). The small space devoted to these topics reflects the scarcity of relevant investigations.

Each chapter has a comprehensive list of references. The literature is taken into account up to the end of 1961, and important work carried out up to the beginning of 1965 has also been added to the translation. The volume of publications to be covered was very large (much more than 10000 being known on Grignard compounds alone), and the authors are to be congratulated on the care that they have taken in this task. For many years they have been among the leading authorities in this field. It is for this very reason, however, that in the reviewer's opinion they might have made greater use of their right to criticize. For example, in the section "Structure of Grignard Reagents" (pp. 84–93), arguments and opinions that have now been revised are listed chronologically alongside those that are still valid. The once amazing ^{28}Mg-exchange experiments are described in detail, together with the (now refuted) conclusion that C_2H_5MgBr has the structure $(C_2H_5)_2Mg \cdot MgBr_2$ (p. 88). On p. 91, however, with no reference to this, we find the exchange experiments with ^{25}Mg, which led to complete equipartition, and on p. 90, without comment, is the remark that the "dominant component ... is the RMgX compound". Some comment by the authors as to what may now be regarded as definite and what may not would be of great value to readers who are unfamiliar with the subject matter.

In view of the importance of this book as a reference work, the author and subject indexes might perhaps have been more detailed. For example, the important keyword "reduction" does not appear. (The book published by *Kharasch* and *Reinmuth* in 1954 contains 30 subsidiary entries related to the reducing action of Grignard compounds under this keyword). The book provides those who are interested with a valuable reference work, which fills a gap in the long-neglected handbook and monograph literature on organometallic chemistry.

W. P. Neumann [NB 734 IE]

The Chemistry of Niobium and Tantalum. By *F. Fairbrother.* Monograph 9 of the series "Topics in Inorganic and General Chemistry". Edited by *P. L. Robinson.* Elsevier Publishing Company, Amsterdam-London-New York 1967. 1st Edit., viii, 243 pp., 16 figures, 6 tables, Dfl. 50.–.

The chemistry of niobium and tantalum is currently developing rapidly. The present compilation and selection of the existing knowledge by an expert is therefore very welcome. The book contains a short section on the separation and preparation of the elements and on the physical properties of the metals (11 pages). The author then discusses compounds containing oxygen, starting with the oxides and proceeding *via* the hydroxides, niobates, and tantalates to the complex compounds (48 pages). The chapter on the oxides is one of the few that leave something to be desired. It would have been better here *e.g.* not to have discussed the modifications of Nb_2O_5 primarily in historical order, and to have given a clearer picture of the latest position. It would also have been useful to include the formulas and structures of the very interesting Magnéli phases in the region from 2.4 to 2.5 O/Nb.

The section on halogen compounds (78 pp.) is very comprehensive. The importance of metal-metal bonds in the structures of the lower halides is also clearly explained.

Further chapters deal with the hydrides (7 pages), carbides, silicides, and borides (17 pages), the compounds of niobium and tantalum with the group V elements (18 pages), and the sulfides, selenides, and tellurides (13 pages). The latest developments are again included in these chapters.

The last chapter presents a survey of analytical methods (10 pages). However, this chapter is probably intended simply to round off the book, and it will be necessary for the analyst to refer to specialized works.

A large number of references facilitate consultation of the original papers. Complete coverage cannot be expected in a monograph of this size; it is therefore all the more important that the author selects his material well. While the essentials have been well selected and arranged, the reader is referred to the literature for other themes. This may be useful to the reader, though it would be very interesting to gain a deeper insight into the author's views on specific problems.

H. Schäfer [NB 730 IE]

Aromatic Rearrangements. By *H. J. Shine.* Monograph No. 6 of the series "Reaction Mechanisms in Organic Chemistry". Edited by *C. Eaborn* and *N. B. Chapman.* Elsevier Publishing Company, Amsterdam-London-New York 1967. 1st Edit., 405 pp., many illustrations, Dfl. 65.–.

The editors have managed to engage an author for this book who has himself made an important contribution to our understanding of the benzidine rearrangement. It is therefore understandable that considerable space in this book is devoted to the reactions of *N*-substituted amino-aromatic compounds (140 pages). Three chapters also deal with rearrangements of alkylaromatic and halogeno-aromatic compounds, aryl esters and ethers, and aromatic amine oxides. The book ends with two sections on base-catalyzed (Smiles, Sommelet, and carboxylate rearrangements, von Richter reaction) and photochemical rearrangements. Ordinary migrations of aryl groups, rearrangements *via* dehydroaromatic intermediates, and Lewis acid-catalyzed rearrangements of polynuclear aromatic compounds are not discussed.

The author has taken into account results from more than 500 original papers and discussed them critically. For reactions whose mechanisms are not yet clarified, the present position is shown and the possible interpretations of the results are considered. The numerous comparisons of rearrangements are particularly valuable.

The following observations were made regarding some of the chapters:

In the discussion of the Fries rearrangement, some reference should have been made to *K. Fries*, particularly since the histories of other reactions are outlined.

Only four of the many papers on the Claisen rearrangement by *H. Schmid* and his co-workers are considered. In the excellent section on the benzidine rearrangement, the author clearly prefers the polar-transition-state theory to the π-complex theory or the radical-cation theory on kinetic grounds. In the reviewer's opinion, there is much to be said for the possibility, mentioned on p. 325, that both the Sommelet and the Stevens rearrangements proceed *via* ion pairs. As was shown in 1966 (reference 50a in Chapter 3), *N,N'*-decamethylenebenzidine (cf. p. 135), which was first described as a monomer (reference 17, Chapter 3), has a dimeric structure.

There are few printing errors either in the text or in the illustrations; however, some of the formulas are very small.

On the whole, this book presents a comprehensive picture of the work on many rearrangements of aromatic compounds

up to about 1965/1966. Its publication will be welcomed by all who wish to learn about this field of organic chemistry, and it should be included at least in the libraries of all universities and colleges. *W. Tochtermann* [NB 738 IE]

The Organic Chemistry of Phosphorus. By *A. J. Kirby* and *S. G. Warren*. Monograph 5 of the series "Reaction Mechanisms in Organic Chemistry". Edited by *C. Eaborn* and *N. B. Chapman*. Elsevier Publishing Company, Amsterdam-London-New York 1967. 1st Edit., xi, 404 pp., 4 figures, 21 tables, Dfl. 65.–.

A great deal of expert knowledge and courage are required to present a monograph on such an extensive topic. However, it is pointed out in the preface that certain mechanistic principles are to be laid down to familiarize the newcomer with the specific problems of organophosphorus chemistry. The authors see the absence of quantitative data in the original papers as one of the limits of their commentary. The experienced reader very soon finds that the discussion of fields that have already been well covered in other monographs (cf. *R. F. Hudson*: Structure and Mechanism in Organophosphorus Chemistry), or that are particularly familiar to the authors from their own experience is of a high scientific standard. This is true of Chapter 1: Electronic Structure; Chapter 2: Structure and Reactivity; Chapter 3: Nucleophilic Attack of Compounds of Trivalent Phosphorus; Chapter 4: Elimination of Compounds of Trivalent Phosphorus; Chapter 5: Free-Radical Reactions on Phosphorus; Chapter 7: Reactions that do not occur on the Central P Atom; Chapter 8: Nucleophilic Attack on Compounds of Tricoordinated Phosphorus; Chapter 10: Nucleophilic Attack on Compounds of Tetrahedral Phosphorus(v), and Chapter 11: Phosphorylation. The last two chapters are particularly impressive for their completeness.

On the other hand, Chapter 6: Four-Center Rearrangements, and to a lesser degree Chapter 9: Nucleophilic Attack on Phosphonium Salts and Compounds of Pentacovalent Phosphorus, seem rather stunted. Chapter 6 deals almost exclusively with olefination *via* phosphonium ylides, with no regard for historical relationships. More recent developments such as PO-activated olefinations are by-passed with references, and their importance in syntheses is not mentioned. No reference is made to later variants by *Zimmer*, *Corey*, *Machleidt*, and *Bergelson*. This chapter also contains many inaccuracies and errors, which should be eliminated for the second edition. The well-informed reader also notices the absence of references to important review articles, particularly in languages other than English. No mention is made in Chapter 9 of the important work by *Hellwinkel* on the anionic hexacovalent phosphorus compounds; the book also lacks any reference to the preparation of phosphabenzene and its derivatives by *G. Märkl*. It is categorically stated on page 336 that no three-membered rings containing phosphorus are known, with complete disregard for the preparation of phosphirane by *Ross* and *Wagner*. Reactions of azides with compounds of tricoordinate phosphorus are repeatedly and wrongly formulated as proceeding *via* nitrenes. If inaccuracies of this nature and mistakes in the formulations, formulas, and literature data were corrected, this monograph could be wholeheartedly recommended. Even in its present state, however, it provides a lively insight into the complexity and vitality of organophosphorus chemistry.

L. Horner [NB 728 IE]

Perspectives in Structural Chemistry. Vol. 1. Edited by *J. D. Dunitz*, and *J. A. Ibers*. John Wiley & Sons, New York-London-Sydney, 1967. 1st Edit., ix, 199 pages, numerous illustrations and tables, bound, 80 s.

This is the first volume of a new series of detailed surveys on topics in structural chemistry. According to the foreword, the emphasis is placed on the results of structural investigations, their accuracy, and their chemical significance, and not on the aspects of methods and techniques. In addition, the results of individual structural determinations are mutually compared to establish relationships wherever possible, and to interpret these relationships.

The first volume contains three surveys, all written with regard to the above concepts: "π-Complexes of Transition Metals with Aromatic Systems" by *P. J. Wheatley*, "Structures of Natural Products" by *A. McL. Mathieson*, and "Structural Chemistry of the C≡N group" by *D. Britton*. The literature up to and including 1965 appears to be reviewed completely. In the last two contributions reference is also made to more recent literature. Characteristically, a large part of the work cited is concerned with X-ray structure analysis. The three authors and the editors are well-known practising crystallographers, who have contributed to the subjects under discussion by their own work.

The value of the book lies not only in the collection and comparative evaluation of the relevant literature, but in the critical manner in which it is presented. For this reason, and because of its emphasis on results, the book will appeal directly to the organic and inorganic chemist interested in general structural and stereo-chemistry, who often finds it difficult to understand and appraise original papers and to assess their accuracy because of the frequently strong emphasis on methodological aspects.

It is to be hoped that further volumes in this series will soon become available. *D. Mootz* [NB 732 IE]

Poly-α-Amino Acids. Protein Models for Conformational Studies. Edited by *G. D. Fasman*. Vol. 1 of the "Biological Macromolecules Series". Marcel Dekker, Inc., New York, 1967. 1st Edit. xv, 764 pages, numerous illustrations and tables, bound $34.50.

This compilation of information about polyamino acids, information that has grown very rapidly in recent years, will be especially welcomed by those who are interested in the structure and stabilization of proteins and in conformational changes. The book consists of 13 chapters written by leading specialists. Each chapter is effectively a separate monograph in its particular field.

The chapters on X-ray structure analysis (*Elliott*), IR-spectroscopy (*Miyazawa*), X-ray small-angle scattering (*Saludjian* and *Luzzati*), and hydrogen exchange (*Erlander*) are excellent both in the description of methods and in the presentation of the results. The treatment of light scattering and hydrodynamic properties by *Benoit et al.* is essentially confined to an outline of method possibilities. The chapters on UV-absorption (*Gratzer*), optical rotatory dispersion (*Yang*), and circular dichroism (*Beychok*) are considered good in themselves; a comprehensive description of these closely related effects from the point of view of the optical properties of polypeptides would certainly have been better. Here we come across the basic disadvantage of the book: the very thorough grouping according to methods, which is only complete when it more or less coincides with a grouping based on the properties of polyamino acids. Hence the individual descriptions are not very well interrelated, and there are many repetitions (even some illustrations occur twice!).

In addition to the method-oriented chapters, there are two interesting chapters on dielectric properties (*Wada*) and biological properties (*Silman* and *Sela*), and also a chapter on polyproline (*Mandelkern*). The difficult problem of presenting the theories on stabilization and conformational changes is well solved by *Poland* and *Scheraga* (with limitations as to kinetics). *Fasman* has succeeded only partially in giving in his chapter an orderly survey of the properties of the polyamino acids and their structures. The construction of the book and a poor and defective index render it impossible for the reader to acquaint himself quickly with a particular polyamino acid. The literature is covered up to 1965, and in certain exceptional cases up to 1966. *J. Engel* [NB 736 IE]

Adsorption from Solutions of Non-Electrolytes. By *J. J. Kipling*, Academic Press, London-New York 1966. 1st Edit., xii, 328 pp., numerous illustrations, 73 s.

This monograph sets out to familiarize the reader with a field that up to now has received little attention, on the one hand because the measurements are difficult to carry out and on the other because the results of such measurements frequently yield only a complex expression that is difficult to interpret. The book offers a good survey of the simultaneous adsorption of components of a liquid, as well as of a solution of a solid in an organic solvent, at the solid/liquid or gas/liquid interface.

The term "solution" in the title can be misleading, since it implies particularly the special case in which one component is normally present in large excess, and this is not the case in many of the systems treated. This term should perhaps only be used, where one component is actually present in excess (*e.g.* a solid in an organic solvent).

Methods of investigation are next considered, and these are principally concerned with the analysis of liquid mixtures. As a result, a clear distinction is made between individual and composite isotherms; the former are concerned with the adsorption of a single component of a mixture or a solution, and the latter with the simultaneous adsorption of all components. The different behavior of polar and nonpolar organic compounds at liquid/solid and gas/liquid interfaces is demonstrated with the aid of many examples. In most cases a monomolecular adsorption layer may be assumed; multimolecular adsorption occurs less frequently, and is thus difficult to estimate quantitatively. The sorption properties of molecular sieves, whose importance in analysis continues to increase, are unfortunately treated only very briefly.

The thermodynamic calculations are useful, particularly the evaluations of various isotherms. However, molecular-physical concepts based on quantum mechanics, which have been applied more recently to adsorbed gases and solids, are completely lacking in the field under consideration.

The purpose of the book – to give to the research worker interested in fundamentals a clear and well arranged exposition of a relatively complex field – is in general fully achieved. It is to be hoped that the book will provide an impetus to wider investigations in the field of adsorption phenomena.

G. Peschel [NB 727 IE]

Halogen Chemistry. By *V. Gutmann*. Academic Press, London-New York 1967. Vol. 1. 1st Edit., xiii, 473 pp., several figures and tables, bound $ 21.00 / £6.

Halogen chemistry has recently become technically and scientifically very interesting, and has consequently undergone a very rapid development. This collection of reviews of important areas of the field by eminent specialists is therefore welcome.

A. G. Sharpe presents a concise but easily understandable discussion of the "Physical Inorganic Chemistry of the Halogens". The author has approached the problems from various angles instead of simply listing the physical data. *M. F. A. Dove* and *D. B. Sowerby* describe "Isotope-Halogen Exchange Reactions". This article contains considerable experimental material, which is particularly valuable in preparative work. The "Physical and Chemical Properties of the Halogen Fluorides" are described by *L. Stein*. This is followed by a very good review by *A. J. Popov* on "Polyhalogen Complex Ions", which should prove an incentive to further investigations. The chapter on "Electronic Structure and MO Treatment of Halogen and Inert Gas Complexes in Positive, Negative, and Indefinite Oxidation States" by *C. Jørgensen* is a clear and understandable account of the theoretical aspects of the halogen complexes. *H. Selig* finally describes the recent "Fluorine Chemistry of the Inert Gases".

The author and subject indexes at the end of the volume are particularly useful. The authors do not all use the same system for references, and in some chapters the references are not indicated by numbers, which makes reading difficult. As is to be expected in a work of this kind, some of the contributions are relatively short, while others give a wider description of the field. The book is a valuable aid to chemists working in every field as a source not only of information on what has already been done, but also of inspiration for new research projects.

O. Glemser [NB 735 IE]

Chemistry and Enzymology of Marine Algal Polysaccharides. By *E. Percival* and *R. H. McDowell*. Academic Press, London-New York 1967. 1st Edit., XII, 219 pages, several figures and tables, bound, 60 s.

The authors have endeavored to present a critical review of the very numerous and widely scattered papers dealing with the polysaccharides found in marine algae and to summarize the results from the chemical and enzymological points of view.

A review of the occurrence and distribution of polysaccharides in algal species and a short chapter on the methods used for elucidating their constitution is followed by a discussion of the neutral polysaccharides, the reserve substances and skeletal substances. Alginic acids, representing the most important polysaccharides carrying carboxyl groups, are discussed next. This is followed by a discussion of the galactan sulfuric acid esters known as agar, and also of polysaccharides containing both carboxyl and sulfate groups. The last chapter is a short one, in which the algal polysaccharides are discussed in the context of their place among the plant carbohydrates.

The authors, both of whom have been working in this field for a long time, have succeeded in presenting a clear picture of the current state of knowledge. They emphasize not only the advances that were made possible by improved methods but also the many problems as yet unsolved. Readers unfamiliar with the methods of macromolecular chemistry would find a more complete treatment of molecular weight determination, and especically of the problems of viscometry – possibly with references to review articles – very helpful.

This is a painstakingly written book, and it is strongly recommended to all chemists and biologists working in this field.

E. Husemann [NB 733 IE]

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Nucleophilic Reactions of Metal Carbonyl Anions with Fluorocarbons

By M. I. Bruce and F. G. A. Stone[*]

This article describes the formation of carbon-metal bonds by reacting carbonylmetalate ions with fluorocarbons. Complex formation depends on the nucleophilic behavior of the anions, and the susceptibility of fluorocarbons to this form of attack.

1. Introduction

It has been known for some time that the metal-metal bonds in polynuclear metal carbonyls (*e.g.* $Mn_2(CO)_{10}$, $Fe_3(CO)_{12}$, *etc.*) and their derivatives may be cleaved by alkali metals, either in dispersion or as an amalgam, to form the corresponding carbonylmetalate ions [1]. Other reducing agents have been used. *King* [2] found that tetrakis(dimethylamino)ethane reduced $Co_2(CO)_8$, $V(CO)_6$, or $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ to the corresponding anions, but concluded that it is a less powerful reducing agent than the alkali metals. It does not react with $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ or $[\pi\text{-}C_5H_5NiCO]_2$, for example. The chemistry of carbonylmetalate ions has recently been reviewed [1].

It is now well known that fluorocarbons have increased susceptibility to nucleophilic attack, compared with the corresponding hydrocarbons, owing to withdrawal of electron density onto the fluorine atoms [3]. Conversely, fluorocarbons show a much lower ability to participate in electrophilic reactions. These tendencies are more pronounced if a site of π-electron density is present, and reach a peak with polyfluoro-aromatic and -heterocyclic compounds, most of the chemistry of which is dominated by nucleophilic reactions. Ionic reactions of fluoroolefins have been summarized by *Chambers* and *Mobbs* [3], and the reactions of aromatic fluorocarbons have been similarly treated by *Tatlow* [4].

Herein we summarize reactions between fluorocarbons and carbonylmetalate ions, the latter having only recently been recognized as nucleophilic reagents. The first reported reaction of this type was that of perfluoroallyl chloride with the anion derived from manganese carbonyl to give pentacarbonyl-*trans*-perfluoropropenylmanganate [5, 6].

$$CF_2{=}CFCF_2Cl + [Mn(CO)_5]^- \rightarrow \textit{trans}\text{-}CF_3CF{=}CFMn(CO)_5 + Cl^-$$

More recently, use of these anions has encompassed a wide range of fluorocarbons, and it is timely to consider the many novel compounds that have been produced. Indeed, it can be said that this type of reaction is now of major importance in the synthesis of fluorocarbon derivatives of transition metals in which carbon is σ-bonded to these metals.

Empirical observations [7, 8] on the reactivity of the various anions employed suggest the following series in order of decreasing nucleophilicity:

$[Re(CO)_5]^- \sim [\pi\text{-}C_5H_5Fe(CO)_2]^- > [\pi\text{-}C_5H_5Ru(CO)_2]^- > [Mn(CO)_4P(C_6H_5)_3]^- > [Mn(CO)_5]^- \sim [\pi\text{-}C_5H_5Mo(CO)_3]^- > [Fe(CO)_4]^{2-} > [Co(CO)_4]^-$.

Consideration of electrochemical data and rates of reaction have recently enabled a semi-quantitative estimate of reactivity to be obtained [9]. The results, based on $[Co(CO)_4]^-$ as unity, are:

$[\pi\text{-}C_5H_5Fe(CO)_2]^-$, 7.0×10^7; $[\pi\text{-}C_5H_5Ru(CO)_2]^-$, 7.5×10^6; $[\pi\text{-}C_5H_5NiCO]^-$, 5.5×10^6; $[Re(CO)_5]^-$,

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[8] *P. W. Jolly*, *M. I. Bruce*, and *F. G. A. Stone*, J. chem. Soc. (London) *1965*, 5830.
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2.5×10^4; $[\pi\text{-}C_5H_5W(CO)_3]^-$, ~500; $[Mn(CO)_5]^-$, 77; $[\pi\text{-}C_5H_5Mo(CO)_3]^-$, 67; $[\pi\text{-}C_5H_5Cr(CO)_3]^-$, 4; $[Co(CO)_4]^-$, 1.

In terms of their practical utility, the anions $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ and $[Re(CO)_5]^-$ are the most useful synthetically. The fluorocarbon-iron complexes are colored, and therefore are more amenable to purification by chromatographic techniques. The rhenium anion gives less complex reaction mixtures, however, with fewer by-products resulting from oxidative degradation of the anion. Where the products are volatile, the rhenium anion gives the highest yield of product.

2. Fluoroalkanes and -alkenes

No reactions between carbonylmetalate ions and fully saturated aliphatic fluorocarbons have been reported so far. On the other hand, fluoroalkenes have been used extensively. Tetrafluoroethylene gives trifluorovinyl complexes with $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ and with $[Re(CO)_5]^-$, but does not react with $[Mn(CO)_5]^-$[8].

$$CF_2{=}CF_2 + [Re(CO)_5]^- \xrightarrow{THF} CF_2{=}CFRe(CO)_5 + F^-$$

Perfluoropropene[8] reacts as expected at the CF_2 group, affording the same *trans*-perfluoropropenyl complexes that are formed with perfluoroallyl chloride, *e.g.*, *trans*-$CF_3CF{=}CFFe(CO)_2(\pi\text{-}C_5H_5)$. Chlorotrifluoroethylene reacts, with replacement of the chlorine atom, with $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ or $[Re(CO)_5]^-$, but with $[Mn(CO)_5]^-$, addition of the elements of $HMn(CO)_5$ occurs giving the chlorotrifluoroethyl complex $HCFClCF_2Mn(CO)_5$[10]. This process is analogous to the base-catalyzed addition of methanol to the same olefin yielding $HCFClCF_2OCH_3$[11].

Perfluorobutadiene reacts with $[Re(CO)_5]^-$ or $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ to give the *trans* and *cis* isomers, respectively, of the corresponding perfluorobutadienyl complexes[12].

$$CF_2{=}CFCF{=}CF_2 + [\pi\text{-}C_5H_5Fe(CO)_2]^- \rightarrow cis\text{-}CF_2{=}CFCF{=}CFFe(CO)_2(\pi\text{-}C_5H_5) + F^-$$

$[Mn(CO)_5]^-$ is too weak a nucleophile to react with perfluorobutadiene.

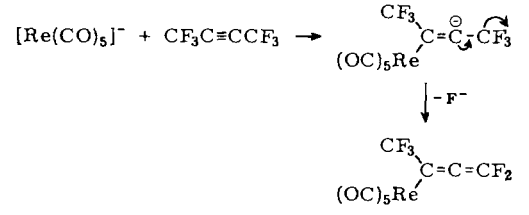
As mentioned above, perfluoroallyl chloride reacts with $[Mn(CO)_5]^-$ or $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ to give *trans*-perfluoropropenyl complexes[5, 6, 13]. With $[\pi\text{-}C_5H_5Ni(CO)]^-$, on the other hand, the product is an inseparable mixture of the perfluoroallyl- and perfluoropropenyl-nickel compounds $C_3F_5Ni(CO)(\pi\text{-}C_5H_5)$[14]. A similar reaction between methoxide ion and perfluoroallyl chloride yields perfluoroallyl methyl ether, which on standing for several days rearranges to the perfluoropropenyl compound[15].

$$CF_2{=}CFCF_2Cl + CH_3O^- \xrightarrow{-Cl^-} CF_2{=}CFCF_2OCH_3 \rightarrow CF_3CF{=}CFOCH_3$$

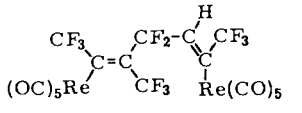
Similar rearrangements are assumed to occur with the metal complexes, either spontaneously, or during work-up and sublimation.

3. Fluoroalkynes

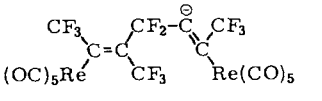
Treatment of hexafluoro-2-butyne with $[Re(CO)_5]^-$ affords the σ-bonded pentacarbonylperfluoro-1-methyl-1-allenylrhenium[12]. This reaction probably proceeds in the following manner,



A second rhenium complex formed in this reaction was thought at first to be a dimer of the allenyl compound, but subsequent studies[16] involving ^{19}F-NMR spin decoupling strongly suggest that the second product has the structure:



This novel complex could be formed by attack of the carbanion $(OC)_5ReC(CF_3){=}C^{\ominus}(CF_3)$ on pentacarbonylperfluoro-1-methyl-1-allenylrhenium to give the intermediate



which then abstracts a proton from the solvent. The anion $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ and hexafluoro-2-butyne afford a single iron complex, $CF_2{=}C{=}C(CF_3)Fe(CO)_2(\pi\text{-}C_5H_5)$.

Trifluoropropyne reacts with the anions $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ and $[Re(CO)_5]^-$ to afford the deriv-

[10] *M. I. Bruce, P. W. Jolly,* and *F. G. A. Stone,* J. chem. Soc. (London) (A) *1966,* 1602.

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[12] *M. Green, N. Mayne,* and *F. G. A. Stone,* Chem. Commun. *1966,* 755; J. chem. Soc. (London) A *1968,* 902.

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Table 1. Reactions of fluoroalkenes and fluoroalkynes with carbonylmetal anions [a].

Fluorocarbon	Anion	Product	M.p. (°C)	References		
				Reaction	IR	NMR
$CF_2=CF_2$	$[cpFe(CO)_2]^-$	$CF_2=CFFe(CO)_2cp$	27	[8]	[8]	[8]
	$[Mn(CO)_5]^-$	no reaction	—	[8]	—	—
	$[Re(CO)_5]^-$	$CF_2=CFRe(CO)_5$	45	[8]	[8]	[8]
$ClCF=CF_2$	$[cpFe(CO)_2]^-$	$CF_2=CFFe(CO)_2cp$	27	[10]	[8]	[8]
	$[Mn(CO)_5]^-$	$ClCFHCF_2Mn(CO)_5$	41–42	[10]	[35]	[35]
	$[Re(CO)_5]^-$	$CF_2=CFRe(CO)_5$	45	[10]	[8]	[8]
$CF_3CF=CF_2$	$[cpFe(CO)_2]^-$	$CF_3CF=CFFe(CO)_2cp$	70–71	[8]	[13]	[13]
	$[cpRu(CO)_2]^-$	$CF_3CF=CFRu(CO)_2cp$	70–71	[22a]	[22a]	[22a]
	$[Mn(CO)_5]^-$	$CF_3CF=CFMn(CO)_5$	71–72	[8]	[36]	[36]
	$[Re(CO)_5]^-$	$CF_3CF=CFRe(CO)_5$	88–89	[8]	[8]	[8]
$ClCF_2CF=CF_2$	$[cpFe(CO)_2]^-$	$CF_3CF=CFFe(CO)_2cp$	69.5–70.5	[13]	[13]	[13]
	$[Mn(CO)_5]^-$	$CF_3CF=CFMn(CO)_5$	71–72 76–76.5	[5] [6]	[5, 6, 36]	[5, 6, 36]
	$[cpNi(CO)]^-$	$CF_3CF=CFNi(CO)cp$ $CF_2=CFCF_2Ni(CO)cp$	liquid	[14]	—	[14]
$CF_2=CFCF=CF_2$	$[cpFe(CO)_2]^-$	$CF_2=CFCF=CFFe(CO)_2cp$	32–34	[12]	[12]	[12]
	$[Re(CO)_5]^-$	$CF_2=CFCF=CFRe(CO)_5$	oil	[12]	[12]	[12]
$CF_3C\equiv CH$	$[cpFe(CO)_2]^-$	*cis*-$CF_3CH=CHFe(CO)_2cp$	oil	[16]	—	—
	$[Mn(CO)_5]^-$	no reaction	—	[16]	—	—
	$[Re(CO)_5]^-$	*cis*-$CF_3CH=CHRe(CO)_5$	~0	[16]	—	—
$CF_3C\equiv CCF_3$	$[cpFe(CO)_2]^-$	$CF_2=C=C(CF_3)Fe(CO)_2cp$	39.5–40	[16]	[16]	[16]
	$[Mn(CO)_5]^-$	no reaction	—	[12]	—	—
	$[Re(CO)_5]^-$	$CF_2=C=C(CF_3)Re(CO)_5$	oil	[12, 16]	[12, 16]	[12, 16]
		$C_8F_{11}H[Re(CO)_5]_2$ [b]	138–138.5	[12, 16]	[16]	[16]

[a] cp = π-C_5H_5; [b] See text for probable molecular structure.

Table 2. Reactions of alicyclic fluorocarbons with carbonylmetal anions [a].

Fluorocarbon	Anion	Product	M.p. (°C)	References		
				Reaction	IR	NMR
Perfluorocyclobutene	$[cpFe(CO)_2]^-$	$C_4F_5Fe(CO)_2cp$	50–51	[8]	[8]	[8]
	$[Mn(CO)_5]^-$	$C_4F_5Mn(CO)_5$	33	[8]	[8]	[8]
	$[Re(CO)_5]^-$	$C_4F_5Re(CO)_5$	55–56	[8]	[8]	[8]
1,2-Dichlorohexafluorocyclobutane	$[cpFe(CO)_2]^-$	$C_4F_5Fe(CO)_2cp$	49–50	[10]	[8]	[8]
	$[Mn(CO)_5]^-$	$C_4F_5Mn(CO)_5$	—	[10]	[8]	[8]
	$[Re(CO)_5]^-$	$C_4F_5Re(CO)_5$	—	[10]	[8]	[8]
1,2-Dichlorohexafluorocyclopentene	$[cpFe(CO)_2]^-$	$C_5F_6ClFe(CO)_2cp$	99–101	[10]	[10]	[10]
	$[Mn(CO)_5]^-$	$C_5F_6ClMn(CO)_5$	—	[10]	[10]	—
	$[Re(CO)_5]^-$	$C_5F_6ClRe(CO)_5$	73–75	[10]	[10]	[10]
Perfluorocyclohexene	$[cpFe(CO)_2]^-$	$C_6F_9Fe(CO)_2cp$	97–98	[8]	[8]	[8]
	$[cpRu(CO)_2]^-$	$C_6F_9Ru(CO)_2cp$	88–89	[22a]	[22a]	[22a]
	$[Mn(CO)_5]^-$	$C_6F_9Mn(CO)_5$	35	[8]	[8]	[8]
	$[Mn(CO)_4P(C_6H_5)_3]^-$	*tert*-$C_6F_9Mn(CO)_4P(C_6H_5)_3$	159–160	[8]	—	[8]
	$[Re(CO)_5]^-$	$C_6F_9Re(CO)_5$	67–70	[8]	[8]	[8]

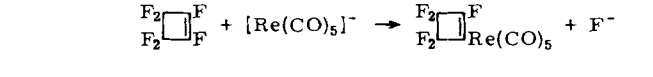
[a] cp = π-C_5H_5.

atives *cis*-$CF_3CH=CHFe(CO)_2(\pi\text{-}C_5H_5)$ and *cis*-$CF_3CH=CHRe(CO)_5$, respectively [17], the reactions proceeding with 100 % stereospecificity.

A variety of reactions occurs also with $C_6F_5C\equiv CH$ [17]. These are discussed in Section 5.

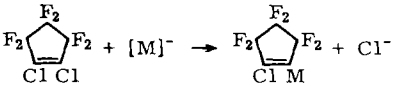
4. Alicyclic Fluorocarbons

Nucleophilic attack of carbonylmetalate ions on cyclic fluoroolefins occurs with substitution of one of the fluorine atoms attached to the C=C double bond [8, 18].



Similar reactions occur with decafluorocyclohexene, but with no anion is more than one fluorine atom replaced.

With 1,2-dichlorohexafluorocyclopentene low yields of the mono-chloro derivatives are obtained [10].



M = π-$C_5H_5Fe(CO)_2$, $Mn(CO)_5$, $Re(CO)_5$

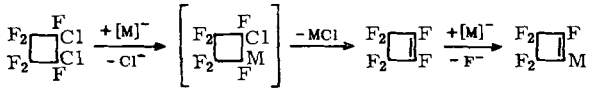
This reaction may be contrasted with the action of alkoxide ion on dichlorohexafluorocyclopentene which rapidly replaces three fluorine atoms, even at −78 °C [10, 19]. Possibly one reason for the low yields of organometallic compound obtained is the tendency of the complexes to eliminate carbonylmetal chloride, the resulting hexafluorocyclopentyne not surviving the reaction conditions. In this connection, it may be

[17] *M. I. Bruce, D. A. Harbourne, F. Waugh*, and *F. G. A. Stone*, J. chem. Soc. (London) A *1968*, 895.

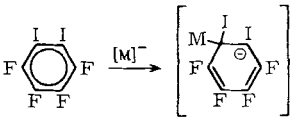
[18] *P. W. Jolly* and *F. G. A. Stone*, Chem. Commun. *1965*, 85.

[19] *A. L. Henne* and *K. A. Latif*, J. Indian chem. Soc. *30*, 809 (1953).

noted that the saturated alicyclic compound 1,2-dichlorohexafluorocyclobutane reacts with carbonylmetalate anions with elimination of carbonylmetal chloride. However, the resulting hexafluorocyclobutene is stable, and reacts further with the anions forming the above mentioned perfluorocyclobutenyl complexes in low yields [10].



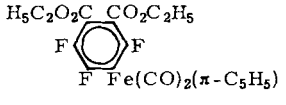
M = π-$C_5H_5Fe(CO)_2$, $Re(CO)_5$, $Mn(CO)_5$



M = π-$C_5H_5Fe(CO)_2$

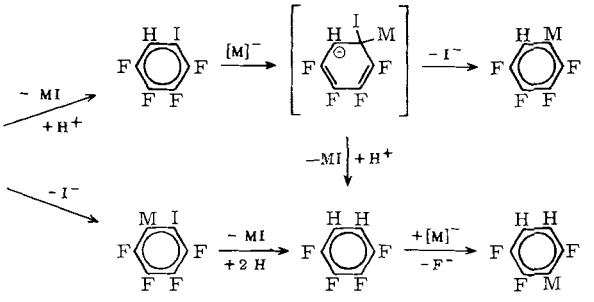
5. Aromatic Fluorocarbons

The recent availability of polyfluoroaromatic compounds has initiated much research on this interesting class of compound [4]. From the earliest investigations, it has been evident that hexafluorobenzene and related compounds are very susceptible to nucleophilic attack, and investigation of their reactions with carbonyl metalate ions followed naturally. The first report of experiments of this type was by *King* and *Bisnette* [20], who found that substitution on the aromatic nucleus occurred when C_6F_6, C_6F_5H, 1,2-$H_2C_6F_4$, or $C_6F_5CF_3$ was treated with the anion $[\pi\text{-}C_5H_5Fe(CO)_2]^-$. Substitution occurred *para* to a group other than fluorine, and it was noted that octafluorotoluene showed no tendency to substitution in the CF_3 group. A subsequent investigation [21] showed that a range of organometallic compounds could be prepared, often in relatively good yields, containing different organic functional groups. Thus pentafluorostyrene with $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ gave *p*-$CH_2{=}CHC_6F_4Fe(CO)_2(\pi\text{-}C_5H_5)$ [22], and diethyl tetrafluorophthalate with the same anion afforded the following complex [21].

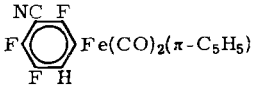


As observed with the alicyclic compounds, substitution to give a carbonylmetal group adjacent to a halogen atom other than fluorine resulted in elimination of carbonylmetal halide. Thus, treatment of 1,2-diiodotetrafluorobenzene with $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ afforded π-$C_5H_5Fe(CO)_2I$ and an inseparable mixture of three complexes, their structures being established by ^{19}F-NMR [21] and mass spectroscopy [23]. The formation of the complexes is in accord with the following reaction scheme, and with the mechanism discussed in Section 7.

The nature of the carbonylmetal anion appears to determine the product formed in reactions with pentafluorophenyl acetylene [17]. Thus with $[Re(CO)_5]^-$



ring substitution occurs to give *p*-$HC{\equiv}CC_6F_4Re(CO)_5$, while with $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ the complex *p*-$HC_6F_4CH{=}CHFe(CO)_2(\pi\text{-}C_5H_5)$ is formed. In the latter case, replacement of one of the ring fluorine atoms with hydrogen has occurred. Examples of this behavior are also found in reactions with C_6F_5X (X = F, Cl, Br, I), when mixtures of the two compounds $C_6F_5Fe(CO)_2(\pi\text{-}C_5H_5)$ and *p*-$HC_6F_4Fe(CO)_2(\pi\text{-}C_5H_5)$ are formed; and with C_6F_5CN, where the product



was identified by ^{19}F-NMR spectroscopy [21,23]. It is not entirely clear why products of this nature should be formed: perhaps elimination of the halide π-$C_5H_5Fe(CO)_2X$ from an S_N2-type intermediate occurs (see Section 7). Alternatively, attack by a hydridic species formed *in situ* may lead to these products.

No instance of disubstitution of an aromatic ring has been reported, even when an excess of carbonyl metal anion is used. Apparently, monosubstitution deactivates the ring towards further substitution. This deactivating effect was observed earlier with pentafluorophenylplatinum complexes [24]. The compound *cis*-$[(C_2H_5)_3P]_2Pt(C_6F_5)_2$ is unaffected by treatment with methyllithium or methylamine. The resistance of the fluorine atoms in these compounds to displacement by nucleophilic reagents can probably be attributed to electron release into the aromatic ring by the transition metal groups, both by an inductive and a mesomeric mechanism [25].

Treatment of pentafluorobenzyl bromide with $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ gives in addition to the expected

[20] *R. B. King* and *M. B. Bisnette*, J. organometallic Chem. *2*, 38 (1964).

[21] *M. I. Bruce* and *F. G. A. Stone*, J. chem. Soc. (London) A *1966*, 1837.

[22] *M. I. Bruce*, unpublished work.

[22a] *T. Blackmore*, *M. I. Bruce*, and *F. G. A. Stone*, J. chem. Soc. (London) A *1968*, 2158.

[23] *M. I. Bruce*, J. chem. Soc. (London) A *1968*, 1459.

[24] *D. T. Rosevear* and *F. G. A. Stone*, J. chem. Soc. (London) *1965*, 5275.

[25] *F. G. A. Stone*, Endeavour *25*, 33 (1966).

Table 3. Reaction of polyfluoroaromatic compounds with carbonylmetal anions [a].

Fluorocarbon	Anion	Product	M.p. (°C)	References		
				Reaction	IR	NMR
C_6F_6	$[cpFe(CO)_2]^-$	$C_6F_5Fe(CO)_2cp$	142–143	[20]	[20]	[20]
		$C_6F_5Fe(CO)_2cp$ + $HC_6F_4Fe(CO)_2cp$	–	[21]	–	–
	$[cpRu(CO)_2]^-$	$C_6F_5Ru(CO)_2cp$	159–160	[22a]	[22a]	[22a]
	$[Mn(CO)_5]^-$	no reaction	–	[20]	–	–
	$[Re(CO)_5]^-$	$C_6F_5Re(CO)_5$	152	[8]	[8]	–
	$[cpMo(CO)_3]^-$	no reaction	–	[20]	–	–
	$[Co(CO)_4]^-$	no reaction	–	[20]	–	–
	$[Fe(CO)_4]^{2-}$	no reaction	–	[20]	–	–
C_6F_5H	$[cpFe(CO)_2]^-$	$HC_6F_4Fe(CO)_2cp$	128–130	[20]	[20]	[20]
C_6F_5Cl	$[cpFe(CO)_2]^-$	$C_6F_5Fe(CO)_2cp$ + $HC_6F_4Fe(CO)_2cp$	–	[21]	–	–
C_6F_5Br	$[cpFe(CO)_2]^-$	$C_6F_5Fe(CO)_2cp$ + $HC_6F_4Fe(CO)_2cp$	–	[21]	–	–
C_6F_5I	$[cpFe(CO)_2]^-$	$C_6F_5Fe(CO)_2cp$ + $HC_6F_4Fe(CO)_2cp$	–	[21]	–	–
C_6F_5CN	$[cpFe(CO)_2]^-$	$CNC_6F_4Fe(CO)_2cp$	99–101	[21]	[21]	[23]
	$[Mn(CO)_5]^-$	$CNC_6F_4Mn(CO)_5$	134–135 (decomp.)	[37]	[37]	[37]
	$[Re(CO)_5]^-$	$CNC_6F_4Re(CO)_5$	152–153 (decomp.)	[37]	[37]	[37]
$C_6F_5CO_2C_2H_5$	$[cpFe(CO)_2]^-$	$C_2H_5O_2CC_6F_4Fe(CO)_2cp$	127–128	[21]	[21]	[23]
$C_6F_5NH_2$	$[cpFe(CO)_2]^-$	no reaction	–	[21]	–	–
$C_6F_5NHNH_2$	$[cpFe(CO)_2]^-$	$HC_6F_4Fe(CO)_2cp$	–	[21]	–	–
C_6F_5NO	$[cpFe(CO)_2]^-$	no reaction	–	[38]	–	–
$C_6F_5NO_2$	$[cpFe(CO)_2]^-$	no reaction	–	[21]	–	–
$C_6F_5CF_3$	$[cpFe(CO)_2]^-$	$CF_3C_6F_4Fe(CO)_2cp$	119–120	[20]	[20]	[20]
$C_6F_5CH{=}CH_2$	$[cpFe(CO)_2]^-$	$CH_2{=}CHC_6F_4Fe(CO)_2cp$	115–117	[22]	–	–
$C_6F_5C{\equiv}CH$	$[cpFe(CO)_2]^-$	$HC_6F_4CH{=}CHFe(CO)_2cp$	59–61	[17]	[17]	[17]
	$[Mn(CO)_5]^-$	$C_6F_5CH{=}CHMn(CO)_5$	–	[17]	–	–
	$[Mn(CO)_4P(C_6H_5)_3]^-$	$C_6F_5CH{=}CHMn(CO)_4P(C_6H_5)_3$	–	[17]	–	–
	$[Re(CO)_5]^-$	$HC{\equiv}CC_6F_4Re(CO)_5$	120	[17]	[17]	[17]
$C_6F_5CH_2Br$	$[cpFe(CO)_2]^-$	$C_6F_5CH_2Fe(CO)_2cp$	70–72 (decomp.)	[26]	[26]	[26]
		$cp(CO)_2FeC_6F_4CH_2Fe(CO)_2cp$	195–197 (decomp.)	[26]	[26]	[26]
$C_6F_5SCH_3$	$[cpFe(CO)_2]^-$	$CH_3SC_6F_4Fe(CO)_2cp$	130	[38]	[38]	[38]
	$[Re(CO)_5]^-$	$CH_3SC_6F_4Re(CO)_5$	155	[38]	[38]	[38]
$C_6F_5SC_6H_5$	$[cpFe(CO)_2]^-$	$C_6H_5SC_6F_4Fe(CO)_2cp$	125	[38]	[38]	[38]
1,2-$C_6F_4H_2$	$[cpFe(CO)_2]^-$	1,2-$H_2C_6F_3$-4-$Fe(CO)_2cp$	73–75	[20]	[20]	[20]
1,3-$C_6F_4H_2$	$[cpFe(CO)_2]^-$	1,3-$H_2C_6F_3$-4-$Fe(CO)_2cp$	121–122	[21]	[21]	[23]
1,4-$C_6F_4H_2$	$[cpFe(CO)_2]^-$	1,4-$H_2C_6F_3$-2-$Fe(CO)_2cp$	90–91	[21]	[21]	[23]
1,2-$C_6F_4(CN)_2$	$[cpFe(CO)_2]^-$	1,2-$(CN)_2C_6F_3$-4-$Fe(CO)_2cp$	180–181 (decomp.)	[21]	[21]	[23]
	$[cpRu(CO)_2]^-$	1,2-$(CN)_2C_6F_3$-4-$Ru(CO)_2cp$	155–157 (decomp.)	[22a]	[22a]	[22a]
	$[Mn(CO)_5]^-$	1,2-$(CN)_2C_6F_3$-4-$Mn(CO)_5$	156 (decomp.)	[21]	[21]	[23]
	$[Re(CO)_5]^-$	1,2-$(CN)_2C_6F_3$-4-$Re(CO)_5$	205–207 (decomp.)	[21]	[21]	[23]
1,2-$C_6F_4(CO_2C_2H_5)_2$	$[cpFe(CO)_2]^-$	1,2-$(CO_2C_2H_5)_2C_6F_3$-4-$Fe(CO)_2cp$	115–116	[21]	[21]	[23]
1,2-$C_6F_4I_2$	$[cpFe(CO)_2]^-$	1,2-$H_2C_6F_3$-4-$Fe(CO)_2cp$ + 1-HC_6F_4-2-$Fe(CO)_2cp$ + 1-IC_6F_4-2-$Fe(CO)_2cp$	–	[21]	–	[21]

[a] cp = π-C_5H_5.

$C_6F_5CH_2Fe(CO)_2(\pi\text{-}C_5H_5)$, small amounts of $(\pi\text{-}C_5H_5)Fe(CO)_2C_6F_4CH_2Fe(CO)_2(\pi\text{-}C_5H_5)$ [26]; this compound contains carbonylmetal groups attached both to the ring and to the side chain, and is stable enough to be sublimed at 200 °C/0.1 torr. This is in contrast to the mononuclear complex, which readily decomposes into decafluorobibenzyl [26].

6. Heterocyclic Fluorocarbon Compounds

The nitrogen heterocyclic compounds perfluoropyridine, perfluoropyridazine, and cyanuric trifluoride are much more susceptible to nucleophilic attack than is hexafluorobenzene; even the relatively unreactive anion $[\pi\text{-}C_5H_5Mo(CO)_3]^-$ has given stable complexes with the two last mentioned compounds [27,28]. Thus perfluoropyridine and $[Mn(CO)_5]^-$ afford *p*-$NC_5F_4Mn(CO)_5$, whereas hexafluorobenzene does not react with this anion [20]. Interestingly, although cyanuric trifluoride appears to be more susceptible to attack by the weaker nucleophilic anions $[Mn(CO)_5]^-$ and $[\pi\text{-}C_5H_5Mo(CO)_3]^-$ than any other fluorocarbon compound so far studied, the strong nucleophile $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ and cyanuric trifluoride afford $\pi\text{-}C_5H_5Fe(CO)_2C_3F_2N_3$ in only very low yield [28]. The

[26] *M. I. Bruce*, J. organometallic Chem. *10*, 495 (1967).

[27] *J. Cooke*, *M. Green*, and *F. G. A. Stone*, Inorg. nuclear Chem. Letters *3*, 47 (1967).

[28] *J. Cooke*, *M. Green*, and *F. G. A. Stone*, J. chem. Soc. (London) A *1968*, 173.

Table 4. Reactions of polyfluoroheterocyclic compounds with carbonylmetal anions [a].

Fluorocarbon	Anion	Product	M.p. (°C)	References		
				Reaction	IR	NMR
Perfluoropyridine	$[cpFe(CO)_2]^-$	$NC_5F_4Fe(CO)_2cp$	209	[28]	[28]	
	$[Mn(CO)_5]^-$	$NC_5F_4Mn(CO)_5$	96—97	[28]	[28, 37]	[37]
			94 (decomp.)	[37]		
	$[Mn(CO)_4P(C_6H_5)_3]^-$	*tert*-$NC_5F_4Mn(CO)_4P(C_6H_5)_3$	166	[28]	[28]	—
	$[Re(CO)_5]^-$	$NC_5F_4Re(CO)_5$	123.5	[28]	[28, 37]	[37]
			117—118	[37]	—	—
Perfluoropyridazine	$[cpFe(CO)_2]^-$	1,2-$N_2C_4F_3$-4-$Fe(CO)_2cp$	147	[28]	[28]	[28]
	$[Mn(CO)_5]^-$	1,2-$N_2C_4F_3$-4-$Mn(CO)_5$	121 (decomp.)	[28]	[28]	[28]
	$[Mn(CO)_4P(C_6H_5)_3]^-$	*tert*-1,2-$N_2C_4F_3$-4-$Mn(CO)_4P(C_6H_5)_3$	120 (decomp.)	[28]	[28]	[28]
	$[Re(CO)_5]^-$	1,2-$N_2C_4F_3$-4-$Re(CO)_5$	144	[28]	[28]	[28]
	$[cpMo(CO)_3]^-$	1,2-$N_2C_4F_3$-4-$Mo(CO)_3cp$	181	[28]	[28]	[28]
Cyanuric fluoride	$[cpFe(CO)_2]^-$	$N_3C_3F_2Fe(CO)_2cp$	not isolated	[28]	—	—
	$[Mn(CO)_5]^-$	$N_3C_3F_2Mn(CO)_5$	85	[28]	[28]	[28]
	$[Mn(CO)_4P(C_6H_5)_3]^-$	*tert*-$N_3C_3F_2Mn(CO)_4P(C_6H_5)_3$	149 (decomp.)	[28]	[28]	—
	$[Re(CO)_5]^-$	$N_3C_3F_2Re(CO)_5$	121	[28]	[28]	[28]
	$[cpMo(CO)_3]^-$	$N_3C_3F_2Mo(CO)_3cp$	110	[28]	[28]	[28]

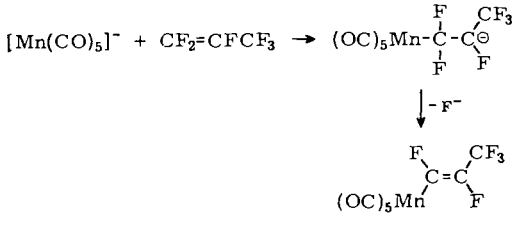
[a] cp = π-C_5H_5.

iron anion apparently brings about breakdown of the heterocyclic ring, or engages in other side reactions. The products from the reactions between the three perfluoroaromatic nitrogen heterocycles and the anion $[Mn(CO)_4P(C_6H_5)_3]^-$ are all complexes in which the triphenylphosphine group is *trans* to the C_5F_4N, $C_4F_3N_2$, and $C_3F_2N_3$ groups, respectively.

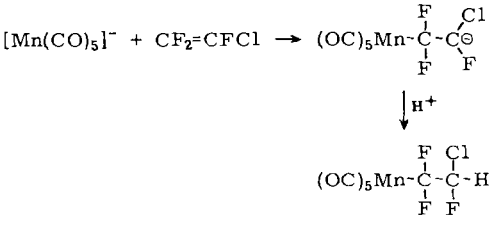
7. Mechanisms of the Reactions

Chambers and *Mobbs* [3] have summarized the three different possible fates of the intermediate carbanion formed by attack of a nucleophile on a fluoroolefin. In the context of this review the different processes can be summarized as follows, considering the anion $[Mn(CO)_5]^-$ as the nucleophile.

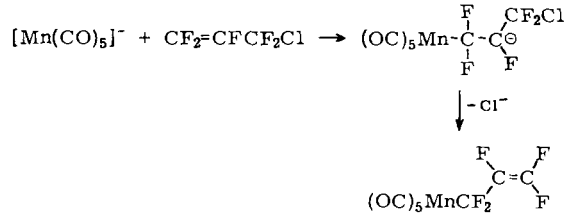
a) Loss of fluoride ion [8]:



b) Addition of a proton [10]:

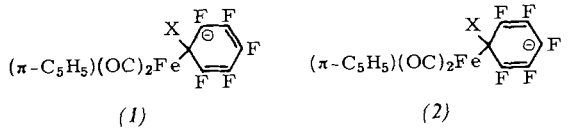


c) Displacement of halogen ions with formation of an allyl compound [5, 6, 13]:



As mentioned previously, pentacarbonylperfluoroallylmanganese rearranges to *trans*-pentacarbonylperfluoropropenylmanganese, and the σ-bonded perfluoroallyl complex is not isolated, although there seems to be some evidence [6] for its existence as an unstable intermediate. However, since NMR spectroscopy has revealed that the product from the reaction between $[\pi\text{-}C_5H_5NiCO]^-$ and perfluoroallyl chloride is a mixture of *trans*-$CF_3CF{=}CFNi(CO)(\pi\text{-}C_5H_5)$ and $CF_2{=}CFCF_2Ni(CO)(\pi\text{-}C_5H_5)$ [14], there seems little doubt that the perfluoropropenyl complexes are formed *via* the perfluoroallyl compounds. Migration of double bonds in the fluorocarbon derivatives of the transition metals is not uncommon. Addition of $HRe(CO)_5$ to perfluorobutadiene affords the complex $HCF_2CF_2CF{=}CFRe(CO)_5$, which is probably formed from $HCF_2CF{=}CFCF_2Re(CO)_5$ by a similar fluorine shift [29].

The products formed in reactions between $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ and C_6F_5X (X = F, Cl, Br, or I) can be rationalized in terms of the intermediates *(1)* or *(2)*.



(1) *(2)*

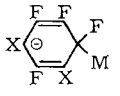
Elimination of X^- would give $C_6F_5Fe(CO)_2(\pi\text{-}C_5H_5)$, the major product [21]. The intermediates could also decompose forming π-$C_5H_5Fe(CO)_2X$ and a species which by abstraction of a proton from the solvent would yield C_6F_5H. On reaction with additional an-

[29] *B. Tattershall, A. J. Rest, M. Green,* and *F. G. A. Stone,* J. chem. Soc. (London) A *1968*, 899.

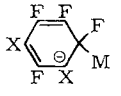
ion, C_6F_5H would give the secondary product p-$HC_6F_4Fe(CO)_2(\pi\text{-}C_5H_5)$. Some support for the suggested mechanism comes from the isolation of π-$C_5H_5Fe(CO)_2I$ when pentafluoroiodobenzene is treated with $[\pi\text{-}C_5H_5Fe(CO)_2]^-$.

The reactivity and the products produced from reactions between carbonylmetal anions and polyfluoroaromatic compounds with substituents such as H, CN, or $CO_2C_2H_5$ on the benzene ring can be understood as proceeding *via* S_N2-type intermediates *(3)–(5)*, with the negative charge centered on a carbon atom having a substituent other than fluorine [30].

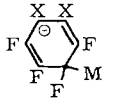
(3)



(4a)



(4b)



(5)

In the case of *monosubstituted* polyfluorobenzenes, *e.g.* C_6F_5H, in addition to *(3)* one can consider an intermediate in which the metal attacks the carbon *ortho* to the substituent (H). However, this intermediate will be less stable than *(3)*, and in accord with this no complexes have as yet been isolated in which the metal atom and the original substituent are *ortho* to each other. Following loss of fluoride, the final product from either *(3)*, *(4)*, or *(5)* is a complex in which a metal atom is substituted *para* to a substituent X. *para*-Disubstituted polyfluoroaromatic compounds, *e.g.* 1,4-$H_2C_6F_4$, react much more slowly with $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ than either the 1,2- or 1,3-isomers. This is as expected, since substitution of the metal group cannot give a derivative in which this group is *para* to a substituent other than fluorine. Moreover, the product is much less stable than those formed by the other two tetrafluorobenzenes, and decomposes even in the solid state. This may be because the hydrogen atom is located at a β position relative to the metal atom, a situation which is known to lead to decomposition by migration of the hydrogen to the metal to form an unstable metal hydride, *e.g.* π-$C_5H_5Fe(CO)_2H$.

It has previously been reported [31] that the only products isolated from the reaction of tropylium bromide with $[Mn(CO)_5]^-$ were bicycloheptatrienyl and $Mn_2(CO)_{10}$. Similarly, reaction of $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ with decafluorobenzhydryl bromide, $(C_6F_5)_2CHBr$, gave moderate yields of $[(C_6F_5)_2CH]_2$ [25]. It appears that if the radical R′ from RX is relatively stable, then only R_2 will be isolated from the reaction of RX with a carbonylmetalate ion. If the radical cannot be stabilized, then an R-metal bond will be formed. In the case cited, stabilization of $(C_6F_5)_2CH$ is enhanced by the presence of fluorine atoms. Even the pentafluorobenzyl radical seems to be stabilized in this way to a certain extent, some $[C_6F_5CH_2]_2$ being isolated from the reaction of $C_6F_5CH_2Br$ with $[\pi\text{-}C_5H_5Fe(CO)_2]^-$, as well as the expected $C_6F_5CH_2Fe(CO)(\pi\text{-}C_5H_5)$. This latter complex is unstable, and in solution decomposes with the formation of decafluorobibenzyl [26].

8. Properties of the Complexes

The known complexes of carbonylmetalate ions with fluorocarbons are listed in Tables 1–4. They contain carbon-metal σ bonds stabilized by the presence of fluorine atoms attached to the carbon atom or adjacent to it [25, 32, 33]. The compounds can usually be sublimed under vacuum, and some are volatile at room temperature and pressure. They are more or less air-stable in the crystalline state, but in solution they are often easily oxidized. The complexes are soluble in non-polar solvents but are generally insoluble in water; most can be recrystallized from petroleum ether, and some may be crystallized from aqueous ethanol.

Few chemical reactions have been reported; methoxide ion does not appear to further substitute the fluorocarbon group in pentacarbonylperfluorophenylrhenium, and the resistance of the platinum compounds to nucleophilic attack has already been mentioned. It has also been reported recently that SO_2 does not insert into the carbon-metal bond in π-$C_5H_5Fe(CO)_2C_6F_5$ [34]; however, it is possible to make the compound π-$C_5H_5Fe(CO)_2SO_2C_6F_5$ by the conventional method, *i.e.* by reaction of $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ with $C_6F_5SO_2Cl$ [22].

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German version: Angew. Chem. *80*, 835 (1968)

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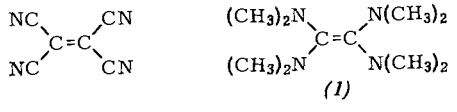
Reactions of Electron-Rich Olefins

BY R. W. HOFFMANN [*]

Olefins are normally preferentially attacked by electrophiles. This trend is strengthened in enol ethers and enamines, and is particularly pronounced in tetramethoxyethylene and in tetraaminoethylenes. These electron-rich olefins are accordingly also excellent reducing agents. In their reactivity, therefore, they behave as counterparts of tetracyanoethylene. This compound shares with the electron-rich olefins a strong tendency to undergo cycloadditions, the electron-rich olefins adding particularly readily to electrophiles.

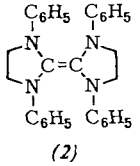
1. Introduction

The reactivity of the olefinic double bond can be strongly influenced by substituents. For example, the four electron-attracting cyano groups in tetracyanoethylene withdraw electrons so effectively from the central double bond that this compound is strongly electrophilic [1]. The opposite situation is found in the "electron-rich olefins" [2], in which four electron-donating substituents are attached to the carbons of



(1)

the central double bond; examples of such compounds are tetraaminoethylenes, particularly tetrakis(dimethylamino)ethylene *(1)* [3] and 1,1′,3,3′-tetraphenyl-2,2′-biimidazolidinylidene *(2)* [4].



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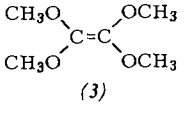
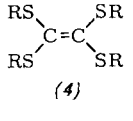
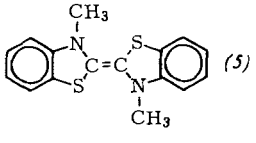


(3)



(4)

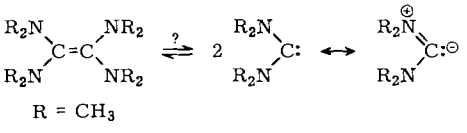


(5)

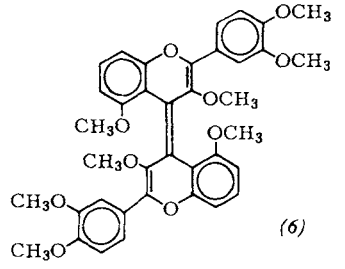
Tetramethoxyethylene *(3)*, in which the double bond is fourfold substituted with oxygen, behaves somewhat differently. Only a few of the corresponding tetraalkylthioethylenes *(4)* have been investigated.

Finally, the chemical behavior of 3,3′-dimethyl-2,2′-bibenzothiazolinylidene *(5)* (configuration not established) indicates that this compound should also be included in the class of electron-rich olefins.

In contrast to tetracyanoethylene, all these compounds should be good reducing agents, and should accordingly be readily attacked by electrophilic reagents. Nevertheless, the chemistry of electron-rich olefins is interesting not merely because it contrasts with that of tetracyanoethylene, but to a large degree because of the idea that with sufficiently strong donation of electrons by the substituents, these olefins should dissociate into two nucleophilic carbenes [4]. A dissociation energy of 40 kcal has been estimated for *(1)* [3] (cf. the estimated value of 70 kcal for tetrafluoroethylene [5]).



R = CH_3



(6)

Though compounds of the type *(2)* and *(6)* give lower results in molecular weight determinations than the calculated values [6–8], dissociation into carbenes has been ruled out in the cases of *(1)* and *(2)* by crossover experiments at 140–175 °C [9, 10]. However, slight exchange between the "carbene halves" of *(2)* and those of the corresponding *p*-tolyl derivative occurs at 225 °C [11].

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[1] *T. L. Cairns* and *B. C. McKusick*, Angew. Chem. *73*, 520 (1961); *D. N. Dhar*, Chem. Reviews *67*, 611 (1967).

[2] The designation "electron-rich olefins" is not quite accurate. These compounds should strictly speaking be described as olefins whose π-electron density on the carbon is distinctly greater than 1.0. (For example, a value of 1.16 has been calculated for *(1)* [3].)

[3] *N. Wiberg*, Angew. Chem. *80*, 809 (1968); Angew. Chem. internat. Edit. *7*, 10 (1968).

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[8] *E. Bayer* and *B. Krämer*, Chem. Ber. *97*, 1057 (1964).

[9] *D. M. Lemal*, *R. A. Lovald*, and *K. I. Kawano*, J. Amer. chem. Soc. *86*, 2518 (1964).

[10] *H. E. Winberg*, *J. E. Carnahan*, *D. D. Coffman*, and *M. Brown*, J. Amer. chem. Soc. *87*, 2055 (1965).

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The positive results obtained in preliminary crossover experiments with *(5)* at 80 °C[12] are not sufficiently unambiguous to constitute proof of the dissociations of *(5)*. Similarly, the occurrence of the ion M/2 in the mass spectra of some electron-rich olefins[12–14] does not, without additional data, provide sufficient grounds for concluding that these compounds undergo thermal dissociation.

2. The Redox Behavior of Electron-Rich Olefins

Owing to the increased charge density on the carbon, the electron-rich olefins should be oxidized much more readily than ordinary olefins. The formation of charge transfer complexes corresponds to partial oxidation, the strength of the π acid that is just still capable of complex formation constituting a measure of the ability of the π base to donate electrons[15].

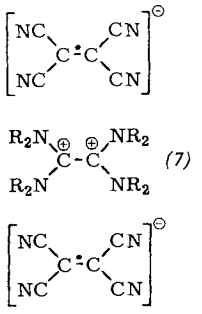
2.1. Charge Transfer Complexes

Tetramethoxyethylene *(3)* forms π complexes with weak π acids, *e.g.* fumaronitrile, in solution, as is shown by the characteristic color that develops. *(3)* gave a crystalline 1:1 complex with 1,3,5-trinitrobenzene[17,18].

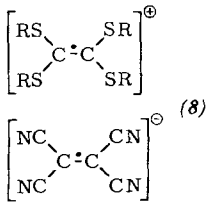
Table 1. π-Complexes of tetramethoxyethylene *(3)* in solution [16, 17].

π-acid	Color
NC–CH=CH–CN	ocher
$NC(CF_3)C=C(CF_3)CN$	violet blue
2,4,7-Trinitro-9-fluorenone	wine red

The tetraaminoethylenes[10] are much stronger π bases, and form π complexes with many π acids having widely different structures[7,10,19,20,20a], the compositions of these complexes varying from 1:1 to 1:3, some of them forming isolable crystals. The complexes exhibit high electric conductivity in the solid state, and some of them are paramagnetic[20], suggesting that electron transfer from the donor to the acceptor is possible even in the ground state. Complete transfer of two electrons is found in the stable 1:2 complexes of *(1)*[21] and *(2)*[22] with tetracyanoethylene, which



(7)

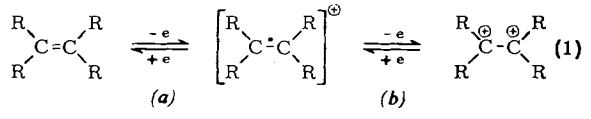


(8)

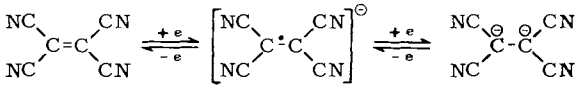
have the structure *(7)*. The reaction of *(4)* with tetracyanoethylene, on the other hand, apparently results in the transfer of only one electron to form *(8)*[23], so that the complex consists of a radical-cation and a radical-anion.

2.2. Stepwise Oxidation

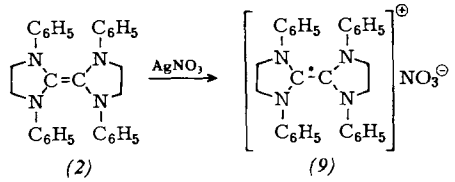
The results described above show that an electron-rich olefin can be oxidized both to a radical-cation and to a dication. This two-step[24] oxidation corresponds to the reduction of tetracyanoethylene, which also proceeds in two steps[25]; like the latter, therefore, it should in principle be reversible[24].



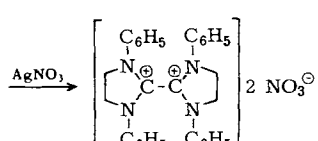
(a) *(b)* (1)



The first observed two-step oxidation of an electron-rich olefin was that of *(2)*[9,26], which is oxidized by one equivalent of silver nitrate to the radical-cation *(9)*, and by two equivalents to the dication *(10)*. The reversibility of the two steps is shown by the fact that *(9)* can also be obtained by combining solutions of *(2)* and *(10)*, *i.e.* by coproportionation. *(10)* with $I^{\ominus}$



(2) *(9)*



(10)

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[22] *H. W. Wanzlick*, personal communication to Prof. *D. M. Lemal*.

[23] *D. Seebach*, personal communication.

[24] *L. Michaelis*, Chem. Reviews *16*, 243 (1935); *S. Hünig*, Liebigs Ann. Chem. *676*, 32 (1964).

[25] *O. W. Webster, W. Mahler*, and *R. E. Benson*, J. Amer. chem. Soc. *84*, 3678 (1962).

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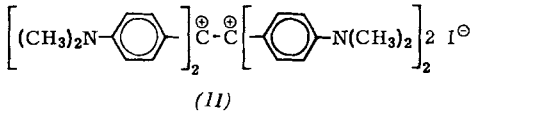
instead of $NO_3^{\ominus}$ can accordingly be reduced to *(2)* by metallic silver, since the resulting silver ions are precipitated as silver iodide [26].

Tetraaminoethylene *(1)* undergoes reversible electrochemical oxidation to the stable radical-cation at only −0.75 V (against the standard calomel electrode) and to the dication at −0.61 V [27]. Thus *(1)* corresponds in its redox behavior to a divalent base metal such as zinc, by which the dication of *(1)* can also be reduced [21,28]. *(1)* can therefore be used in batteries in place of the baser metal [29].

This oxidation potential of *(1)*, being very negative, is in agreement with calculations [3] according to which *(1)* possesses two electrons in an antibonding orbital (−0.19 β). The level of this highest occupied orbital is lowered by phenyl substituents on the nitrogen. Consequently *(2)* is no longer such a strong reducing agent as *(1)*, while *(11)* exists in equilibrium with *(12)* in apolar media [30]. *(12a)*, on the other hand, should be a much stronger reducing agent than *(1)* [30a].



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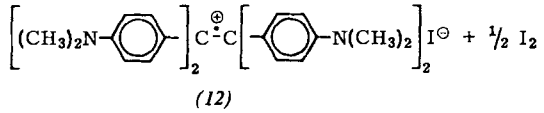
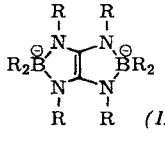


(12)



(12a) R = C_2H_5

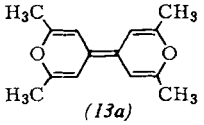
The question of whether the radical-cation reaches such an equilibrium concentration as to be detectable in the oxidation of an electron-rich olefin depends on the difference in the redox potentials of steps (a) and (b) in eq. (1). The equilibrium between the different oxidation states can be expressed by the semiquinone formation constant K [24].

K = [radical-cation]^2/[olefin] [dication]

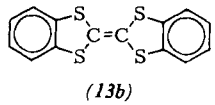
The greater the value of K, the higher is the equilibrium concentration of radical-cation. Some values of K are given in Table 2.

Table 2. Semiquinone formation constants for the two-step oxidation of electron-rich olefins.

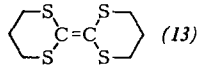
(2)	25 [31]
(1)	230 [27]
(5)	1000 [32]
(13a)	6×10^4 [32]
(13b)	10^8 [32]



(13a)



(13b)

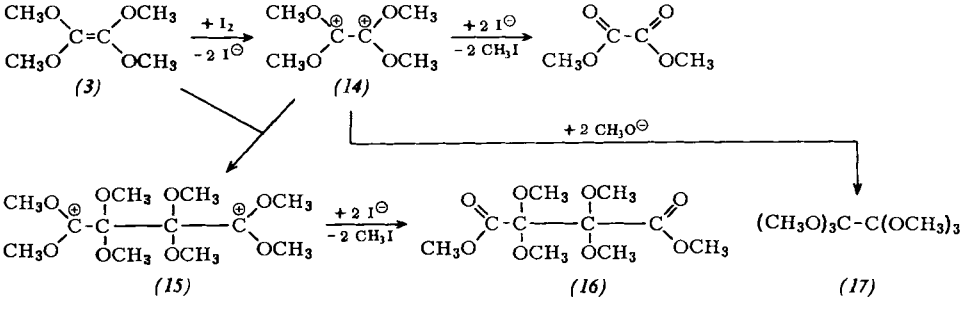


(13)

Whereas the two oxidation stages are quite distinct in the polarographic oxidation of *(13)* [32], they can no longer be separated in the oxidation of tetramethoxyethylene *(3)* [33] or of 1,1,4,4-tetrakis(dimethylamino)buta-1,3-diene [33a], *i.e.* the semiquinone formation constants for these compounds are probably lower than 100 [34].

2.3. Formation and Reaction of Dications

As expected, tetramethoxyethylene *(3)* is oxidized by iodine to the dication *(14)* [35], which, as an ambident cation [36], is demethylated in 61 % yield by the iodide formed to give dimethyl oxalate. However, *(14)* also attacks the tetramethoxyethylene *(3)* present to give 10 % of dimethyl tetramethoxysuccinate *(16)* *via* the octamethoxybutane dication *(15)* [37]. If, for example, by addition of silver tetrafluoroborate, the absence of nucleophiles is ensured during the oxidation of *(3)* with iodine, *(14)* can no longer be demethylated. The reaction then leads mainly to *(15)*, from which *(16)* is



(3) *(14)* *(15)* *(16)* *(17)*

[27] *K. Kuwata* and *D. H. Geske*, J. Amer. chem. Soc. *86*, 2101 (1964).

[28] The reduction can also be carried out with $Na_2Fe(CO)_4$ [3].

[29] *W. R. Wolfe jr.*, US-Pat. 3156587 (Nov. 10, 1964), Du Pont; Chem. Abstr. *62*, 4913 (1965).

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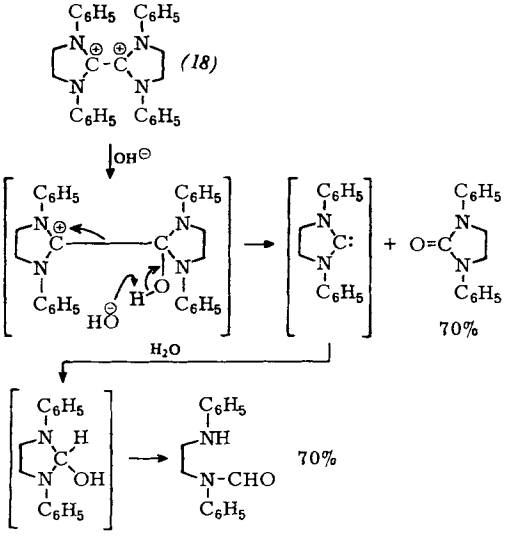
[35] *R. W. Hoffmann* and *J. Schneider*, Chem. Ber. *100*, 3689 (1967).

[36] *S. Hünig*, Angew. Chem. *76*, 400 (1964); Angew. Chem. internat. Edit. *3*, 548 (1964).

[37] Cf. the similar process in the autoxidation of *(1)*: *A. N. Fletcher* and *C. A. Heller*, J. physic. Chem. *71*, 1507 (1967).

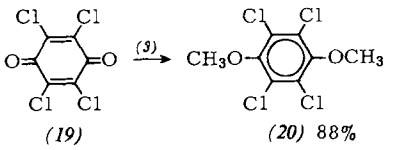
formed during workup. The assumption that *(14)* is formed on oxidation of *(3)* with iodine is finally supported by the fact that *(14)* can be intercepted with sodium methoxide to give hexamethoxyethane *(17)* in 73 % yield [35].

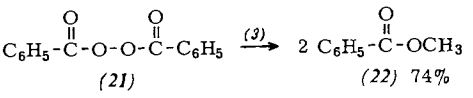
The dication *(14)* formed on oxidation of tetramethoxyethylene is so reactive [38] that its existence is only concluded from indirect evidence. On the other hand, the dications formed on oxidation of *(1)* [10,21,40], *(2)* [26,41], and *(5)* [42] with iodine or bromine can be isolated as salts. These dications are no longer dealkylated by nucleophiles; bases add instead to the positively charged C atom. Thus the addition of 2 molecules of sodium methoxide to the dication of *(5)* [42] corresponds to the addition of sodium methoxide to *(14)*. If the added base still contains mobile protons, the adduct is cleaved after only one molecule of base has been added to the dication *(18)* [26,41]. In certain circumstances the base may abstract a proton from a position α to the nitrogen [43]. (For detailed discussion see [3].)



2.4. Electron-Rich Olefins as Reducing Agents

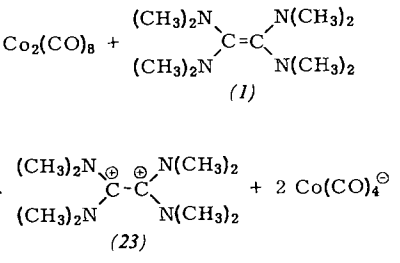
Because of their low redox potential, the electron-rich olefins can be used as strong reducing agents that are soluble in organic solvents. When used in this capacity the olefins are generally oxidized to the dications. The dication *(14)* formed in reductions with tetramethoxyethylene *(3)* is in turn a strong methylating agent [44]. Thus *(19)* and *(21)* are converted directly into *(20)* and *(22)* respectively by reductive methylation with *(3)* [35].





Sulfonyl and nitro groups are also reduced by *(3)* in a complex reaction [35]. Nitro groups, like HNO_2 [45], azidinium salts [46], and diazonium groups [46], are also reduced by *(5)*. *(2)* reduces *e.g.* peroxides, thionyl chloride, and sulfuryl chloride [41].

All electron-rich olefins are oxidized by $Ag^{\oplus}$ [9,26,35,42] and by other heavy metal ions [21,35]. *(1)* is so reactive that, like the alkali metals, it reduces complexes of zero-valent transition metals [47]. As expected, *(1)*



readily reduces a number of compounds that contain positively polarized NO_2 groups [48], but it is interesting to note that considerable quantities of *(23)* are formed in the reaction of *(1)* with various Lewis acids [21,49,50].

The reductive cleavage of carbon-halogen bonds by tetraaminoethylenes [51–54] is of great preparative value. The ease with which the halogen is released increases from fluorine to iodine. The reactivity of the substrates also increases in the order $R_3CX < R_2CX_2 < RCX_3 < CX_4$. Since secondary products of $Cl_3C^{\ominus}$ *(24)*, but not of $Cl_3C\cdot$, can be detected in the reduction of $BrCCl_3$, the reaction must proceed by an ionic mechanism.

$$(1) + BrCCl_3 \rightarrow (23) + Br^{\ominus} + [Cl_3C^{\oplus}] \quad (24)$$

(1) can be used for selective reductive dehalogenation, particularly of perhalogenated hydrocarbons [*e.g.* *(25)*]. One advantage of these substrates is that no competing dehydrohalogenation [53] is possible.

$$CF_3{-}CCl_2{-}CCl_2{-}CF_3 \xrightarrow{(1)} CF_3{-}CCl{=}CCl{-}CF_3 \quad (97\,\%)$$
(25)

[38] The products of the oxidation of tetraphenoxyethylene with bromine [39] have not yet been studied in detail.

[39] *H. Scheibler* and *M. Depner*, Ber. dtsch. chem. Ges. *68*, 2151 (1935).

[40] *R. L. Pruett, J. T. Barr, K. E. Rapp, C. T. Bahner, D. H. Gibson*, and *R. H. Lafferty jr.*, J. Amer. chem. Soc. *72*, 3646 (1950).

[41] *H. W. Wanzlick, B. Lachmann*, and *E. Schikora*, Chem. Ber. *98*, 3170 (1965).

[42] *J. Metzger, H. Larivé, R. Dennilauler, R. Baraqe*, and *C. Gaurat*, Bull. Soc. chim. France *1964*, 2857.

[43] *W. H. Urry* and *J. Sheeto*, Photochem. and Photobiol. *4*, 1067 (1965).

[44] Cf. *S. Kabuss*, Angew. Chem. *78*, 714 (1966); Angew. Chem. internat. Edit. *5*, 675 (1966).

[45] *W. Friedrich, H. Kehr, F. Kröhnke*, and *P. Schiller*, Chem. Ber. *98*, 3808 (1965).

[46] *H. Quast* and *S. Hünig*, Chem. Ber. *99*, 2017 (1966).

[47] *R. B. King*, Inorg. Chem. *4*, 1518 (1965).

[48] *W. E. Thun*, J. org. Chemistry *32*, 503 (1967).

[49] *N. Wiberg* and *J. W. Buchler*, Chem. Ber. *96*, 3000 (1963).

[50] *N. Wiberg* and *J. W. Buchler*, Z. Naturforsch. *19b*, 9 (1964).

[51] *H. W. Wanzlick* and *F. Esser*, Angew. Chem. *76*, 614 (1964).

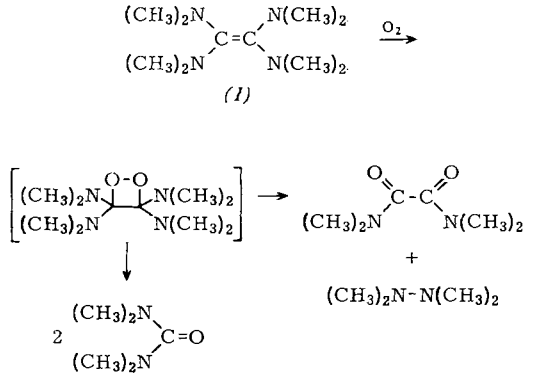
[52] *H.-K. Chiang, C.-I. Chang*, and *Y. Shih*, Acta chim. sinica *31*, 42 (1965); Chem. Abstr. *63*, 6993 (1965).

[53] *W. Carpenter*, J. org. Chemistry *30*, 3082 (1965).

[54] *W. Carpenter, A. Haymaker*, and *D. W. Moore*, J. org. Chemistry *31*, 789 (1966).

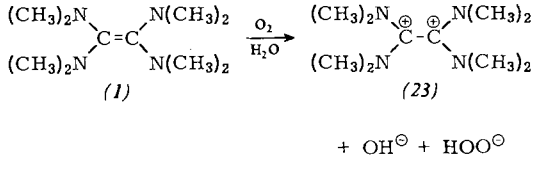
2.5. Autoxidation of Electron-Rich Olefins

All electron-rich olefins are easily autoxidized. The autoxidation of tetrakis(dimethylamino)ethylene *(1)* is particularly spectacular, since it is accompanied by an intense green chemiluminescence [40, 55]. The products formed in organic solvents are 45–65 % of tetramethylurea, 20–30 % of *N,N,N',N'*-tetramethyloxamide, and small quantities of tetramethylhydrazine and bis(dimethylamino)methane [10, 43]. The scheme [43, 55] presents only a greatly simplified picture



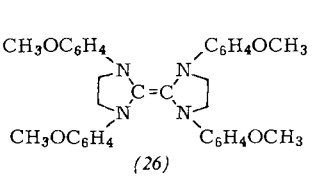
of the reaction. The various steps of the chemical process [43, 55–57] and of the steps connected with the emission of light [58–61] have now been extensively studied. (For detailed discussion see [3]).

The autoxidation of *(1)* in aqueous medium stops at the stage of the tetrakis(dimethylamino)ethylene dication *(23)*, and derivatives of the latter are obtained as the products [43, 57].

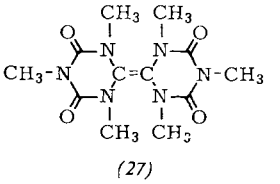


The autoxidation of *(2)* in glacial acetic acid leads to the dication *(18)* [43], whereas the reaction proceeds further in aprotic solvents to give 1,3-diphenyl-2-imidazolidinone (90 %) [6].

The autoxidation rate of a tetraaminoethylene is strongly dependent on the availability of electrons, and hence on the substituents on the nitrogen [7, 62, 63]. Thus *(26)* is autoxidized much more rapidly, and *(27)* much more slowly, than *e.g. (2)*.

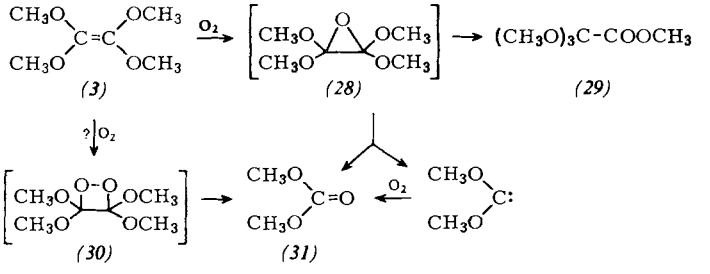


(26)



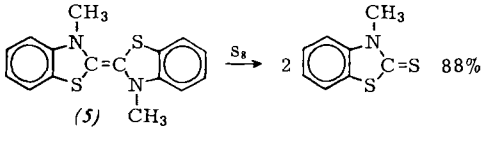
(27)

The autoxidation of tetramethoxyethylene *(3)* differs considerably from that of the tetraminoethylenes. In this case *(29)* and *(31)* are formed in yields of 51 and 39 % respectively [64].



If one compares this reaction with the autoxidation of tetrahalogenoolefins [65], which leads *via* an epoxide [66] to trihalogenoacetyl halides [67], the formation of *(29)* on autoxidation of *(3)* seems plausible if the epoxide *(28)* is assumed to occur as an itnermediate. *(31)* is probably also formed partly *via (28)*, since the reaction of *(3)* with tetracyanoethylene oxide, which can transfer only one oxygen atom onto *(3)*, yields both *(31)* and *(29)* [64]. It is not yet known whether the formation of *(31)* also involves *(30)* or polymeric peroxides.

The ozonization of *(3)* also leads to *(31)* and *(29)* [64]. The action of H_2O_2 on *(5)* [42, 68] and the reaction of *(29)* with performic acid [69] also lead to oxidative cleavage of the central double bond.



The reaction of tetramethoxyethylene with sulfur yields the *S* analogs of *(31)* and *(29)* [64]. The tetraaminoethylenes [10, 70] and *(5)* [14, 42] readily undergo oxidative cleavage by sulfur; this reaction does not, however, take place *e.g.* with tetraphenylethylene [71]. However, the autoxidation of *(5)* is a complex reaction leading to numerous products [14, 72].

[55] *N. Wiberg* and *J. W. Buchler*, Z. Naturforsch. *19b*, 5 (1964).

[56] *C. A. Heller* and *A. N. Fletcher*, J. physic. Chem. *69*, 3313 (1965).

[57] *A. N. Fletcher* and *C. A. Heller*, J. Catalysis *6*, 263 (1966).

[58] *H. E. Winberg*, *J. R. Downing*, and *D. D. Coffman*, J. Amer. chem. Soc. *87*, 2054 (1965).

[59] *A. N. Fletcher* and *C. A. Heller*, J. physic. Chem. *71*, 1507 (1967).

[60] *A. N. Fletcher* and *C. A. Heller*, Photochem. and Photobiol. *4*, 1051 (1965).

[61] *J. P. Paris*, Photochem. and Photobiol. *4*, 1059 (1965).

[62] *H. W. Wanzlick*, *F. Esser*, and *H. J. Kleiner*, Chem. Ber. *96*, 1208 (1963).

[63] *A. Piskala* and *J. Gut*, Collect. czechoslov. chem. Commun. *29*, 2794 (1964).

[64] *R. W. Hoffmann* and *J. Schneider*, Chem. Ber. *100*, 3698 (1967).

[65] *H. Cohn* and *E. D. Bergmann*, Israel J. Chem. *2*, 355 (1964).

[66] *W. Müller* and *E. Walaschewsky*, German Pat. 947364 (Aug. 16, 1956), Farbenfabriken Bayer, Chem. Abstr. *53*, 4299 (1959).

[67] *D. M. Frankel*, *C. E. Johnson*, and *H. M. Pitt*, J. org. Chemistry *22*, 1119 (1957).

[68] *W. H. Mills*, *L. M. Clark*, and *J. A. Aeschlimann*, J. chem. Soc. (London) *123*, 2353 (1923).

[69] *A. Piskala*, Tetrahedron Letters *1964*, 2587.

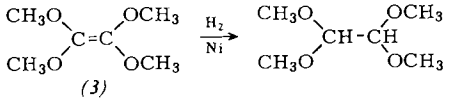
[70] *H. W. Wanzlick* and *B. König*, Chem. Ber. *97*, 3513 (1964).

[71] *A. Schönberg* and *W. Asker*, J. chem. Soc. (London) *1942*, 272.

[72] *J. J. Vorsanger*, Bull. Soc. chim. France *1964*, 119.

2.6. Reduction of Electron-Rich Olefins

Practically no experiments on the reduction of electron-rich olefins have been reported. *(1)* is not reduced *e.g.* by lithium diethylamine[21]. *(3)*, on the other hand, readily undergoes catalytic hydrogenation to give symmetric tetramethoxyethane[73].



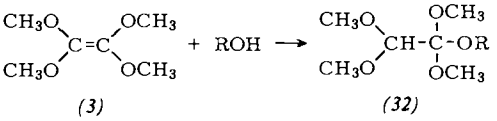
(3)

3. Reactions of Electron-Rich Olefins with Electrophiles

3.1. Reactions in which the Molecular Skeleton remains Intact

Simple olefins are preferentially attacked by electrophilic reagents. Electron-rich olefins should therefore react particularly readily with electrophiles. The reaction with Brönsted acids may be taken as a model, since this reaction involves the simplest of all electrophiles, the proton.

Benzoic acid adds readily to tetramethoxyethylene *(3)* to form *(32a)*. This adduct is an α-alkoxyalkyl ester, and so readily undergoes thermal cleavage into methyl dimethoxyacetate and methyl benzoate, which is formed in 80 % yield[73]. The weaker acid methanol is added rapidly to *(3)* only above 0 °C, to form *(32b)*, whereas no reaction occurs with *tert*-butanol even at 80 °C[74]. Nevertheless, CH acids may be sufficiently

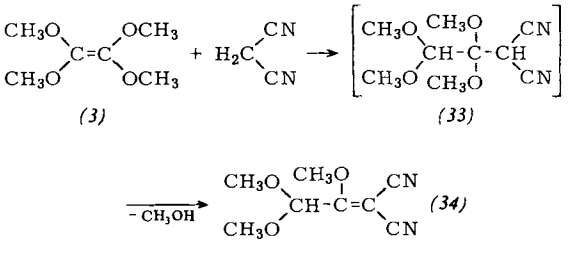


(3) *(32)*

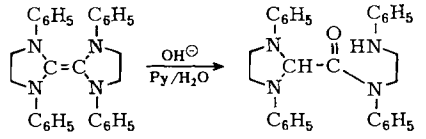
(a), R = COC_6H_5
(b), R = CH_3

acidic to add to *(3)*, as is shown by the reaction with malononitrile, during which the primary adduct *(33)* loses methanol to form *(34)*[75].

The addition of methanol and of water[76] to *(5)* is reversible[42]. Corresponding to the hydrolysis of *(3)* to give methyl dimethoxyacetate[74] (cf. also[39]), the hydrolysis of *(2)* in

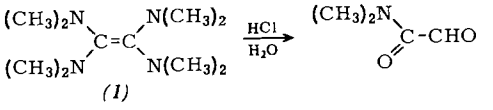


(3) *(33)* *(34)*



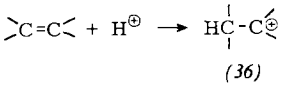
(2) *(35)*

alkaline media leads to *(35)*[4], whereas acid hydrolysis results in more extensive cleavage (see Section 3.2). Only in the case of *(1)* has cleavage to *N,N*-dimethylglyoxylamide been achieved by acid hydrolysis[50].



(1)

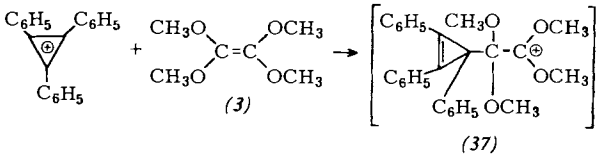
These reactions probably all begin with the addition of a proton to the electron-rich olefin. The resulting primary adduct *(36)* has been intercepted as the iodide[42] or perchlorate[72] in the case of *(5)*.



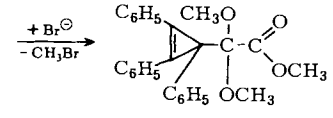
(36)

The possibility of diprotonation has been discussed for *(1)*[31] to explain differences between the acidic and neutral hydrolyses (see Section 3.2) of this compound. With Lewis acids such as BF_3, BH_3[49], $Al(CH_3)_3$[77], $AlCl_3$[49], $ZnCl_2$[49], or TiF_4[78], *(1)* forms stable adducts, the Lewis acid in some cases being bound to the nitrogen. (The structures of some of the adducts have not yet been established.)

The alkylation of electron-rich olefins, *e.g.* of *(3)* with carbonium ions, proceeds very vigorously even under mild conditions[79]. The primary adduct such as *(37)* is demethylated as a carbonium-oxonium ion by nucleophiles to form α-substituted methyl α,α-dimethoxyacetates, which can be hydrolyzed to give the corresponding α-keto acids in good yields. The positive charge in *(37)* is stabilized to such a degree that tetramethoxyethylene is no longer alkylated by *(37)*. For this reason the alkylation of *(3)* by the tetramethoxyethylene dication *(14)* (see Section 2.3) stops, once the primary adduct *(15)* is formed.



(3) *(37)*



The rate of alkylation of *(3)* depends on the tendency of the alkylating agent to form carbonium ions[79]. The fact that *(3)* is inert to *n*-butyl iodide or phenacyl bromide shows that *(3)* itself is not nucleophilic,

[73] *J. Schneider*, Dissertation, Universität Heidelberg, 1966.

[74] *R. W. Hoffmann*, *J. Schneider*, and *H. Häuser*, Chem. Ber. *99*, 1892 (1966).

[75] *J. Gehlhaus*, Diplomarbeit, Universität Heidelberg, 1967.

[76] Several structures have been proposed for the adduct of *(5)* with H_2O [14, 72].

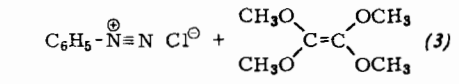
[77] *N. R. Fetter* and *D. W. Moore*, Canad. J. Chem. *42*, 885 (1964).

[78] *E. L. Muetterties*, J. Amer. chem. Soc. *82*, 1082 (1960).

[79] *R. W. Hoffmann* and *J. Schneider*, Chem. Ber. *99*, 1899 (1966).

though it is instantaneously attacked by electrophiles. *(5)*, on the other hand, possesses nucleophilic properties, since it is alkylated by dimethyl sulfate or ethyl iodide [42]. However, the choice of alkylating agents is restricted by the reducing properties of the electron-rich olefins.

The reactions of electron-rich olefins with electrophiles, particularly their acylation [79], coupling with diazonium ions [79], and formation of cyanine dyes [80], offer interesting routes for preparative chemistry.



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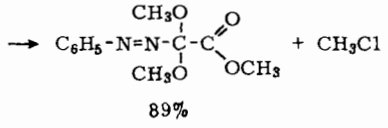

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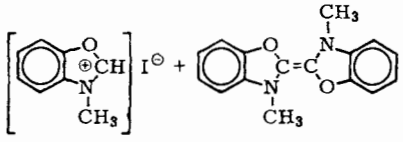
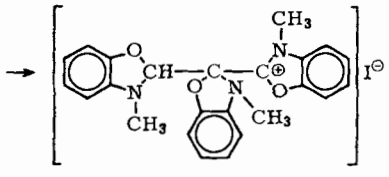
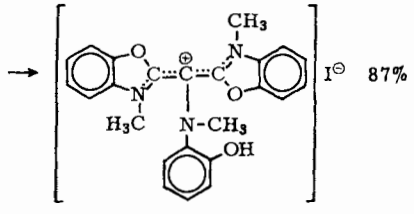


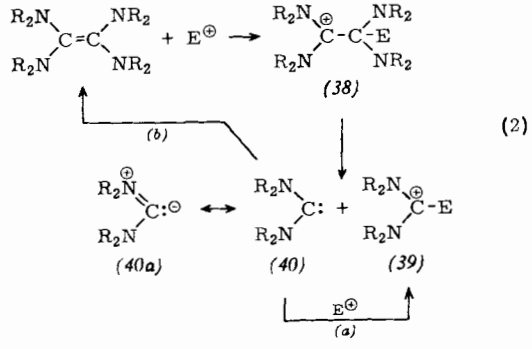




87%

3.2. Reaction in which the Molecule is Cleaved

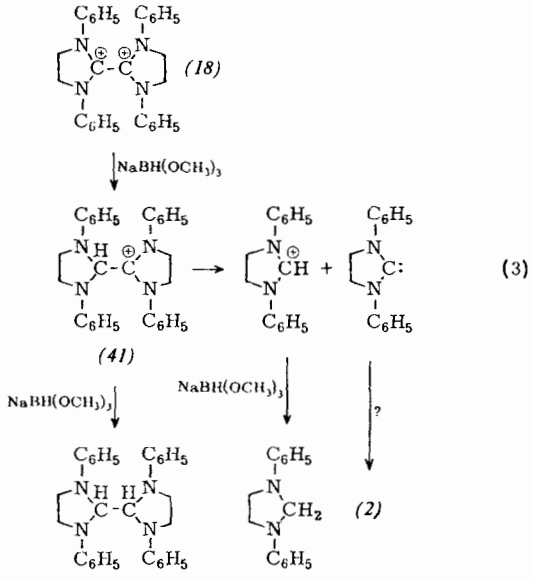
The primary adduct *(38)* formed by the reaction of *(1)* or *(2)* with electrophiles, and partly also the adduct formed from *(5)*, exhibits a strong tendency to dissociate into a amidinium ion *(39)* and a nucleophilic carbene *(40)* [9].



(2)

[80] *H. W. Wanzlick* and *H. Steinmaus*, Chem. Ber. *101*, 244 (1968).

As is shown by the few reactions described in Section 3.1, *(38)* can be intercepted before cleavage occurs only in the presence of high concentrations of active nucleophiles. The cleavage of the molecule actually starts from the intermediate *(38)*, since cleavage products are also obtained on the reduction of *(18)*, which proceeds *via* the intermediate *(41)* corresponding to *(38)* [31].

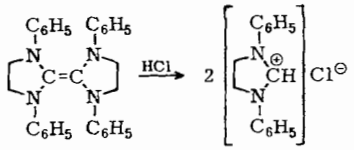


(3)

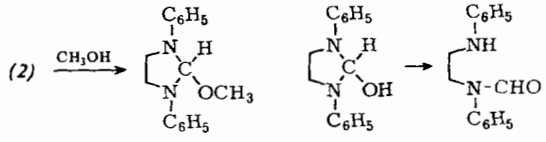
The cleavage of *(38)* into *(39)* and *(40)* is possible only because *(40a)* is so strongly stabilized by the participation of low-energy ylid structures that it becomes a good leaving group [81].

The nucleophilic carbene *(40)* liberated immediately adds on any strong electrophiles present to form *(39)* [path *(a)* in eq. (2)]. At lower electrophile concentrations or in the presence of only weak electrophiles, *(40)* might dimerize with regeneration of the original electron-rich olefin [31] [path *(b)* in eq. (2), cf. also eq. *(3)*]. The competition between paths *(a)* and *(b)* has not yet been investigated.

Mineral acids cleave *(5)* [42, 72], *(29)* [69], and *(2)* [4, 82], quantitatively in some cases, into formamidinium salts in accordance with eq. (2).



(2)



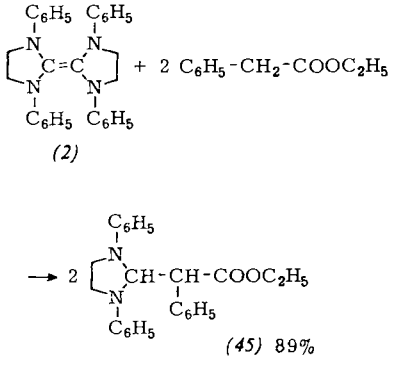
(42) *(43)* *(44)*

[81] *R. Breslow*, J. Amer. chem. Soc. *80*, 3719 (1958).

[82] *Z. Z. Ma*, *C. Y. Chen*, *H. K. Jiang*, and *M. Y. Ma*, Sci. sinica *17*, 299 (1966); Chem. Abstr. *65*, 13463 (1966).

The reaction of *(2)* with methanol yields *(42)*. In weakly acidic [7] or even weakly alkaline media, the proton activity is sufficient to hydrolyze *(2)* to *(44)*, presumably *via (43)*. The neutral hydrolysis of *(1)* at 160 °C proceeds similarly [50].

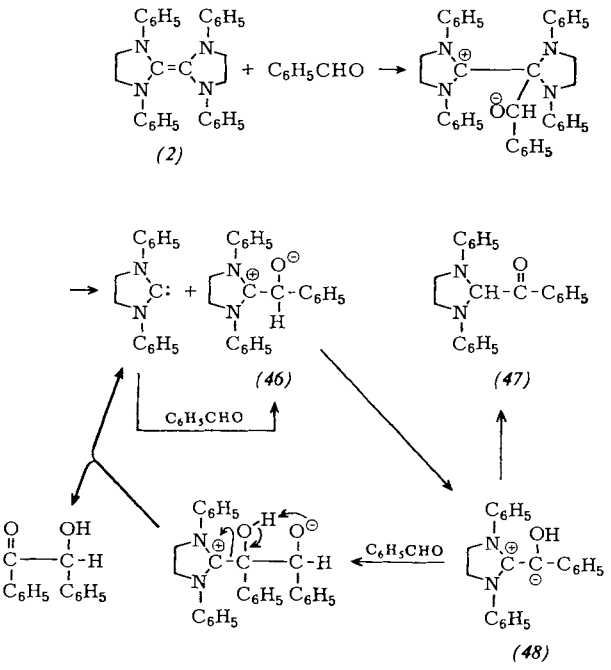
A large variety of CH acidic compounds react readily in a similar manner with *(2)* [6, 83–86], *(29)* [63], or *(5)* [42], the reaction resulting in cleavage of the molecule. It has been shown in the case of *(2)* → *(45)* that the reaction is reversible [85]. Since the aminal group in *(45)* is readily hydrolyzed to give an aldehyde, these reactions have gained some importance for the synthesis of α-substituted aldehydes.



(2) *(45)* 89%

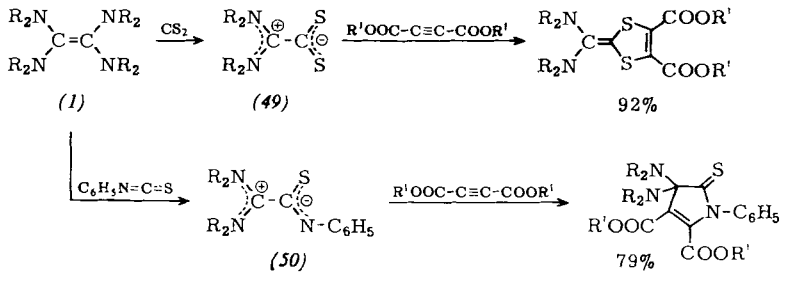
With aldehydes having no acidic α-hydrogen, electrophilic attack by the carbonyl group on *(5)* [42] or *(2)* [4, 6, 84] ensues. Corresponding to eq. *(2)*, the reaction *e.g.* of *(2)* with benzaldehyde proceeds *via* the adduct *(46)* to give *(47)* in 90 % yield [84].

The ketonization of the enol *(48)* to *(47)* is in competition with the attack of further benzaldehyde on

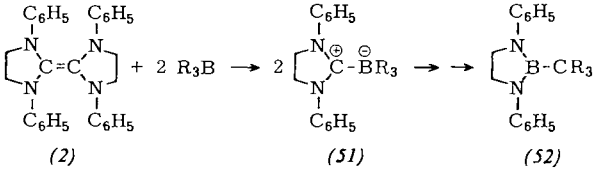


(48) to form benzoin; this process, which corresponds to the thiamine-catalyzed formation of benzoin [81], is favored to such an extent in the presence of electron-donating substituents on the nitrogen atoms, and hence by stabilization of the positive charge in *(48)*, that the formation of benzoin becomes the principal reaction [84, 87].

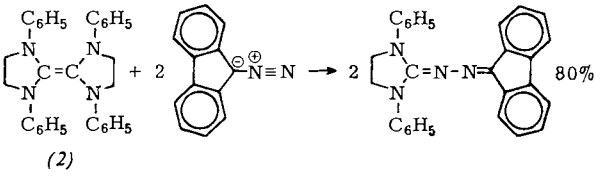
Under the action of carbon disulfide or phenyl isothiocyanate, *(1)* is cleaved in high yields in accordance with eq. *(2)* to give the stable betaines *(49)* and *(50)*, which can be readily alkylated on the sulfur [88], and which readily also undergo 1,3-dipolar additions [88, 88a, 89].



Whereas *(2)* suffers acylation and cleavage by acyl chlorides in accordance with eq. (2), acetic anhydride acts on *(2)* as a CH acid [83]. Trialkylboranes cleave *(2)* in boiling toluene to give the ylid *(51)*, which undergoes a series of inverse Stevens rearrangements to give the 1,3,2-diazaborolidines *(52)* in 85 to 95 % yield [90].



(2) [70, 91, 92] and *(5)* [14] are cleaved even by diazo compounds such as diazofluorene, which are only weakly electrophilic, to form azines in good yields.



(2)

Unlike the reaction of electron-rich olefins with azides (see Section 5.3), the reaction with diazofluorene probably does not proceed by cycloaddition, since the adduct *(53)*, as a

[83] *H. W. Wanzlick, H. Ahrens, B. König,* and *M. Riccius,* Angew. Chem. *75*, 685 (1963); Angew. Chem. internat. Edit. *2*, 560 (1963).

[84] *H. W. Wanzlick* and *H. J. Kleiner,* Chem. Ber. *96*. 3024 (1963).

[85] *H. W. Wanzlick* and *H. Ahrens,* Chem. Ber. *97*, 2447 (1964).

[86] *H. W. Wanzlick* and *H. Ahrens,* Chem. Ber. *99*, 1580 (1966).

[87] *H. W. Wanzlick* and *H. Steinmaus,* private communication.

[88] *H. E. Winberg* and *D. D. Coffman,* J. Amer. chem. Soc. *87*, 2776 (1965).

[88a] *A. Takamizawa, K. Hirai,* and *S. Matsumoto,* Tetrahedron Letters *1968*, 4027.

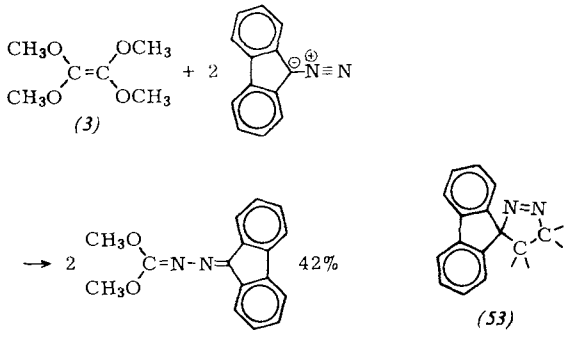
[89] *H. Behringer* and *J. Falkenberg,* Tetrahedron Letters *1967*, 1895.

[90] *G. Jesse* and *A. Haag,* Tetrahedron Letters *1965*, 1123.

[91] *H. Reimlinger,* Chem. Ber. *97*, 3503 (1964).

[92] *M. Regitz, A. Liedhegener,* and *D. Stadler,* Liebigs Ann. Chem. *713*, 101 (1968).

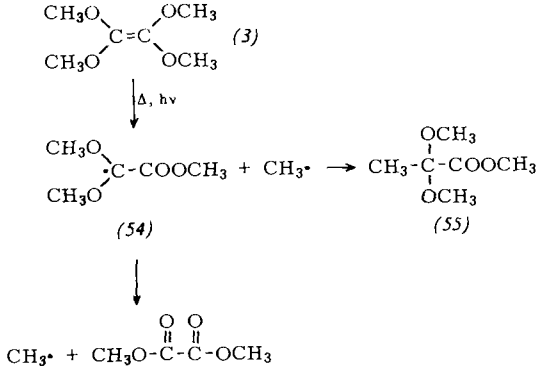
1-pyrazoline[93], should preferentially split of nitrogen and not a carbene.



Tetramethoxyethylene *(3)* also reacts with diazofluorene to give an azine[94], but it is questionable, in view of the low yield, whether the azine is formed in accordance with eq. (2), since *(3)* is not cleaved according to eq. (2) by much stronger electrophiles even in the absence of nucleophilic anions (see Section 3.1). This would support the argument that cleavage of the molecule in the course of the addition of an electrophile to an electron-rich olefin [eq. (2)] becomes increasingly favored with increasing resonance stabilization of the resulting nucleophilic carbene. The results described here accordingly lead to the conclusion that the tendency toward cleavage in accordance with eq. (2) increases in the order *(3)* < *(5)* < *(2)* ≈ *(1)*.

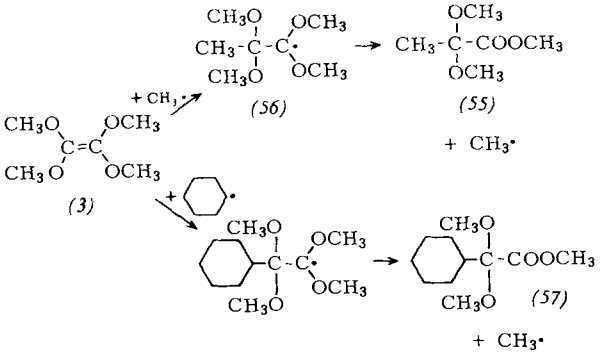
4. Free Radical Reactions of Electron-Rich Olefins

Simple ketene acetals undergo homolysis when heated to about 250 °C[95]. Tetramethoxyethylene *(3)*, on the other hand gives 17–31 % of dimethyl oxalate and 25–50 % of methyl α,α-dimethoxypropionate *(55)*[74] at 165 °C in a reaction that presumably begins with homolysis of a methyl-oxygen bond. The resulting resonance-stabilized radical *(54)* can partly recombine with the methyl radical to give *(55)*.

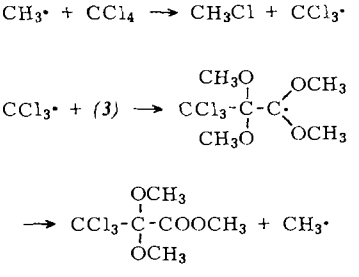


On the other hand, *(54)* decomposes very readily into dimethyl oxalate and another methyl radical, as can be shown independently by generation of *(54)* from methyl dimethoxyacetate and di-*tert*-butyl peroxide[35]. A small quantity of *(54)* also dimerizes to form dimethyl tetramethoxysuccinate *(16)*.

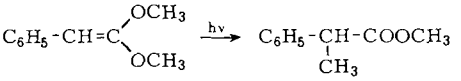
(16) is also formed on thermal decomposition of *(3)* in cyclohexane, where some of the methyl radicals recombine with *(54)* and some undergo chain transfer with the solvent. Both the methyl and the cyclohexyl radicals can add to *(3)* in a chain reaction. The reaction leads *e.g.* to 8 % of *(57)* and 24 % of *(55)*, since the primary adduct, *e.g.* *(56)*, as an α,α-dimethoxyalkyl radical[96], readily decomposes into a methyl



radical and *(55)*. In any case, the ratio of the yields of dimethyl oxalate (product of the initiation reaction) to *(55)* (product of the chain reaction), which has a value of 1:1 to 1.5:1, shows that the kinetic chain length[*] is short. The ratio of the yields gives an upper limit for this quantity. When tetramethoxyethylene is heated in carbon tetrachloride, no dimethyl oxalate is found, but more than 95 % of methyl β,β,β-trichloro-α,α-dimethoxypropionate can be isolated[74, 97], indicating that the kinetic chain length of the following reaction is >25, since the addition of a trichloromethyl radical to *(3)* is favored by polarity factors.



Thus the thermal decomposition of *(3)* is neither a pure radical chain reaction nor a pure radical cage reaction. Since the photolysis and the thermolysis of *(3)* yield the same products in comparable yields[74], this conclusion is probably also valid for the photolysis of *(3)*. This reaction thus differs from the formally analogous photolysis of the phenylketene acetals, which proceeds purely intramolecularly as a radical cage reaction[98].



[93] *C. G. Overberger, J. P. Anselme,* and *J. G. Lombardino*: Organic Compounds with Nitrogen-Nitrogen Bonds. Ronald Press, New York 1966, p. 37.

[94] *R. W. Hoffmann* and *H. Häuser*, Tetrahedron Letters *1964*, 1365.

[95] *S. M. McElvain* and *C. L. Stevens*, J. Amer. chem. Soc. *68*, 1917 (1946).

[96] See *e.g.*, *E. S. Huyser, R. M. Kellogg,* and *D. T. Wang*, J. org. Chemistry *30*, 4377 (1965).

[*] The kinetic chain length is the average number of cycles of the reaction chain initiated by one initiation step.

[97] Cf. the reaction of *(1)* or *(2)* with CCl_4, which is quite different (Section 2.4).

[98] *J. E. Baldwin* and *L. E. Walker*, J. Amer. chem. Soc. *88*, 3769, 4191 (1966).

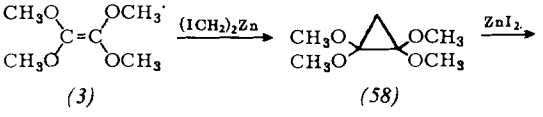
It is not yet certain whether *(1)*, which is sensitive to light [55], decomposes in the same way on irradiation. *(2)* evidently forms free radicals when heated, and may be used as a thermal initiator for the oligomerization of perfluoroolefins [82].

5. Cycloadditions to Electron-Rich Olefins

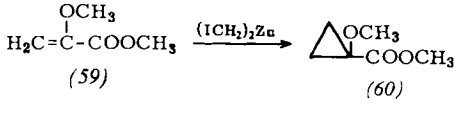
In some cycloadditions the transition states are slightly, but nevertheless definitely, polar [99]. The electron-rich olefins should therefore preferentially undergo cycloadditions with electrophilic partners. In this respect they are again counterparts of tetracyanoethylene [1], which is widely used for its pronounced tendency to enter into cycloadditions with electron-rich compounds.

5.1. Formation of Three-Membered Rings

The reaction of tetramethoxyethylene *(3)* with carbenoids [100] leads to derivatives of tetramethoxycyclopropane [16]. For example, the action of bis(iodomethyl)zinc on *(3)* yields a mixture of the compounds *(58)*, *(59)*, and *(60)*, *(59)* being formed from *(58)* by the action of zinc iodide, as has been shown independently. Thus if the zinc iodide formed by the



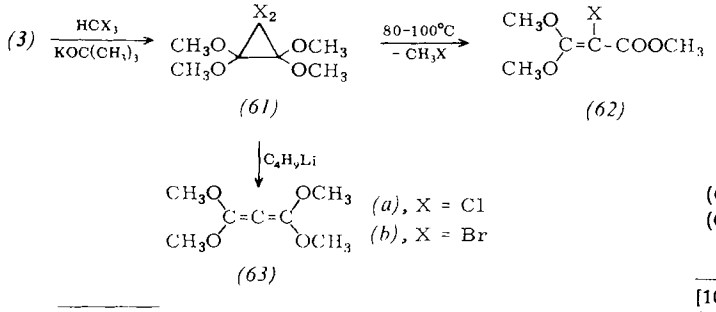
(3) *(58)*



(59) *(60)*

reaction of *(3)* with bis(iodomethyl)zinc is partly bound by complex formation with 1,2-dimethoxyethane, the yields of *(58)* can be increased to 20 %.

Dibromo- and dichlorocarbenoid (from potassium *tert*-butoxide and haloform [101]) add to *(3)* with formation of 1,1-dihalogenotetramethoxycyclopropanes



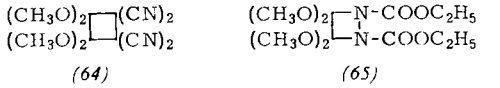
(61) *(62)* *(63)*

(61) [102], which are cleaved on heating to form the methyl 2-halogeno-3,3-dimethoxyacrylates *(62)*.

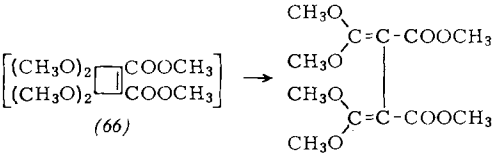
(61) is the starting material for the preparation of the electron-rich tetramethoxyallene *(63)*, which is formed in 72 % yield on reaction of *(61b)* with butyllithium [102]. (For the possibility of a reaction of *(1)* with dichlorocarbene, see [53].)

5.2. Formation of Four-Membered Rings

Tetramethoxyethylene enters extremely readily into 2 + 2-cycloadditions with electrophiles. Thus the reaction at 0 °C with tetracyanoethylene leads instantaneously to the adduct *(64)* (63 %), while addition to diethyl azodicarboxylate yields diazetidine *(65)* (98 %) [103].



(64) *(65)*

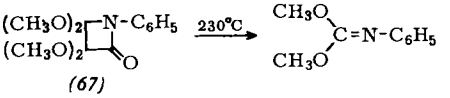


(66)

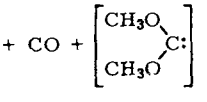
The adduct *(66)* formed by *(3)* and dimethyl acetylenedicarboxylate undergoes ring opening during workup to yield dimethyl 1,1,4,4-tetramethoxy-1,3-butadiene-2,3-dicarboxylate (97 %) [75, 104].

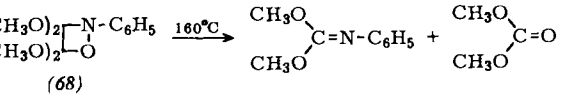
Interesting adducts of *(3)* include not only those with ketene and diphenylketene, but also those with phenyl isocyanate *(67)* [103] and with nitrosobenzene *(68)* [103], which are formed in high yields. On heating or on exposure to light, *(67)* and *(68)* do not undergo retrocleavage to *(3)* but are split to form dimethyl *N*-phenylimidocarbonate [73, 75].

According to the *Woodward-Hoffmann* rules [105], the thermal 2'+ 2-cycloadditions to *(3)* should proceed in two steps. In view of the difference in the polarity of the addends, the intermediate may be expected to be a 1,4-dipole [99]. The forma-



(67)





(68)

[99] *R. Huisgen, R. Grashey*, and *J. Sauer* in *S. Patai*: The Chemistry of Alkenes. Interscience, London 1964, p. 739.

[100] See *G. Köbrich*, Angew. Chem. *79*, 15 (1967); Angew. Chem. internat. Edit. *6*, 41 (1967).

[101] The compound *(62)* is obtained directly by reaction of *(3)* with phenyl(bromodihalogenomethyl)mercury in boiling benzene.

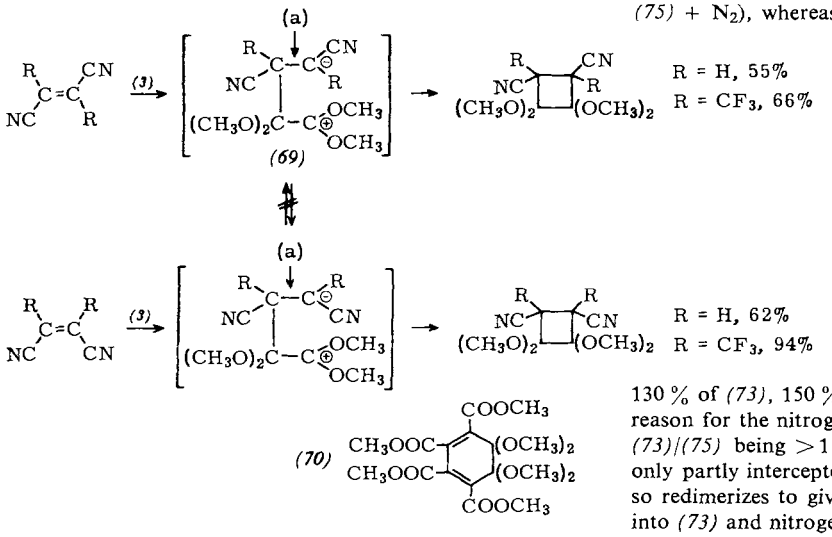
[102] *R. W. Hoffmann* and *U. Bressel*, Angew. Chem. *79*, 823 (1967); Angew. Chem. internat. Edit. *6*, 808 (1967).

[103] *R. W. Hoffmann* and *H. Häuser*, Angew. Chem. *76*, 346 (1964); Angew. Chem. internat. Edit. *3*, 380 (1964).

[104] This is a revision of our earlier formulation [103].

[105] *R. Hoffmann* and *R. B. Woodward*, J. Amer. chem. Soc. *87*, 2046 (1965).

tion of a 1,4-dipole *(69)* should be recognizable from the fact that rotation about the bond (a) is possible in this species. Thus on addition of *(3)* to a pair of *cis,trans*-isomeric electrophilic olefins, the *cis* and the *trans* adduct should be formed together in each case. However, the addition of *(3)* both to 1,2-dicyanoethylenes and to 1,2-dicyano-1,2-bis(trifluoromethyl)ethylenes was found to be more than 95 % stereospecific[16,106]. The rotation about the bond (a) in *(69)* is evidently much slower than the ring closure to form cyclobutane derivatives. This is probably mainly due to the fact that the ends of the 1,4-dipole are fixed in relation to each other by electrostatic forces[99]. However, the idea that 2 + 2-cycloadditions to *(3)* proceed *via* a 1,4-dipole is supported[107] by the fact that on addition of *(3)* to dimethyl acetylenedicarboxylate, it was possible under certain conditions to obtain the 1,2-adduct *(70)* in 45 % yield [75].



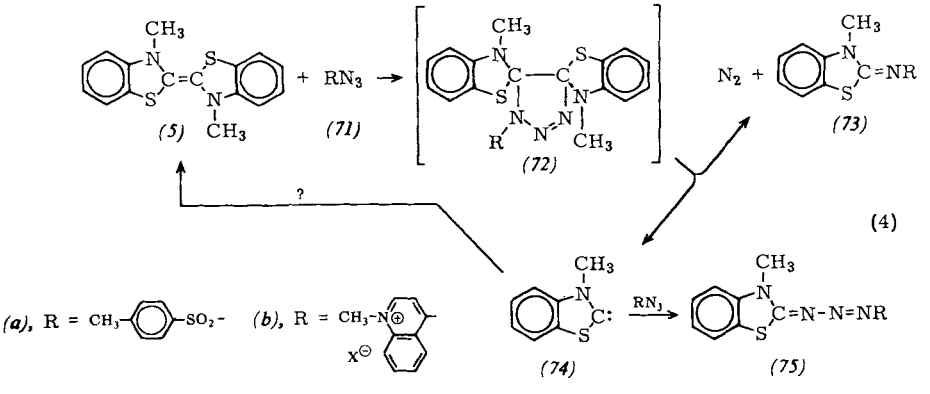
5.3. Formation of Five-Membered Rings

Adducts of 1,3-dipoles with electron-rich olefins have not yet been isolated as such. However, *Quast* and *Hünig*[46] have shown that cycloadducts are probably formed in the reaction of *(5)* with azides *(71)*. By analogy with the reaction of enol ethers[108] or enamines[109] with azides, the reaction of *(5)* with an azide *(71)* should lead first to a triazoline *(72)*. Compound *(72)* then decomposes into an imine *(73)*, nitrogen, and the nucleophilic carbene *(74)*; it is not certain whether *(73)* and *(74)* are liberated *via* a diazo compound as a further intermediate[109,110]. In any case, the induction time for the evolution of nitrogen points to the formation of an intermediate[111].

The carbene *(74)* can now add on the azide *(71)* to form the triazene derivative *(75)*, the formation of which has been shown to be characteristic of the carbene *(74)*. On the other hand, the carbene can enter into other reactions, including redimerization under certain circumstances to form *(5)*. The principal reaction path followed by *(74)* depends on the electrophilicity of the azide used. Thus *(5)* and *p*-toluenesulfonyl azide *(71a)* give 79 % of *(73)*, 107 % of N_2, and 46 % of *(75)* (based on the stoichiometry *(5)* + 2 *(71)* → *(73)* + *(75)* + N_2), whereas with the less electrophilic azide *(71b)*, 130 % of *(73)*, 150 % of N_2, and no *(75)* are obtained. The reason for the nitrogen yield exceeding 100 % and the ratio *(73)*/*(75)* being >1 may be either that the carbene *(74)* is only partly intercepted by the azide *(71)* to form *(75)*, and so redimerizes to give *(5)*, or that *(75)* partly decomposes into *(73)* and nitrogen.

This dependence of the product yield on the electrophilicity of the azide can be satisfactorily explained if a triazoline is assumed as an intermediate. If on the other hand, the reaction of *(71)* had followed eq. (2), the only product would have been the triazene derivative *(75)*, irrespective of the electrophilicity of the azide used.

The reaction of tetraaminoethylenes with azides similarly yields both guanidine and triazene derivatives[88]; if the triazenes predominate in this case, however, a reaction in accordance with eq. (2) could compete with one corresponding to eq. (4).



Much less information can be deduced from the reaction of *(3)* with azides, which yields only derivatives of dimethyl imidocarbonate *(76)*[94]. Until it is known

[106] The configurations of the adducts were assigned on the assumption that the configuration is retained on cycloaddition.

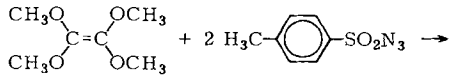
[107] *R. Huisgen, K. Herbig,* and *M. Morikawa,* Chem. Ber. *100,* 1107 (1967), and earlier communications.

[108] *R. Huisgen* and *G. Szeimies,* Chem. Ber. *98,* 1153 (1965).

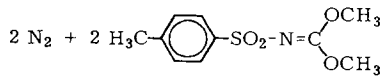
[109] *R. Fusco, G. Bianchetti, D. Pocar,* and *R. Ugo,* Chem. Ber. *96,* 802 (1963).

[110] *G. Bianchetti, D. Pocar, P. D. Croce,* and *A. Vigevani,* Chem. Ber. *98,* 2715 (1965); *K. D. Berlin* and *M. A. R. Khayat,* Tetrahedron *22,* 975 (1966); *J. Kučera* and *Z. Arnold,* Tetrahedron Letters *1966,* 1109.

[111] *H. Quast,* private communication.



(3) (71a)

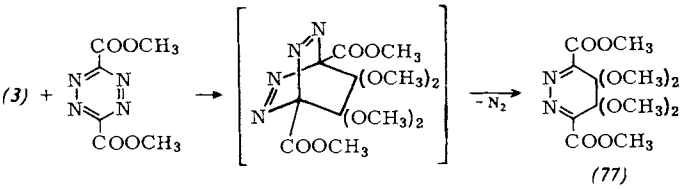


(76) 74%

whether the triazene derivative corresponding to *(75)* is stable under the reaction conditions or readily decomposes into *(76)* and nitrogen, the only way to determine whether the reaction of *(3)* with *(71a)* also follows eq. (4) is by labeling experiments. In this case the dimethoxycarbene should redimerize to form tetramethoxyethylene. However, *(76)* certainly is not formed because of prior dissociation of tetramethoxyethylene into two dimethoxycarbene fragments, since a kinetic study has shown [112] that the reaction is first order with respect to both tetramethoxyethylene and *p*-toluenesulfonyl azide. This is compatible with the reaction proceeding in accordance with either eq. (2) or eq. (4).

5.4. Formation of Six-Membered Rings

If electron-rich olefins do in fact enter into Diels-Alder additions, these should be additions with "inverse electron demand" [113]. Whereas *(3)* was alkylated by



(77)

hexachlorocyclopentadiene because of the presence of chlorine in an allylic position [79], the reaction of *(3)* with dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate leads *via* the Diels-Alder adduct to a 70 % yield of *(77)* [114].

[112] *U. Bressel*, Diplomarbeit, Universität Heidelberg, 1966.

[113] *J. Sauer*, Angew. Chem. *79*, 76 (1967); Angew. Chem. internat. Edit. *6*, 16 (1967).

[114] *J. Sauer*, private communication.

6. Concluding Remarks

The investigation of electron-rich olefins has been decisively influenced by the desire to liberate nucleophilic carbenes from them. Though the latter occur in many reactions of the electron-rich olefins, it has been found that the original idea of generating them by dissociation of electron-rich olefins cannot generally be realized. On the other hand, these investigations have uncovered many novel reactions; the examples discussed here should provide some idea of the wide range of possible uses of electron-rich olefins in synthetic organic chemistry.

The electron-rich olefins discussed here and tetrafluoroethylene exhibit a characteristic gradation of reactivity (see Table 3).

Table 3. Reactivity of olefins having four (+M) substituents.

	$(R_2N)_2C{=}C(NR_2)_2$	$(RO)_2C{=}C(OR)_2$	$F_2C{=}CF_2$
Addition of electrophiles	+++	++	–
Cleavage of the molecule on reaction with electrophiles	++	–	–
Addition of free radicals	?	+	++
Cycloadditions	?	++	+++
Addition of nucleophiles	?	?	++

The many question marks in this table show that the investigation of electron-rich olefins has by no means reached an end, rather it is fairly certain that this branch of organic chemistry still has surprises in store.

Our own investigations described here were carried out with the generous support of the Deutsche Forschungsgemeinschaft.

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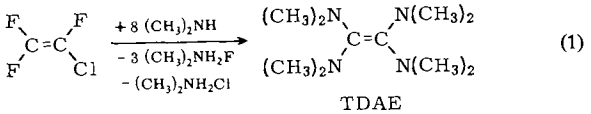
Tetraaminoethylenes as Strong Electron Donors

BY N. WIBERG[*]

Depending on the nature of the electron acceptor and of the tetraaminoethylene (TAE), the electron pairs of the ethylenic double bond (A), of the nitrogen (B), or of the entire electronic system (C) of TAE react with the acceptor. Thus oxidizing agents convert TAE into the mono- and dications TAE^+ and TAE^{2+} by path (A); acids add on to the ethylenic carbon (A) or the amine nitrogen (B) (the addition of acid is often followed by cleavage of the C=C or C–N bond); organic π-electron acceptors form deeply colored donor-acceptor complexes with TAE (C).

1. Introduction

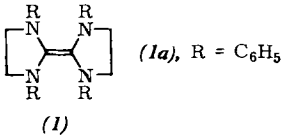
In 1950, when *Pruett et al.* [1] allowed dimethylamine to act on trifluorochloroethylene [reaction (1)], they obtained pale green, liquid tetrakis(dimethylamino)-ethylene (TDAE [2]), the first of the tetraaminoethylenes (TAE). In qualitative experiments on this product,



TDAE (1)

Pruett et al. [1] observed behavior that was unexpected in an ethylene derivative: "This (TDAE) ... was strongly luminescent in contact with air. It reacted with oxygen to form a white solid..." If a little tetrakis(dimethylamino)ethylene is placed on a filter paper, intense luminescence begins after a few minutes in contact with atmospheric oxygen. A small room can even be dimly lit for over an hour in this way with about 10 ml of TDAE [61, 61a]. *Pruett et al.* did not further examine the compound TDAE.

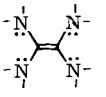
The systematic study of the properties of tetraaminoethylenes only began in 1960 with the discovery of a second member of this class of compounds, 1,1',3,3'-tetraphenyl-2,2'-biimidazolidinylidene *(1a)*, by *Wanzlick et al.* [3]. More than 30 extensively studied compounds of this class are now known.



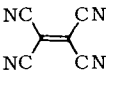
(1a), R = C_6H_5

(1)

The following is a review of the reactive tetraaminoethylenes (TAE) [5], which are found in many (often surprising) reactions to act as strong electron donors, and whose chemistry contrasts strongly with that of the electron acceptor tetracyanoethylene (TCNE) [4].



TAE



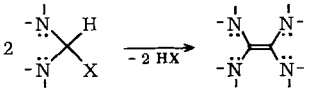
TCNE

The discussion will concentrate on tetrakis(dimethylamino)ethylene, which is a particularly simple and thoroughly studied tetraaminoethylene.

2. Preparation of Tetraaminoethylenes

The simple preparation method used by *Pruett* [reaction (1)] cannot be used as a general route to tetraaminoethylenes. The only amines that have so far been successfully used for the preparation of tetraaminoethylenes with trifluorochloroethylene are dimethylamine [1, 9] and *N,N'*-dimethylethylenediamine [10]. It appears that successful syntheses by means of reaction (1) are possible only with amines R_2NH having very small ligands R.

A general method [reaction (2)] for the preparation of tetraaminoethylenes is the elimination of acids HX



(2) (2)

TAE

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[1] *R. L. Pruett, J. T. Barr, K. E. Rapp, C. T. Bahner, J. D. Gibson,* and *R. H. Lafferty,* J. Amer. chem. Soc. *72,* 3646 (1950).

[2] We have chosen this abbreviation by analogy with that commonly used for tetracyanoethylene (TCNE) (cf. *J. W. Buchler,* Dissertation, Universität München, 1963). *Flechter* and *Heller* use TMAE [46], while *Winberg, Paris,* and *Geske et al.* use TDE [12, 37, 27].

[3] *H.-W. Wanzlick* and *E. Schikora,* Angew. Chem. *72,* 494 (1960).

[4] *T. L. Cairns* and *B. C. McKusick,* Angew. Chem. *73,* 520 (1961).

[5] For further reviews see [6–8].

[6] *H.-W. Wanzlick,* Angew. Chem. *74,* 129 (1962); Angew. Chem. internat. Edit. *1,* 75 (1962).

[7] *D. M. Lemal* in *S. Patai*: The Chemistry of the amino Group. Interscience, New York-London, in press.

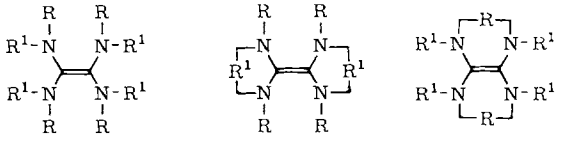
[8] *R. W. Hoffmann,* Angew. Chem. *80,* 823 (1968); Angew. Chem. internat. Edit. *7,* 754 (1968).

[9] *N. Wiberg* and *J. W. Buchler,* Z. Naturforsch. *19b,* 5 (1964).

[10] *D. M. Lemal, R. A. Lovald, K. I. Kawano,* and *J. P. Lokensgard,* J. Amer. chem. Soc., in press.

from aminals *(2)* (examples of X: see Table 1, column four). HX can be eliminated by heating of *(2)* to 80–250 °C [6, 11–14, 19], by acid catalysis [15], or by treatment of *(2)* with strong bases [16–19]. The starting compound *(2)* required for the synthesis in accordance with equation (2) is generally first prepared as such and then made to react further as shown [20].

Table 1. Preparation of tetraaminoethylenes.



A B C

Type of compound	R	R^1	X in reaction (2)	Ref.
A	CH_3	CH_3	[a]	[1, 9]
			$N(CH_3)_2$	[13]
			OCH_3	[22]
A	CH_3	C_6H_5	OC_2H_5	[15]
A	C_2H_5	C_6H_5	OC_2H_5	[15]
A	CH_3	$N(CH_3)_2$	OCH_3	[14]
A	$[(CH_3)_2N]_2C=$		OCH_3	[14]
A	$-(CH_2)n-$, $n = 2, 3, 5, 6$		OCH_3	[14]
A	$-(CH_2)_4-$		OCH_3, CN	[12, 14, 22]
A	$-CH_2-CH=CH-CH_2-$		OCH_3	[14]
A	$-(CH_2)_2-O-(CH_2)_2-$		OCH_3	[12, 14]
A	$-(CH_2)_2-NCH_3-(CH_2)_2-$		OCH_3	[12, 14]
B	CH_3	$-(CH_2)_2-$	OCH_3	[12, 14, 14a]
B	C_2H_5	$-(CH_2)_2-$	OCH_3	[12, 14, 14a]
B	[b]	$-(CH_2)_2-$	OCH_3	[12, 14]
B	n-C_3H_7	$-(CH_2)_2-$	OCH_3	[12]
B	n-C_4H_9	$-(CH_2)_2-$	OCH_3	[12]
B	n-C_6H_{13}	$-(CH_2)_2-$	OCH_3	[12]
B	$CH_2C_6H_5$	$-(CH_2)_2-$	OCH_3	[12, 14]
B	C_6H_5	$-(CH_2)_2-$	OC_2H_5, CCl_3	[6, 11]
			ClO_4	[10, 16, 17]
B	p-$CH_3-C_6H_4$	$-(CH_2)_2-$	OC_2H_5, CCl_3	[6, 11]
			ClO_4	[10, 16, 17]
B	p-$CH_3O-C_6H_4$	$-(CH_2)_2-$	OC_2H_5, CCl_3	[11]
B	p-$Cl-C_6H_4$	$-(CH_2)_2-$	OC_2H_5, CCl_3	[11]
B	p-$NO_2-C_6H_4$	$-(CH_2)_2-$	OC_2H_5, CCl_3	[11]
B	α-Naphthyl	$-(CH_2)_2-$	OC_2H_5, CCl_3	[11]
B	CH_3	$-(CH_2)_3-$	OCH_3	[12, 14]
B	C_6H_5	$-(CH_2)_3-$	OC_2H_5	[11]
B	p-$CH_3-C_6H_4$	$-(CH_2)_3-$	OC_2H_5	[11]
B	CH_3	$-CO-NCH_3-CO-$	OCH_3, I	[19]
C	$-(CH_2)_2-$	CH_3	[a]	[10]

[a] Preparation by reaction (1).

[b] Two of the four groups R are CH_3 groups, and the other two are C_2H_5 groups.

In the reaction of $(C_2H_5O)_3CH$ [6, 11, 15] or $(CH_3)_2NCH(OCH_3)_2$ [12, 14] with amines, tetraaminoethylenes are formed *via (2)*, also directly if the amine does not exhibit strong steric hindrance.

The tetraaminoethylenes prepared so far (see Table 1) with the exception of the liquid tetrakis(dimethylamino)ethylene, are solids. They are sparingly soluble in apolar solvents, and apart from TDAE (pale green) and *(1)*, R = $CH_2C_6H_5$ (yellow), p-$NO_2C_6H_4$ (red), and α-naphthyl (red), they are colorless. TDAE is a strongly refracting, fluorescent, lipophilic, hydrophobic oil (n_D^{25} = 1.4785), which solidifies at 0 °C and boils at 30 °C/0.01 torr. It decomposes slowly with loss of dimethylamine at about 100 °C [9].

3. Reactivity of the Tetraaminoethylenes

Tetraaminoethylenes (TAE) are strong organic electron donors. The chemistry of these compounds is therefore dominated by the effort to give up some of their electrons to an oxidizing agent O (redox reaction) or to share them with an acid S (acid-base reaction).

$$\text{TAE} \xrightarrow[(+O)]{\text{Redox reaction}} \text{TAE}^{n+}\text{O}^{n-} \quad (3)$$

$$\text{TAE} \xrightarrow[(+S)]{\text{Acid-base reaction}} \text{TAE} \rightarrow \text{S} \quad (4)$$

3.1. Redox Reactions

3.1.1. The Tetraaminoethylene Dication

Oxidizing agents such as halogens, dinitrogen tetroxide, copper^{I}, silver^{II}, carbon tetrachloride, and tetracyanoethylene withdraw two electrons from tetrakis(dimethylamino)ethylene (TDAE) [18, 25–31]. TDAE is converted into the dication $TDAE^{2+}$, the octamethyloxamidinium ion, [reaction (5)] and is thus a chemical counterpart of tetracyanoethylene (TCNE), which can be readily reduced to the radical-anion $TCNE^{-}$, and even to the dianion $TCNE^{2-}$ [4, 23, 24] [reaction (6)].

[11] *H.-W. Wanzlick, F. Esser*, and *H.-J. Kleiner*, Chem. Ber. *96*, 1208 (1963).

[12] *H. E. Winberg, J. E. Carnahan, D. D. Coffman*, and *M. Brown*, J. Amer. chem. Soc. *87*, 2055 (1965).

[13] *H. Bredereck, F. Effenberger*, and *H. J. Bredereck*, Angew. Chem. *78*, 984 (1966); Angew. Chem. internat. Edit. *5*, 971 (1966).

[14] *H. E. Winberg*, US-Pat. 3239519 (March 8, 1966) Du Pont; Chem. Abstr. *64*, 15854h (1966).

[14a] *H. E. Winberg*, US-Pat. 3361757 (Jan. 2, 1968), Du Pont; Chem. Abstr. *69*, 19155a (1968).

[15] *I. Hagedorn* and *K. E. Lichtel*, Chem. Ber. *99*, 524 (1966).

[16] *K. I. Kawano* and *D. M. Lemal*, J. Amer. chem. Soc. *84*, 1761 (1962).

[17] *D. M. Lemal, R. A. Lovald*, and *K. I. Kawano*, J. Amer. chem. Soc. *86*, 2518 (1964).

[18] *N. Wiberg* and *J. W. Buchler*, Z. Naturforsch. *19b*, 953 (1964).

[19] *A. Piskala*, Tetrahedron Letters *1964*, 2587.

[20] For example, when X = OCH_3: $(CH_3)_2NCHO + (CH_3)_2SO_4 \rightarrow (CH_3)_2NCH(OCH_3)OSO_3CH_3 + (CH_3)_2NH \rightarrow [(CH_3)_2N]_2CHOSO_3CH_3 + NaOCH_3 \rightarrow$ *(2)* [21, 22].

[21] *H. Bredereck, F. Effenberger*, and *G. Simchen*, Chem. Ber. *98*, 1078 (1965).

[22] *H. E. Winberg*, US-Pat. 3239534 (March 8, 1966), Du Pont; Chem. Abstr. *64*, 17425d (1966).

[23] *W. Liptay, G. Briegleb*, and *K. Schindler*, Z. Elektrochem., Ber. Bunsenges. physik. Chem. *66*, 331 (1962).

[24] *O. W. Webster, W. Mahler*, and *R. E. Benson*, J. Amer. chem. Soc. *84*, 3678 (1962).

[25] *N. Wiberg* and *J. W. Buchler*, Angew. Chem. *74*, 490 (1962); Angew. Chem. internat. Edit. *1*, 406 (1962).

[26] *N. Wiberg* and *J. W. Buchler*, Chem. Ber. *96*, 3223 (1963).

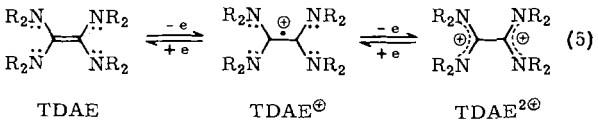
[27] *K. Kuwata* and *D. H. Geske*, J. Amer. chem. Soc. *86*, 2101 (1964).

[28] *W. H. Urry* and *J. Sheeto*, Photochem. and Photobiol. *4*, 1067 (1965).

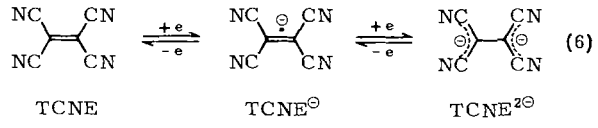
[29] a) *W. Carpenter*, J. org. Chemistry *30*, 3082 (1965); b) *W. Carpenter, A. Haymaker*, and *D. W. Moore*, *ibid. 31*, 789 (1966).

[30] *W. E. Thun*, J. org. Chemistry *32*, 503 (1967).

[31] *R. B. King*, Inorg. Chem. *4*, 1518 (1965).



TDAE $\quad$ $TDAE^{\oplus}$ $\quad$ $TDAE^{2\oplus}$ $\quad$ (5)



TCNE $\quad$ $TCNE^{\ominus}$ $\quad$ $TCNE^{2\ominus}$ $\quad$ (6)

$R = CH_3$

This unusual readiness of the TDAE system to give up electrons is due to the presence of the four amino groups, which stabilize the positive charge by partial transfer of their free electron pairs onto the two central C atoms (the strong electron affinity of the TCNE system can similarly be attributed to the four electron-attracting cyanide groups [4]). However, the "inverse analogy" between TDAE and TCNE is not quantitative; thus the easier accessible ionization stage is the second for TDAE and the first for TCNE.

The salts of $TDAE^{2+}$ are reviewed in Table 2.

Table 2. Octamethyl oxamidinium salts $[TDAE]^{2+}X_2^-$.

X	M.p. (°C)	Color	Soluble in H_2O	Ref.
Cl	166	colorless	+	[26]
Br	263	colorless	+	[1,25,26,27]
I [a]	257	lemon yellow	+	[18]
BF_4	273	colorless	−	[25, 26, 30]
PF_6	278	colorless	−	[25, 26]
ClO_4	294–297	colorless	−	[27–30]
NO_2	209	cream	÷	[30]
NO_3	266	colorless	+	[30]
$Co(CO)_4$ [b]	[c]	orange	?	[31]
$V(CO)_6$	[c]	brown	?	[31]
$Mo(CO)_3Cp$	171–173	orange brown	−	[31]
$W(CO)_3Cp$	152–153	red	?	[31]
$Mo(CO)_3(C_9H_7)$ [d]	?	brown	−	[31]
Picrate	200	ocher	−	[25, 26]
TCNE	125–127	violet black	−	[26]
$C(NO_2)_3$	122–124	?	−	[30]

[a] Polyiodides TDAE $[I_n]$ (n = 4, 5, 7) can also be obtained [26].

[b] TDAE$[Fe(CO)_4]$ cannot be prepared, since $TDAE^{2+}$ is reduced by $Fe(CO)_4^{2-}$ [38].

[c] No definite m.p.

[d] C_9H_7 = indenyl.

The TDAE salts are obtained by oxidation of TDAE *e.g.* with Hal_2, $CHal_4$, and $Co_2(CO)_8$ in organic solvents or by metathetic reaction from $TDAE(Hal)_2$. TDAE evidently reacts with carbon compounds CX_4 in accordance with reaction (7).

$$TDAE + CX_4 \rightarrow TDAE^{2+}X^-CX_3^- \qquad (7)$$

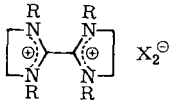
(3)

The salt *(3)* is stable when X = NO_2; it can be decomposed by water into water-insoluble $TDAE[C(NO_2)_3]_2$ and water-soluble $TDAE(NO_2)_2$ [30]. When X = Hal, *(3)* is unstable; the basic $CHal_3^-$ ion removes a proton from the $TDAE^{2+}$ (see below) or loses a halide ion to form $CHal_2$ [29]. For example, TDAE and CCl_4 give $TDAE(Cl)_2$ and $CHCl_3$ in high yields, together with other products that have not been investigated. The reaction of polyhalogenoethanes with TDAE [29] leads to dehalogenation with formation of polyhalogenoethylenes. For example, tetrachloroethylene is formed in a high yield, together with $TDAE(Cl)_2$, from hexachloroethane and TDAE [29].

Special mention should be made of octamethyloxamidinium bis (tetracyanoethylenide), $TDAE(TCNE)_2$, which precipitates out when solutions of TDAE and TCNE in acetonitrile are mixed at 0 °C. According to IR, NMR, UV, and ESR spectroscopic results and chemical investigations, this compound has a salt-like structure [26]: $TCNE^-$ $TDAE^{2+}$ $TCNE^-$. The curious reaction of TDAE with TCNE again illustrates the difference in the redox behavior [reactions (5) and (6)] of the two systems. It should also be noted that a complete electron transfer between two ethylene derivatives has been achieved in $TDAE(TCNE)_2$.

Like TDAE, 1,1′,3,3′-tetraorganyl-2,2′-biimidazolidinylidenes *(1)* can also be converted into dications (Table 3).

Table 3. 1,1′,3,3′-Tetraorganyl-2,2′-biimidazolidinylidene salts.



R	X	Color	Ref.
C_6H_5	Cl	yellow	[32, 33]
C_6H_5	Br	yellow	[32, 33]
C_6H_5	I	orange red	[16, 33]
C_6H_5	NO_3	yellow	[16]
C_6H_5	ClO_4	yellow	[16]
C_6H_5	BF_4	yellow	[10, 34]
C_6H_5	TCNE [a]	?	[35]
p-CH_3—C_6H_4	NO_3	orange yellow	[17]
Alkyl	Br, I	?	[12]

[a] TCNE is present in the first reduction stage.

The reverse process, *i.e.* the reduction of $TDAE^{2+}$, can be achieved with strong reducing agents such as zinc dust [26] or $Na_2Fe(CO)_4$ [38]. The diiodide of *(1a)* can even be discharged with silver to form *(1a)* [16]. Thus equation (5) represents a true redox equation; the oxidation process in (5) could be formally compared to the ionization of a metal:

$$TDAE \underset{\text{Red.}}{\overset{\text{Oxid.}}{\rightleftharpoons}} TDAE^{2+} + 2e$$

$$Mg \underset{\text{Red.}}{\overset{\text{Oxid.}}{\rightleftharpoons}} Mg^{2+} + 2e$$

The "quasimetal" TDAE gives up two electrons from a high energy level and retains a stable "octet of electrons" in the next lower shell (cf. Section 4.1). The electrons liberated in accordance with reaction (5) can be used to produce an electric current in a special apparatus [36a].

The dications TAE^{2+} are thermally very stable, and are also resistant to water and to acids. They can, on the other hand, be attacked by bases [reaction (8)].

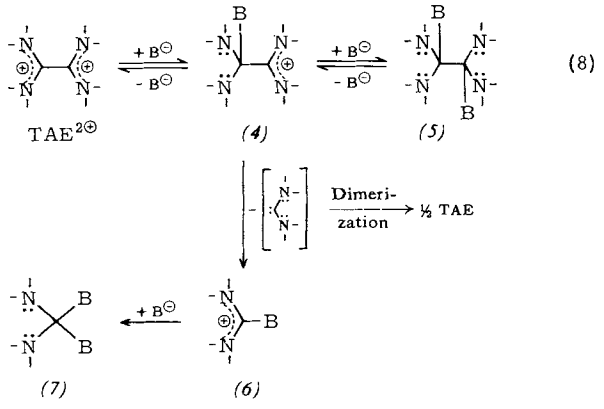
[32] *H.-W. Wanzlick, B. Lachmann,* and *E. Schikora,* Chem. Ber. *98,* 3170 (1965).

[33] *Hsi-Kuei Chiang, Chun-I Chang,* and *Yy Shih,* Hua Hsueh Hsueh Pao (Acta chim. sinica) *31,* 42 (1965); Chem. Abstr. *63,* 6993a (1965).

[34] *N. Wiberg,* unpublished.

[35] Contrary to an earlier view [6], the reaction of *(1a)* with TCNE appears to lead to a compound corresponding to TDAE $(TCNE)_2$ (*H.-W. Wanzlick,* private communication).

[36a] *W. R. Wolfe, jr.,* US-Pat. 3156587 (Nov. 10, 1964), Du Pont; Chem. Abstr. *62,* 4913b (1965).

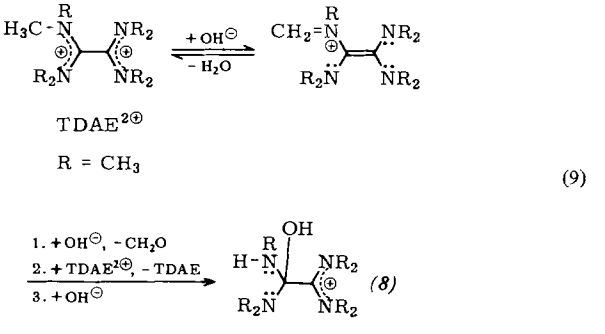


(8)

Of the compounds *(4)* and *(5)* initially formed by the addition of bases to the central carbon atoms of $TAE^{2\oplus}$, *(4)* is unstable. It formally loses the carbene $C(NR_2)_2$ (which dimerizes to give TAE (cf. Section 5)) to form the compound *(6)*, which also reacts with bases. Thus the reaction of the dinitrate of *(1)*, R = C_6H_5 or *p*-$CH_3C_6H_4$, with hydride ions ($B^- = H^-$, introduced in the form of $B(OCH_3)_3H^-$) leads to the tetraaminoethane *(5)* and the diaminoethane *(7)* in yields of 50 and 25 % respectively[10]. Unchanged tetraaminoethylene *(1)* is also formed.

Compound *(5)* is evidently formed only in the presence of extremely strong bases. If the base is only strong, *(4)* is formed and converted into *(7)* and TAE; *e.g.*, if $[TDAE]Br_2$ is heated for 5 minutes (50 °C) in 50 % sodium hydroxide solution, only tetramethylurea [—B, —B in *(7)* is =O in this case] and TDAE are formed in the expected molar ratio of 2:1[36b]. The dication of *(1)*, R = C_6H_5 or *p*-$CH_3C_6H_4$ decomposes in a similar manner in the presence of sodium hydroxide solution; however, the resulting tetraaminoethylene *(1)*, unlike TDAE, is unstable to bases and reacts further to give the *N*-formyl compound $RNH-CH_2-CH_2-NR-CHO$ *(13c)* [cf. reaction (25)]. Since the uncharged compounds TAE form the radical-cation TAE^+ reversibly with the dication TAE^{2+} (cf. Section 3.1.2), the characteristic color of TAE^+ is observed during reaction (8).

Unlike the concentrated alkali, dilute sodium hydroxide solution converts $[TDAE]Br_2$ not into tetramethylurea but into TDAE, the compound *(8)*, formaldehyde, oxalic acid bis(dimethylamide), bis(dimethylamino)methane, and dimethylamine[28]. Isotope experiments indicate that *(8)* is formed from $TDAE^{2+}$ in accordance with reaction (9), with simultaneous formation of CH_2O and TDAE.



(9)

The other reaction products result from the hydrolysis of *(8)*. The failure of reaction (8) to occur in this case is evidently connected with the fact that the equilibrium $TAE^{2+} + B^- \rightleftharpoons$ *(4)* is strongly displaced to the left in dilute alkali.

[36b] As has been shown experimentally, no free carbenes occur in this reaction (cf. Section 5). The carbenes must therefore dimerize during the reaction. *D. M. Lemal* proposes the reaction sequence 2 *(4)* → *(4)* − *(4)* → 2 *(7)* + TAE [7], and *R. W. Hoffmann* the sequence *(5)* + TAE^{2+} → 2 *(7)* + TAE.

3.1.2. The Tetraaminoethylene Radical Cation

The intermediate in the complete oxidation of tetrakis(dimethylamino)ethylene to $TDAE^{2+}$, the radical-cation $TDAE^+$, can also be prepared; it is formed as the only detectable particle in the mass spectrograph *e.g.* of TDAE at an electron collision potential of 6.5–8.0 eV (TDAE is increasingly fragmented at collision potentials >8.5 eV; rather oddly, however, no strong peak is found for the dication $TDAE^{2+}$[38]). Moreover, the ESR spectrum of a dilute solution of the compound $TDAE(TCNE)_2$ in acetonitrile indicates the existence of the cation $TDAE^+$, since the background of the $TCNE^-$ nonet contains many small signals (multiplet) due to the $TDAE^+$ cation, which is present in equilibrium with $TDAE^{2+}$ in accordance with reaction (10)[38] (cf. Section 3.1.3).

$$TDAE^{2+} + 2\,TCNE^- \rightleftharpoons TDAE^+ + TCNE^- + TCNE \qquad (10)$$

Kuwata and *Geske*[27] obtained the radical-cation $TDAE^+$ by the coproportionation reaction (11).

$$TDAE + TDAE^{2+} \rightleftharpoons 2\,TDAE^+ \qquad (11)$$

The orange solution of the cation $TDAE^+$ ($\lambda_{max}^{CH_3CN}$ = 385 nm) obtained from TDAE $(ClO_4)_2$ and TDAE in dimethylformamide gives an ESR spectrum with a multiplet consisting of 300 signals (line width: 0.04 G, cf. Section 4.2). The equilibrium constant for reaction (11) is 2.3×10^2, *i.e.* 89 % of $TDAE^+$ exists in equilibrium with 5.5 % of TDAE and 5.5 % of $TDAE^{2+}$[39]. The half-wave potentials ε_0 are[27]:

$$TDAE \rightarrow TDAE^+ + e \qquad \varepsilon_0 = -0.75\ V$$

$$TDAE^+ \rightarrow TDAE^{2+} + e \qquad \varepsilon_0 = -0.61\ V$$

The radical-cation is surprisingly stable. For example, the ESR spectrum of $TDAE^+$ in dimethylformamide does not change when the solution is heated to 120 °C.

The partial oxidation of *(1a)* with iodine, Ag^+, or the dication of *(1a)* gives the violet radical-cation of *(1a)* ($\lambda_{max}^{CH_3CN}$ = 517 nm), which, unlike $TDAE^+$, gives only a single broad ESR signal (line width: 5.4 G)[16]. Solutions of the monocation of *(1a)* in acetonitrile satisfy the Beer-Lambert law[7]; the radical-cation therefore does not dimerize with increasing concentration.

The distinctly negative potential of TDAE (which roughly corresponds to the standard potential of zinc: $Zn \rightarrow Zn^{2+} + 2e$; $\varepsilon_0 = -0.76$ V) is a quantitative indication of the electron-donor character of the tetraaminoethylene system. The surprisingly low appearance potential of TDAE in comparison with those of other tetrasubstituted ethylenes also confirms that the atomic grouping $(\rangle N)_2C{=}C(N\langle)_2$ is an "electron-rich" system. The appearance potentials of ethylene, tetramethylethylene, and TDAE are 10.5, 8.4, and <6.5 eV respectively.

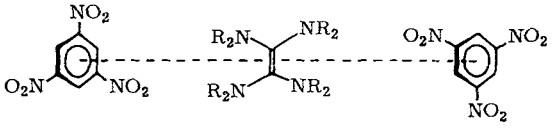
[37] *J. P. Paris*, Photochem. and Photobiol. *4*, 1059 (1965).

[38] *N. Wiberg* and *J. W. Buchler*, unpublished.

[39] The equilibrium (11) cannot be established unless TDAE and $TDAE^{2+}$ are soluble in the reaction medium.

3.1.3. Electron Donor-Acceptor Complexes of Tetraaminoethylenes

The reaction of TDAE with organic molecules having a lower oxidation potential than TCNE no longer results in complete electron transfer from the donor TDAE to the organic acceptor, but leads instead to the formation of electron donor-acceptor complexes [40]. For example, reaction with trinitrobenzene (TNB) in acetonitrile yields the crystalline, blackish-red, light-sensitive, diamagnetic [42] complex $TDAE(TNB)_2$ (m.p. 84–86 °C) [41]. Spectroscopic studies characterize it as an electron donor-acceptor complex, and are compatible with a sandwich arrangement of the molecules.



$TDAE(TNB)_2$, R = CH_3

Stronger electron acceptors such as oxygen or halogen can displace the weaker electron acceptor TNB from the TDAE and so complete the oxidation of TDAE [41], *e.g.*:

$$TDAE(TNB)_2 + Br_2 \rightarrow TDAE^{2+}\ 2\ Br^- + 2\ TNB \qquad (12)$$

The difference in the electronic structure of $[TDAE^{2+}][TCNE^-]_2$ (salt) and $TDAE(TNB)_2$ (electron donor-acceptor complex) is clear from the IR, ^{1}H-NMR, and UV spectra [26, 41] (see Table 4).

Table 4. Comparison of the spectra of $[TDAE^{2+}][TCNE^-]_2$ and $TDAE(TNB)_2$.

Spectrum	$[TDAE^{2+}][TCNE^-]_2$	$TDAE(TNB)_2$
IR (in Nujol)	$TDAE^{2+}$ and $TCNE^-$ bands	no $TDAE^{2+}$ bands
^{1}H-NMR (in CH_3CN)	$TDAE^{2+}$ signals [a]	TDAE signal [b]
UV (in CH_3CN)[c]	$TCNE^-$ absorption [24]	2 new CT bands [d]

[a] Considerably broadened and displaced to higher field strengths because of the paramagnetism of $TCNE^-$.
[b] Another signal is due to trinitrobenzene.
[c] Dilute solution.
[d] Charge-transfer bands at 545 (ε = 210) and 442 nm (ε = 300).

result indicates that the ionization of $TDAE(TCNE)_2$ is reversible (formation of ion pairs and electron donor-acceptor complexes). $TDAE(TCNE)_2$ probably exists in the solid state as an electron donor-acceptor complex of the ions $TDAE^{2+}$ and $TCNE^-$, *i.e.* as a complex in which more ionic limiting structures are involved in the ground state than in the excited state ("inverse" electron donor-acceptor complex [23]).

Electron donor-acceptor complexes of tetrakis(dimethylamino)ethylene and other tetraaminoethylenes are generally formed by the action of organic molecules containing π electrons and electron-attracting substituents (*e.g.* chloranil, cyanoethylenes, nitroaromatic compounds) on tetraaminoethylenes in organic solvents [43, 43a]. The very strong organic electron acceptors form deeply colored electron donor-acceptor complexes that are stable to above 200 °C, frequently stable to air, and generally paramagnetic, and which are probably comparable in their structure to

Table 5. Strong electron donor-acceptor complexes with tetraaminoethylenes [43].

Donor (D)	Acceptor (A)	D:A	Color	Decomp. pt. (°C)
TDAE	Chloranil	1:3	green	?
TDAE	Bromanil	1:2	green	220–230
TDAE	3,4,5,6-Tetrabromo-3,5-cyclohexadiene-1,2-dione	1:1	light brown	250
Tetrapyrrolidinoethylene	3,6-Bis(dicyanomethylene)-1,4-cyclohexadiene	1:1	blue black	185
Tetrapiperidinoethylene	3,6-Bis(dicyanomethylene)-1,4-cyclohexadiene	1:1	blue black	243
1,1',3,3'-Tetramethyl-2,2'-biimidazolidinylidene	3,6-Bis(dicyanomethylene)-1,4-cyclohexadiene	1:1	deep blue	220

$TDAE(TCNE)_2$ is evidently on the borderline between a salt and an electron donor-acceptor complex. In dilute solution it must be described as salt. However, the ESR spectra of increasingly concentrated solutions of $TDAE(TCNE)_2$ in CH_3CN show that the structure of the compound changes. At concentrations of 2.6×10^{-4} and 1.3×10^{-3} mole/l, the spectra show a nonet having line widths of 0.1 and 0.2 G respectively and at 1.3×10^{-1} mole/l a singlet having a line width of 5 G [38].

By analogy with the case of tetramethyl-*p*-phenylenediamine tetracyanoethylene (TMPD) (TCNE) [23], this

$TDAE[TCNE]_2$ [44]. TDAE is also a sufficiently strong electron donor to give electron donor-acceptor complexes with very weak electron acceptors such as tetrachloroethylene [43], anthracene [43a], or acrylonitrile [41]; however, these complexes readily decompose when

[40] *G. Briegleb*: Elektronen-Donator-Acceptor-Komplexe. Springer, Berlin 1961.

[41] *N. Wiberg* and *J. W. Buchler*, Chem. Ber. *97*, 618 (1964).

[42] In solution. In the solid state, the complex exhibits weak electron spin resonance at $g = 2$.

[43] *H. E. Winberg*, US-Pat. 3239518 (March 8, 1966), Du Pont; Chem. Abstr. *64*, 15898c (1966).

[43a] *P. R. Hammond* and *R. H. Knipe*, J. Amer. chem. Soc. *89*, 6063 (1967).

[44] Electron donor-acceptor complexes in which substantial transfer of the electrons from the donor to the acceptor has occurred are paramagnetic or diamagnetic, according as the spins of the unpaired electrons of the donor and acceptor molecules are parallel or antiparallel. The question of whether the complex is paramagnetic or diamagnetic may depend on the state (pure substance, solution), the nature of the solvent, the concentration in a solvent, and the temperature [45].

[45] *F. Schneider*, *K. Möbius*, and *M. Plato*, Angew. Chem. *77*, 888 (1965); Angew. Chem. internat. Edit. *4*, 856 (1965).

heated. The "weak" electron donor-acceptor complexes are only "slightly" colored [TDAE$(C_2Cl_4)_n$: yellow; TDAE$(C_{14}H_{10})_n$: yellow; TDAE(acrylonitrile)$_n$: orange], and unlike the very strong complexes they must evidently be regarded as "normal" electron donor-acceptor complexes, in which the excited state involves more ionic limiting structures than the ground state.

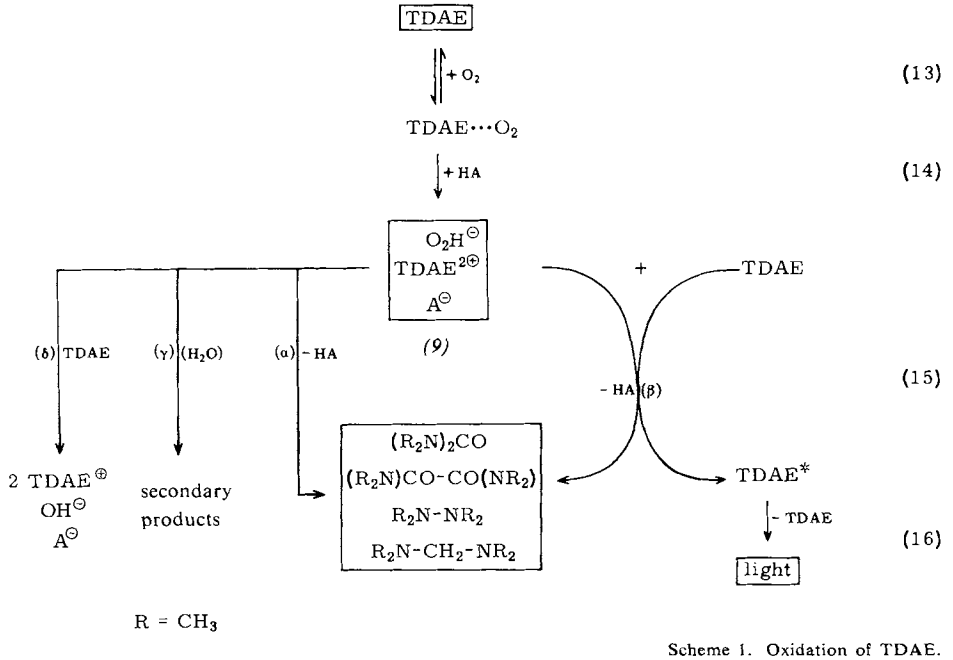
Some typical examples of strong electron donor-acceptor complexes with tetraaminoethylenes are listed in Table 5.

These complexes are not only of theoretical interest, but can also be used in practice[43], *e.g.* for the production of duplicates without the use of carbon paper. A sheet of paper impregnated with a TAE donor and another impregnated with a π acceptor are brought together, and the top sheet is written on with a hard pencil; the colored electron donor-acceptor complex appears where pressure was applied. The complex can also be used as a pigment for colored inks. Writing executed in such inks can be readily thermographically reproduced, since the complexes, unlike the pigments of most ordinary inks, absorb strongly between 500 and 2000 nm.

3.1.4. Autoxidation of Tetraaminoethylenes

Tetrakis(dimethylamino)ethylene reacts vigorously with oxygen in the presence of protonic compounds, with emission of pale green chemiluminescence; the products (based on the TDAE initially present) are 68 % of tetramethylurea, 16 % of oxalic acid bis(dimethylamide), 10 % of tetramethylhydrazine, and 4 % of bis(dimethylaminomethane)[28]. Many investigations[12,28,37,46–50] have been aimed at the elucidation of this unusual reaction. The investigations by *Urry* and *Sheeto*[28] and by *Flechter* and *Heller*[49] will now be discussed in some detail.

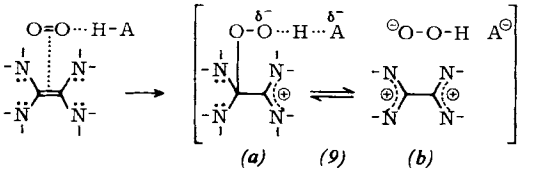
The oxidation of pure tetrakis(dimethylamino)ethylene dissolved in organic solvents or emulsified in water can be best represented by Scheme 1.



Scheme 1. Oxidation of TDAE.

Reaction (13): Colorless dilute solutions of TDAE in *n*-decane turn brown when oxygen is introduced[46]: a fast reaction leads to a low equilibrium concentration of an electron donor-acceptor complex TDAE$\cdots\cdots O_2$ (broad absorption maximum at $\lambda = 450$ nm, enthalpy of formation $\Delta H \approx -1.2$ kcal), which in vacuum can be reversibly decomposed into TDAE and O_2 at 0 °C.

Reaction (14): In the presence of protonic compounds HA (alcohol, water, silanol, acetylene, *etc.*), the complex TDAE$\cdots\cdots O_2$ changes irreversibly into *n*-decane[46]: the molecules HA induce an electron transfer from TDAE to the oxygen[51].



(14)

The oxidation to *(9)* takes place only in the presence of protonic compounds[49,50]. Corresponding to their catalytic function, the HA molecules are not consumed, except in oxidations of concentrated TDAE solutions; according to their activity and their concentration, they regulate the rate of the process (14), which evidently determines the rate of the

[46] *C. A. Heller* and *A. N. Flechter*, J. physic. Chem. *69*, 3313 (1965).

[47] *A. N. Flechter* and *C. A. Heller*, J. Catalysis *6*, 263 (1966).

[48] *A. N. Flechter* and *C. A. Heller*, Photochem. and Photobiol. *4*, 1051 (1965).

[49] *A. N. Flechter* and *C. A. Heller*, J. physic. Chem. *71*, 1507 (1967).

[50] *H. E. Winberg*, *D. R. Downing*, and *D. D. Coffman*, J. Amer. chem. Soc. *87*, 2054 (1965).

[51] The question of whether the zwitterion *(9a)* [28] or the ion pair *(9b)* [47, 49] is formed in inert solvents (both *(9a)* and *(9b)* must be thought of as being solvated by other molecules HA) has not been settled. Both compounds appear reasonable as products of the ionic reaction (14) on energy grounds ($\Delta F \approx -20$ kcal; free-radical reactions can be ruled out, since the oxidation of TDAE is not suppressed by free-radical interceptors [28]). Other ionic reactions, such as TDAE·$O_2 \rightarrow$ TDAE$^+O_2^-$ ($\Delta F = -0.9$ kcal) or TDAE·$O_2 \rightarrow$ TDAE$^{2+}O_2^{2-}$ ($\Delta F = +81.4$ kcal), are less likely [47].

overall reaction. The reaction (14) can even be catalyzed by the OH groups of the glass apparatus (HA = HO-glass)[52]. The complex TDAE·O_2 thus decomposes slowly in decane above 0 °C even in the absence of added substances HA, *i.e.* apparently without a catalyst.

Reaction (15), path γ: The ion pair $[TDAE^{2+}O_2H^-A^-]$ *(9)* formed in accordance with (14) can be extracted from the organic medium with water during the oxidation of TDAE. In the aqueous phase, *(9)* dissociates into the independent ions $TDAE^{2+}$, O_2H^-, and A^- (= OH^-), and $TDAE^{2+}$ can be precipitated in a high yield as the perchlorate[28]. If the cation $TDAE^{2+}$ is not precipitated, it reacts slowly in water (unlike in inert organic solvents, see below) with its basic counter-ions O_2H^- and OH^- to give the cation *(8)*, formate[53], dimethylamine, oxalic acid bis(dimethylamide), and bis(dimethylamino)methane [cf. reaction (9)].

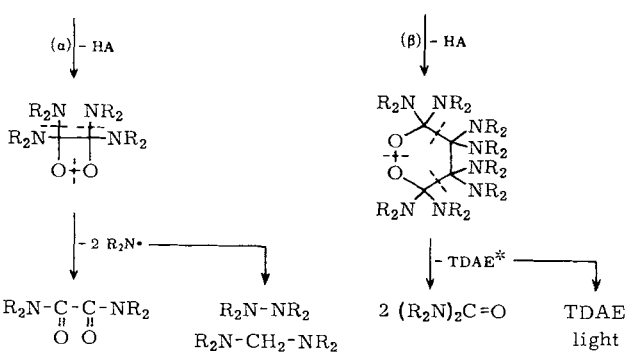
Reaction (15), path δ: In suitable solvents, the dication $TDAE^{2+}$ can also enter into an equilibrium reaction with unreacted TDAE to form the monocation $TDAE^+$ [cf. Reaction (11)]. For example, the oxidation of TDAE in alcohols is accompanied by the formation of an intensely orange solution ($\lambda_{max}^{CH_3OH}$ = 383 nm) and the appearance of ESR signals[9]. The color effect and the paramagnetism are due to the intermediate formation of $TDAE^+$.

Reaction (15), paths α *and* β: In inert solvents, the intermediate *(9)* rapidly reacts further to form the "normal" products of the oxidation of TDAE, *i.e.* tetramethylurea, oxalic acid bis(dimethylamide), tetramethylhydrazine, and bis(dimethylamino)methane. From the measured time-dependence of the intensity of the light produced during the oxidation of TDAE/*n*-decane/*n*-octanol solutions, *Flechter* and *Heller*[49] believe that the formation of the reaction products is preceded by the fast equilibrium (17)[54]:

$$\left[TDAE^{2\oplus}, O_2H^{\ominus}, A^{\ominus}\right] \underset{-TDAE}{\overset{+TDAE}{\rightleftharpoons}} \left[(TDAE)_2^{2\oplus}, O_2H^{\ominus}, A^{\ominus}\right] \quad (17)$$

(9) *(10)*

The decomposition of *(10)* (the structure of which is unknown) and of *(9)* leads to the products of the oxidation of TDAE. The formation of these products is illustrated in Scheme 2.



Scheme 2. Consecutive reactions of *(9)* in inert organic solvents [cf. Scheme 1, reactions (15α) and (15β)].

In this case the formation of tetramethylurea as a final product of the chemiluminescence reaction that proceeds *via (10)* appears probable from the following observation. The oxidation of some tetraaminoethylenes containing *N*-alkyl groups is accompanied by chemiluminescence and leads only to urea derivatives (see below)[55]. The reaction course shown in Scheme 2 is also supported by energy considerations. Thus the exothermic decomposition of *(9)* leads to high-energy amine radicals, and the exothermic decomposition of *(10)* leads to high-energy TDAE*; the simultaneous formation of $R_2N\cdot$ and TDAE* in one step consequently seems unlikely.

The formation of the complex *(10)* can be "seen" if a TDAE solution is rapidly freed from oxygen during the oxidation and allowed to solidify at −30 °C. The solid solution continues to luminesce faintly for several hours, owing to the slow (1st order) decomposition of *(10)* into TDAE* and other products. If the oxygen is withdrawn from the uncooled solution, the intensity of the chemiluminescence increases for a short time before dying away, since the quantum yield of reaction (16) is increased by the absence of the oxygen, which extinguishes the fluorescence[49].

Reaction (16): The oxidation of TDAE can proceed with emission of light (in the case of pure TDAE or solutions in hydrocarbons; λ_{max}^{decane} = 485 nm[49]) or without emission of light (*e.g.* in the solvents pyridine, tetrahydrofuran, dioxane, dichloromethane). The overall oxidation of TDAE yields 140 kcal/mole; thus the oxidation energy is easily sufficient for the emission of light wavelength ≈500 nm (57 kcal/mole of photons). The quantum yield of the reaction (16) (0.35 ± 0.05) is decreased by many substances, such as oxygen, alcohol, tetramethylurea, and oxalic acid bis(dimethylamide)[49, 57, 57a, 58]. The reason for the absence of chemiluminescence during the oxidation of TDAE in many organic solvents is probably due to the fluorescence-extinguishing action of the solvents.

All tetraaminoethylenes are sensitive to oxygen. In the case of the 1,1′,3,3′-tetraorganyl-2,2′-biimidazolidinylidenes *(1)*, the oxidation leads only to urea derivatives.

[52] This can be seen *e.g.* from the fact that the intensity of the chemiluminescence of the solution still adhering to the glass wall after pouring out the TDAE/*n*-decane solution falls only to about 20% of its original value [47].

[53] Secondary product of the oxidation of CH_2O with O_2H^-.

[54] Over a wide concentration range, the intensity of the chemiluminescence is proportional to the square of the TDAE concentration. Thus two molecules of TDAE are involved in the formation of electronically excited TDAE (= TDAE*). Since it has been conclusively shown that only one type of excited molecule is formed, *i.e.* TDAE* (identity of the chemiluminescence spectrum with the fluorescence spectrum of TDAE), TDAE* must be formed on oxidation of a complex containing two molecules of TDAE [49]. The equilibrium (17) thus expresses the experimental observation that the yield of excited molecules TDAE* increases with increasing TDAE concentration, since the equilibrium (17) must be displaced to the right with increasing TDAE concentration.

[55] The configuration of excited TDAE*, which is certainly different from that of TDAE in the ground state (cf. Section 4.3) [49, 50], could be approximately formed in the complex *(10)* or a secondary product. According to *Chandross* and *Sonntag* [56], similarity between the configurations of the reactant and the excited product increases the probability of chemiluminescence.

[56] *E. A. Chandross* and *F. I. Sonntag*, J. Amer. chem. Soc. *88*, 1089 (1966).

[57] *H. E. Winberg*, US-Pat. 3264221 (Aug. 6, 1966), Du Pont; Chem. Abstr. *65*, 13000f (1966).

[57a] *W. R. Carpenter* and *E. M. Bens*, US Clearing House Federat. Sci. Tech. Inform. AD 806625; Chem. Abstr. *68*, 104362q (1968).

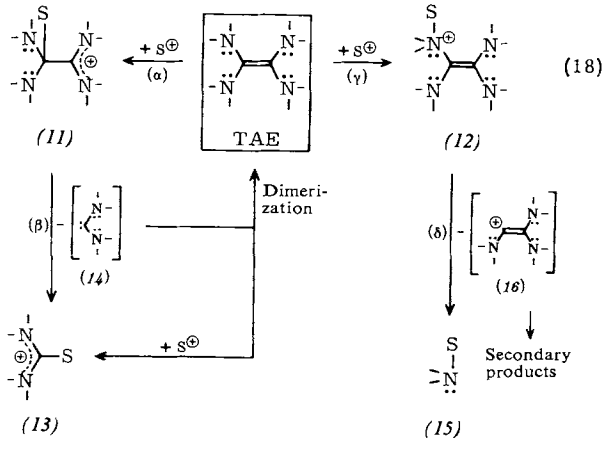
[58] For example, if 1–2 mole-% (based on the TDAE) of tetramethylurea or oxalic acid bis(dimethylamide) are added to chemiluminescing pure TDAE, the chemiluminescence is completely suppressed [50, 57]. The chemiluminescence is restored on extraction of the reaction mixture with water, which is immiscible with TDAE, but dissolves tetramethylurea and oxalic acid bis(dimethylamide).

(Similarly, compounds of the type *(1)* react with sulfur (S_8) to give thioureas[12, 59, 60]). However, chemiluminescence has been observed only in the oxidation of 1,1′,3,3′-tetraalkyl-2,2′-biimidazolidinylidenes (*e.g.* for *(1)*, R = C_2H_5: $\lambda_{max}^{cyclohexane}$ = 506 nm[12]).

The high sensitivity of TDAE and other tetraaminoethylenes to oxygen and their ability to chemiluminesce in the presence of oxygen can be used *e.g.* for the removal of traces of oxygen[14, 22], for the detection of traces of oxygen[6], for the quantitative determination of oxygen (quantitative determination of the carbonyl compounds formed)[14, 22], or for the production of light[61, 61a]. It has also been suggested[14, 22] that TDAE should be used as a high-energy rocket fuel.

3.2. Acid-Base Reactions

Tetrakis(dimethylamino)ethylene and other tetraaminoethylenes react vigorously, often at room temperature, with Brønsted and Lewis acids S. The TAE system donates either the pair of π electrons from the carbon atoms (α) or the four (nonbonded) n-electron pairs of the four nitrogen atoms (γ) to the acids [reaction (18)].



(18)

This reaction type formally also includes the additions of acceptor molecules (π acids) to the complete system of π- or n-electrons of the base TAE to form electron donor-acceptor complexes (cf. Section 3.1.3). The formation of electron donor-acceptor complexes is an illustration of the fact that it is often impossible to distinguish oxidations from acid-base reactions.

The products *(11)* and *(12)* initially formed by the addition of acid to the TAE system are unstable, and react further to give secondary products. Thus the electrophilic attack of S leads in most cases to cleavage of the C=C (β) or C–N (δ) bond; the products include compounds of the type *(13)* or *(15)* (formamidinium cations or amines, when S=H^+).

According to a suggestion by *Lemal*[7, 17], the C=C bond is cleaved by path (18α), (18β), the intermediate *(11)* losing a diaminocarbene *(14)* to form the compound *(13)*. *(14)* can then dimerize or react with the acid S to give *(13)*. It is not certain whether the carbene is formed as such or is simply transferred during the step β in accordance with

$$2\,(11) \rightarrow 2\,(13) + \text{TAE}$$

or

$$(11) + S \rightarrow 2\,(13)$$

However, cleavage of the double bond in an equilibrium

$$\text{TAE} \rightleftarrows 2\,(14)$$

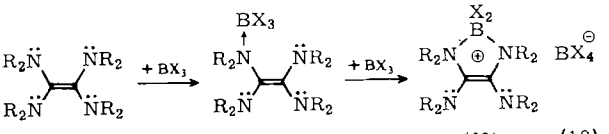
can be definitely ruled out (cf. Section 5). Since the ion *(11)* is also formed when the base B^- is added to the dication TAE^{2+}, it is not surprising that TAE^{2+} is converted into *(13)* and TAE (or its reaction products with bases) by bases [cf. reaction (8), *(4)* and *(5)*].

The cleavage of the C–N bond is probably initiated by the reaction sequence (18γ), (18δ)[62], the hypothetical cation *(16)*, as well as the carbene *(14)*, possibly being resonance-stabilized[63]. The secondary reactions of cation *(16)* are very complex (cf. Section 3.2.2), and have not been elucidated in detail[64].

Reactions with acids leading to stable addition compounds will be discussed first. Reactions with acids involving cleavage of the C–N or C=C bond of the tetraaminoethylene system are then described.

3.2.1. Addition of Acids to Tetraaminoethylenes

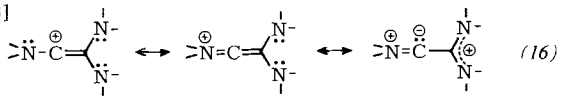
Whereas no stable addition products of Brønsted acids (S = H^+) with the TAE system have been obtained[66], adducts with Lewis acids can be isolated as such. Thus boron trifluoride and diborane (S = BX_3; X = F, H) react by a multistep process (19) to give the salt *(18)*, whose cation, according to spectroscopic and chemical investigations, is cyclic[62].



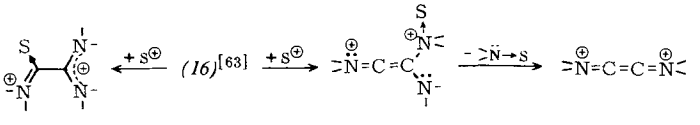
(19)

The cation in *(18)* (X = F), whose fluorine atoms are not substituted on reaction with phenylmagnesium bromide, differs from TDAE in its high thermal stability and stability to solvolysis and oxidation. The dimethylamino groups can be

[62] *N. Wiberg* and *J. W. Buchler*, Chem. Ber. *96*, 3000 (1966).

[63]  *(16)*

[64] It may be assumed that the secondary reactions are introduced by the addition of acid to a carbon or nitrogen atom of *(16)* (cf. Section 3.2.2 and [63,65]):



[59] *H.-W. Wanzlick*, *H. Ahrens*, *B. König*, and *M. Riccius*, Angew. Chem. *75*, 685 (1963); Angew. Chem. internat. Edit. *2*, 560 (1963).

[60] *H.-W. Wanzlick* and *B. König*, Chem. Ber. *97*, 3513 (1964).

[61] *D. D. Coffman* and *H. E. Winberg*, US-Pat. 3239406 (March 8, 1966), DuPont; Chem. Abstr. *64*, 16090h (1966).

[61a] *E. T. Cline*, US-Pat. 3236698 (March 16, 1967), Du Pont; Chem. Abstr. *67*, 16684v (1967).

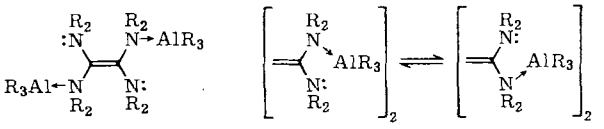
[65] *H. G. Viehe*, Angew. Chem. *79*, 744 (1967); Angew. Chem. internat. Edit. *6*, 767 (1967).

[66] When S = H^+ in reaction (18), *(11)* and *(12)* evidently decompose rapidly with cleavage of the C–C or C–N bond (cf. Sections 3.2.2 and 3.2.3).

removed only with concentrated hydrochloric acid, and $KMnO_4$ is necessary for oxidation of the compound [67].

The indicated path for the formation of the compound *(18)* *via* the intermediate *(17)* is shown by the reaction of TDAE with zinc chloride (S = $ZnCl_2$), since the reaction stops in this case at the stage of the primary addition product TDAE·$ZnCl_2$. The lability of TDAE·$ZnCl_2$ (luminesces in air, yields ZnO and [TDAE]Cl_2 on careful autoxidation) and the very strong double bond stretching vibration [68] oppose the structure *(18)* with $ZnCl_2$ instead of BX_2 for this adduct [38].

Unlike trimethylboron [62], trimethylaluminum [S = $Al(CH_3)_3$] reacts with TDAE at room temperature, again to form a 2:1 adduct [69]. This adduct is not, however, an analog of the salt *(18)*, X = CH_3, as is clear even from the low sublimation point of TDAE·[$Al(CH_3)_3]_2$ (60 °C/0.05 torr) in comparison with *(18)* [m.p. 200 °C/(dec.)]. The ^{1}H-NMR spectrum contains two proton signals of equal area for the



(19) *(19a)* *(19b)*

R = CH_3 (20)

N-methyl protons and only one signal for the *Al*-methyl protons. This leads to the structure *(19)* with two molecules of $Al(CH_3)_3$ bound to the TDAE in the same manner. Rather surprisingly the two *N*-methyl proton signals fuse when the recording temperature is raised from 3 to about 50 °C. *Mole* [70] explains this effect by a rapid change in the coordination of the aluminum from one nitrogen atom to the other in accordance with reaction (20); the life of *(19a)* or *(19b)* at 50 °C should be short in relation to the "exposure time" in the NMR spectrometer [71].

As well as 1:1 and 2:1 adducts of Lewis acids with TDAE, 4:1 adducts evidently also exist, as is shown by the complex TDAE[$TiF_4]_4$ described by *Muetterties* [73], which has not been investigated in detail.

No products formed by the addition of acid to the carbon atoms of the TAE system have been obtained, though such adducts should in fact have a certain stability, since the positive charge on the system after the addition of the acid can be stabilized by resonance [cf. *(11)*] [74].

[67] *N. Wiberg* and *J. W. Buchler*, J. Amer. chem. Soc. *85*, 243 (1963).

[68] This indicates asymmetrically substituted TDAE; the band ν(C=C), as expected, is absent or very weak for TDAE and *(18)*.

[69] *N. R. Fetter* and *D. W. Moore*, Canad. J. Chem. *42*, 885 (1964).

[70] *T. Mole*, Chem. and Ind. *1964*, 281.

[71] *Schmidbaur* and *Wolfsberger* [72] recently reported a similar case of a complex with an oscillating coordinate bond.

[72] *H. Schmidbaur* and *W. Wolfsberger*, Angew. Chem. *79*, 411 (1967); Angew. Chem. internat. Edit. *6*, 448 (1967).

[73] *E. L. Muetterties*, J. Amer. chem. Soc. *82*, 1082 (1960).

[74] Adducts of acids to one of the ethylenic carbon atoms are, however, known in the case of 1,2-diaminoethylene-1,2-dithiols [75].

3.2.2. Cleavage of the C–N Bond of Tetraaminoethylenes with Acids

The compounds formed by the addition of acids to the TAE system are unstable in many cases. Thus an unstable adduct is first formed with the Lewis acid boron trichloride (S = BCl_3) [62]. Unlike the boron trifluoride adduct *(17)*, however, this rapidly decomposes to form dimethylaminoboron dichloride in accordance with the overall equation

$$\text{TDAE} + 2\ BCl_3 \longrightarrow \approx {}^4/_5\ (CH_3)_2NBCl_2 + \approx {}^1/_2\ TDAE^{2+} \quad 2\ Cl^- + \text{tars} \qquad (21)$$

Trimethylborane [S = $B(CH_3)_3$] reacts slowly with TDAE at 150 °C with cleavage of C–N bonds to form $(CH_3)_2N-B(CH_3)_2$. The decomposition is evidently introduced in both cases by the reaction (18γ), (18δ). Another interesting reaction is that of TDAE with methyl iodide, which leads to $(CH_3)_4NI$, [TDAE]I_2, and $[(CH_3)_3N-CH_2-CON(CH_3)_2]\ I$ [76].

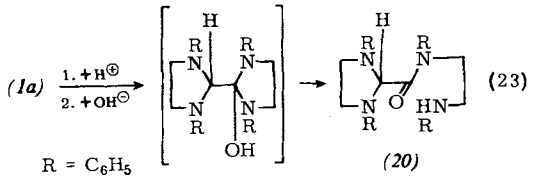
No explanation has yet been found for the formation of the dication $TDAE^{2+}$ in the decomposition of TDAE with BCl_3 (up to 50 % yield) and with CH_3I. $TDAE^{2+}$ salts are also formed in yields of up to 13 % (based on the TDAE used) in the reaction of TDAE with BF_3 or $ZnCl_2$ [but not with BH_3 or $B(CH_3)_3$]. The reaction of tetraphenyl-2,2′-biimidazolidinylidene *(1a)* with BF_3 also leads to dications [34].

TDAE reacts with the Brønsted acid hydrogen chloride (S = H^+) to form dimethylamine together with glyoxalic acid dimethylamide and [TDAE]Cl_2, probably by the reaction sequence (18γ), (18δ) [77]

$$\text{TDAE} \xrightarrow{H_2O/HCl} (CH_3)_2NH_2Cl + \approx {}^1/_2\ (CH_3)_2NCO-CHO + \approx {}^1/_4\ [\text{TDAE}]Cl_2 + ? \qquad (22)$$

Glyoxalic acid dimethylamide may be regarded as the hydrolysis product of the cation *(16)*. The oxidation mechanism is again unclear [78].

Brønsted acids of low acidity (H_2O, ROH) act on TDAE only around 160 °C (see below). The reaction rate evidently decreases rapidly with decreasing acidity of the acid used. *(1a)*, on the other hand, reacts even with concentrated sodium hydroxide solution to give cleavage of a C–N bond in accordance with reaction (23).



(1a) *(20)* (23)

R = C_6H_5

According to *Lemal* [7], the formation of *(20)* is introduced by proton addition to an ethylenic carbon atom of *(1a)*.

[75] *J. Metzger*, *H. Larivé*, *R. Dennilauler*, *R. Baralle*, and *C. Gaurat*, Bull. Soc. chim. France *1964*, 2857.

[76] *W. H. Urry*, unpublished.

[77] *N. Wiberg* and *J. W. Buchler*, Z. Naturforsch. *19b*, 9 (1964).

[78] It has been shown that the oxidation is not effected by oxygen or by protons (no H_2 is formed). In certain circumstances the cation *(16)* or a secondary product of *(16)* (dication?, cf. [64]) accepts the electrons from TDAE.

3.2.3. Cleavage of the C=C Bond of Tetraaminoethylenes by Acids

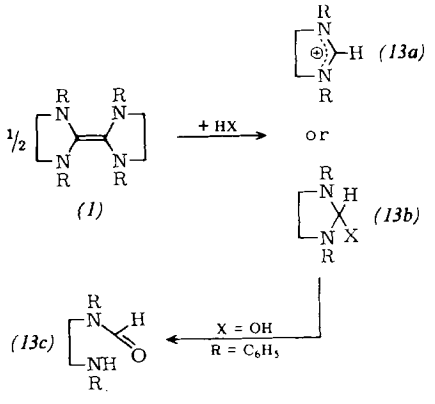
Tetrakis(dimethylamino)ethylene reacts quantitatively with water at 160 °C to form dimethylamine and dimethylformamide [77].

$$TDAE + 2\,H_2O \rightarrow 2\,(CH_3)_2NH + 2\,(CH_3)_2N{-}CHO \qquad (24)$$

No other reactions in which the C=C bond of TDAE is cleaved by acids are known [79].

The reaction of 1,1',3,3'-tetraorganyl-2,2'-biimidazolidinylidenes *(1)* with acids, on the other hand, leads preferentially to cleavage of the C=C bond. Thus acids evidently preferentially attack TDAE on the nitrogen atoms, but *(1)* on the ethylenic carbon atoms.

Thus reactions of *(1)* with Brønsted acids [apart from the case of (23)] lead to the compounds *(13a)*, *(13b)*, or *(13c)* probably by the path (18α), (18β).

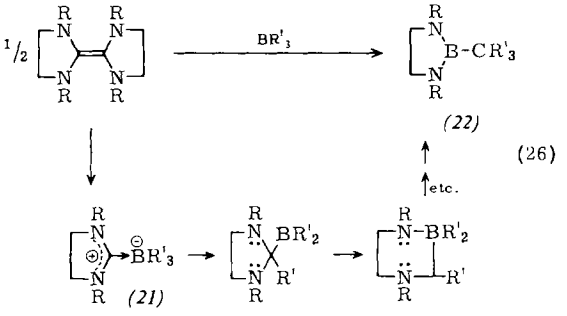


For example, the reaction of *(1a)* with hydrochloric acid (HX = HCl) leads to *(13a)* (containing the formamidinium grouping), and the reactions with methanol (HX = $HOCH_3$) or CH acids (HX = HC<) lead to *(13b)* (aminal) [6, 80–82]. The reaction with aqueous pyridine (HX = HOH) proceeds in accordance with equation (25), with cleavage of both the C=C and the C–N bonds and formation of the *N*-formyl compound *(13c)* [6]. Special mention should be made of the reaction of TDAE and *(1a)* with water, the course of which appears to be decided by the pH (cf. Table 6).

Table 6. Reaction of tetraaminoethylenes with water with retention (ret.) or cleavage (cl.) of the central C–C bond (reaction equations in parentheses).

Medium	TDAE	*(1a)*
acidic	ret. (22)	cl. (25)
neutral	cl. (24)	cl. (25)
alkaline	no reaction	ret. (23)

Lewis acids also react readily with compounds of the type *(1)* in accordance with the reaction sequence (18α), (18β). Thus carbonyl and thiocarbonyl functions can be made to react with *(1)* with cleavage of the central C=C bond [6, 52, 81, 83]. Electrophilic diazo compounds and azides react with *(1)* [53, 83–85]. Finally, an interesting course is followed by the reaction of *(1a)* with trialkylboranes [86]. The trialkylborane-carbene complex *(21)* expected from reaction (26) evidently rearranges in a multistep reaction to give *(22)*.



R = C_6H_5; R' = CH_3, n-C_4H_9, CH_2-C_6H_5

The difference in the behavior of TDAE and compounds of the type *(1)* toward acids is also seen in the reaction with trialkylboranes. TDAE reacts with BR_3 with cleavage of C–N bonds (cf. Section 3.2.2). A detailed discussion of reactions leading to cleavage of the C=C double bond may be found in ref. [8].

4. Structure of Tetraaminoethylenes

Our knowledge of the structure of tetraaminoethylenes in the charged, uncharged, or excited state is still very poor. The only compound of this class that has been studied in any detail is tetrakis(dimethylamino)-ethylene.

The foregoing discussions show that TDAE is a strong electron donor. This is also shown by a simple HMO calculation [34], the results of which are summarized in Figure 1 and in Table 7 and discussed below together with experimental data.

4.1. Electron Donor Strength of the Tetraaminoethylenes

Figure 1 shows how the energies of the six π molecular orbitals of the system $(\ddot{N})_2C{=}C(\ddot{N})_2$ varies with the parameter h (which takes into account the difference in the ionization energies of carbon ($\alpha_C = \alpha$) and nitrogen (α_N) in accordance with $\alpha_N = \alpha + h\beta$). The six energy levels (thick horizontal lines) $E = \alpha + m\beta$ (m = 2.69, 2.14, 1.50, 1.50, –0.19, –1.64) are then obtained for the value h = 1.5 recommended in [87]. As expected, two electrons occupy a high-

[79] TDAE is reported to react with CH_3OH to form $[(CH_3)_2N]_2CH(OCH_3)$. *H. E. Winberg*, unpublished.

[80] *H.-W. Wanzlick* and *H. Ahrens*, a) Chem. Ber. *99*, 1580 (1966); b) Liebigs Ann. Chem. *693*, 176 (1966).

[81] *H.-W. Wanzlick* and *J.-J. Kleiner*, Chem. Ber. *96*, 3024 (1963).

[82] *H.-W. Wanzlick* and *H. Ahrens*, Chem. Ber. *97*, 2447 (1964).

[83] *H. E. Winberg* and *D. D. Coffman*, J. Amer. chem. Soc. *87*, 2776 (1965).

[84] *H. Reimlinger*, Chem. Ber. *97*, 3503 (1964).

[85] *H. Quast* and *S. Hünig*, Chem. Ber. *99*, 2017 (1966).

[86] *G. Hesse* and *A. Haag*, Tetrahedron Letters *1965*, 1123.

[87] *A. Streitwieser*: Molecular Orbital theory. Wiley, New York 1961.

energy antibonding molecular orbital (b_{1u}), and can therefore be readily removed from the TAE system. Consequently, the ionization energy of TDAE (<6.5 eV)[38] is significantly lower than that of ethylene (10.5 eV). The electron donor character of TDAE is also demonstrated quantitatively by the oxidation potential (Table 7).

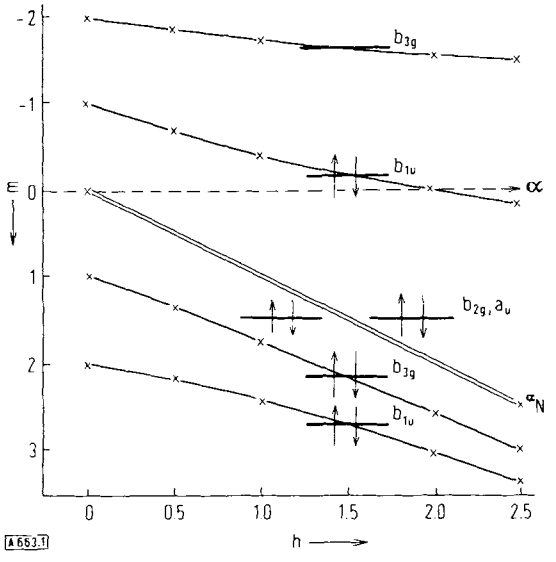
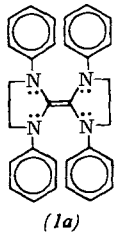
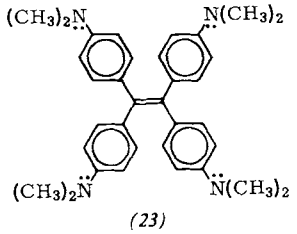


Fig. 1. π energy level scheme of the tetraaminoethylene system.

The HMO scheme also permits the comparison of the electron donor TDAE with other donors of similar structures. As the size of a carbon π system increases, the energy of the first antibonding orbital decreases. Lower donor strengths should therefore be expected for compounds derived from TDAE by the insertion of conjugated organic systems instead of the methyl groups [such as *(1a)*] the C–N bond [such as *(23)*], or the C=C bond [such as tetramethylphenylenediamine (TMPD)].



(1a)



(23)

TMPD

The monoiodide of *(1a)* can in fact be reduced even with silver[16] (Zn is required for TDAE); the half-wave potential of *(1a)* is only −0.3 V[27] (TDAE: −0.75 V). The oxidation of *(23)* with iodine is so readily reversible that in solvents having low dielectric constants, the diiodide exists in equilibrium with singly charged and uncharged *(23)* and elementary iodine[88,89]; *(23)* even exhibits a certain acceptor character, and adds on two atoms of sodium in ether [90] (TDAE does not react with lithium in diethylamine[38]). Reversible electron transfers have also been observed for the mono(tetracyanoethylenide) of TMPD, $TMPD^+$ $TCNE^-$[23,91] (→TMPD + TCNE). The ionization potential of TMPD is 6.6 V[92].

It should, however, be noted that the position of the upper b_{1u} energy level is influenced, not only by conjugative effects, but also by inductive and steric effects and by effects due to ring strain, since these factors also influence the parameter *h*. The donor strength must thus increase or decrease in accordance with Figure 1 when the dimethylamino groups of TDAE are replaced by more electropositive or more electronegative amino groups. Since methoxy groups are more electronegative than dimethylamino groups, tetramethoxyethylene should be a weaker donor than TDAE. The properties of the compound *(1a)* are undoubtedly strongly influenced by steric effects and ring strain[93].

4.2. Bonding in the System TAE^{n+} (n = 0, 1, 2)

The resonance energy of the system $TDAE^{n+}$ increases with increasing *n* (cf. Table 7). Even uncharged TDAE has the appreciable resonance energy of 24 kcal/mole if the entire system $(C_2N)_2C{=}C(NC_2)_2$ lies in a single plane. The vibration spectrum contains no IR absorption in the C=C region[9], whereas an intense $\nu_{C=C}$ band (1630 cm^{-1}) appears in the Raman spectrum[50]. This indicates that the TDAE molecule has a centrosymmetric structure. However, this does not necessarily mean that the TDAE skeleton is planar, since the dimethylamino groups could also rotate rapidly about the C–N bonds (see below and ref.[43a]). The vibration spectrum also confirms a centrosymmetric structure for $TDAE^{2+}$[34].

According to the HMO calculation, the bond order of the C=C bond decreases and that of the C–N bond increases in the order TDAE, $TDAE^+$, $TDAE^{2+}$ (Table 7). The change in the $C{-}N(CH_3)_2$ bond order can be detected in the ^{1}H-NMR spectrum. Whereas TDAE gives only one sharp proton signal at δ = −2.55 ppm[*][50] (−2.32 ppm[**][9]), the spectrum of $TDAE^{2+}$ contains two signals of equal intensity (δ = −2.90, −3.18 ppm[**], acetonitrile)[26]. The dimethylamino groups can evidently still rotate about

[88] *D. H. Anderson, R. M. Elofson, H. S. Gutowsky, S. Levine,* and *R. B. Sandin,* J. Amer. chem. Soc. *83,* 3157 (1961).

[89] *R. M. Elofson, D. H. Anderson, H. S. Gutowsky, R. B. Sandin,* and *K. F. Schulz,* J. Amer. chem. Soc. *85,* 2622 (1963).

[90] *W. Schlenk* and *E. Bergmann.* Liebigs Ann. Chem. *463,* 40 (1928).

[91] The optical spectrum of [TMPD][TCNE] solutions, unlike that of TDAE[TCNE]$_2$ solutions, changes with time, since the TCNE formed in accordance with [TMPD][TCNE] ⇌ TMPD + TCNE is consumed by side reactions.

[92] *G. Briegleb* and *J. Czekalla,* Z. Elektrochem., Ber. Bunsenges. physik. Chem. *63,* 6 (1959).

[93] A Stuart model of *(1a)* shows strong mutual steric hindrance of the phenyl groups.

[*] TMS as internal standard.

[**] TMS as external standard.

Table 7. Experimental and calculated data for tetrakis(dimethylamino)ethylene.

		TDAE	(→)	$TDAE^+$	(→)	$TDAE^{2+}$
Ionization energy (eV)	found [a]		<6.5			
	calculated [b]		5.7			
Oxidation potential (V)	found [27]		−0.75		−0.61	
	calculated [c]		−0.44			
UV-Absorption (nm)	found	221 [46]		385 [27] [e]		205 [26]
(in solution)		270				273
	calculated [d]	330				284
Resonance energy (kcal/mole)	calculated [f]	24		47		69
Degree of bonding	found [g]	NC 1.13				1.89
		CC 1.94				1.43
	calculated	NC 1.265		1.439		1.613
		CC 1.818		1.526		1.233
Charge density (π system)	calculated	N +0.081		+0.184		+0.288
		C −0.164		+0.128		+0.421

[a] From mass spectroscopy [34].

[b] Ionization potential IP = 4.0 m + 6.5 eV [87].

[c] Oxidation potential $\varepsilon_0 = 2.05\ m - 0.05$ V [87].

[d] β = 60 kcal/mole = 2.61 eV/molecule [87].

[e] For the radical-cation of *(1)*, $\lambda^{CH_3CN} = 517$ nm [10].

[f] β = 19 kcal/mole [87].

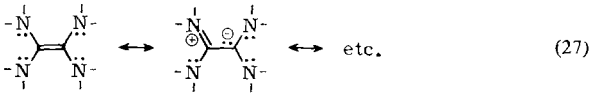
[g] Vibration spectrum (cm^{-1})

	νCC(A_g)	$\nu_s CN_2(A_g/B_{2u})$	$\nu_{as} CN_2(B_{1g}, B_{3u})$
TDAE	1630	?/1095	?/1337
$TDAE^{2+}$	1109	1541/1456	1671/1672

The following force constants have been calculated from the positions of the vibration bands [34]:
TDAE: f_{CN} = 5.80; f_{CC} = 9.4 mdyn/Å; $TDAE^{2+}$: f_{CN} = 9.71; f_{CC} = 6.85 mdyn/Å.

the C–N bond in TDAE[94], whereas they are sterically fixed in $TDAE^{2+}$ by the high C–N bond order. ESR spectroscopic studies indicate that the dimethyl amino groups in $TDAE^+$ are also fixed in the N_2C plane of the cation; thus the spectrum shows two types of hydrogen atoms in equal numbers (coupling constants a_N = 4.85 ± 0.01, $a_{H(1)}$ = 3.28 ± 0.01, $a_{H(2)}$ = 2.84 ± 0.01 G)[27]. Whereas the ESR spectroscopic studies indicate that the two N_2C halves in $TDAE^+$ lie in one plane[27], the NMR and vibration spectra of $TDAE^{2+}$ do not rule out the possibility of twisting of the N_2C halves about the central C–C bond[26]. The ESR spectrum of the compound *(1)* shows no fine structure (one signal, line width 5.4 G)[16].

The bond orders found experimentally from the vibration spectra for the CN and CC bonds (Table 7) agree with the "mobile bond orders" found from the HMO calculation. It can be seen from the table that the bond order of the TDAE double bond does not quite reach a value of 2, whereas the C–N bonds have additional double bond components. The free electron pairs on the nitrogen thus belong to the π system of TDAE:



(27)

The nitrogen accordingly also carries positive charge components and the carbon negative charge components of the π system (Table 7). However, the "mobile bond order", and hence the positive charge on the nitrogen, will be smaller than that calculated, since the HMO calculation did not take into account the rotation of the dimethyl groups around the C–N bond, which weakens the π interaction. Since the electronegative nitrogen also attracts electrons to itself *via* the σ-bond system, the nitrogen atoms in TDAE must again be regarded as negative centers of the molecule. The correctness of this view is also confirmed experimentally by the reaction of TDAE with acids (cf. Sections 3.2.1 and 3.2.2.). However, the situation is somewhat different for ethylenes of the type *(1)*, possibly because of ring strain and the impossibility of rotation of the nitrogen about the C–N bond (cf. Section 3.2.3).

[94] The energy barrier for rotation of the dimethylamino groups about the C–N bond is probably not very high since the resonance energy lost when the dimethylamino group is twisted out of the $(C_2N)_2C{=}C(NC_2)_2$ plane (max. 24 kcal/mole, see above) is counteracted by the energy gained on reduction of steric hindrance (cf. ref. [43a]).

4.3. Electronic Spectra of the System TAE^{n+} (n = 0, 1, 2)

The positions of the UV absorption maxima are given in Table 7. The UV spectrum of TDAE contains two bands: λ_{max}^{gas} = 265, 350 nm (shoulder)[50] ($\lambda_{max}^{n\text{-decane}}$ = 221, 270 nm[46]). TDAE*, life 1.9×10^{-8} sec, emits blue-green fluorescence. The position of the emission band depends on the solvent: $\lambda_{max}^{n\text{-decane}}$ = 485, $\lambda_{max}^{\text{no solvent}}$ = 505, $\lambda_{max}^{\text{dioxane}}$ = 550 nm[49]. The configuration of TDAE* is unknown. (The absorption band shows no fine structure.) It is assumed, however, that the N_2CCN_2 skeleton in TDAE* is not planar, but that the two N_2C halves are mutually perpendicular[49]. This is shown in particular by the large frequency shift of the absorption and emission bands (485–270 = 215 nm[95].) In the case of $[(C_6H_5)(CH_3)N]_4C_2$, the positions of the absorption and emission bands are almost identical[96].

According to the HMO scheme (Fig. 1), the transitions $b_{1u} \rightarrow b_{3g}$ and $b_{2g} \rightarrow b_{1u}$ in TDAE and $TDAE^{2+}$ should give absorptions in comparable positions; this is qualitatively confirmed in practice [λ (TDAE) = 221, 270; λ ($TDAE^{2+}$) = 205, 273 nm]. In view of the "rough calculation", only a very approximate agreement between the calculated and experimental UV data can be expected.

[95] ν(C=C) = 1630 cm^{-1}.

[96] *C. A. Heller*, unpublished.

Thus on the basis of the discussion in Sections 4.1–4.3, uncharged, charged, and excited TDAE probably have the structures shown in Figure 2.

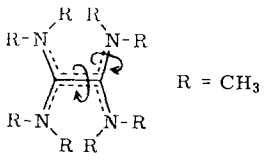
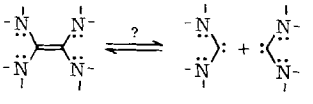


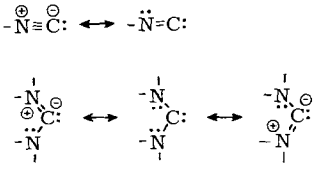
Fig. 2. Probable structures.
TDAE: rotation of the R_2N groups; $TDAE^+$: completely planar skeleton; $TDAE^{2+}$: N_2C halves may be twisted with respect to each other; $TDAE^*$: N_2C halves twisted through 90° with respect to each other.

5. The Question of an Equilibrium TAE ⇌ 2 Carbene

We shall now consider the question of whether the TAE system exists in equilibrium with two diaminocarbene halves [reaction (28)].

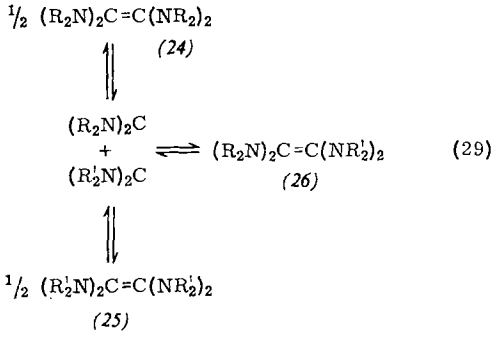

(28)

In recent years, a number of schools have been concerned with the answer to this question. The existence of carbon monoxide and of isocyanides, both of which are chemically related to diaminocarbene, and the stability of which is normally explained by resonance structures for the sake of simplicity, may be regarded as some justification for the posing of this question. If the doubly-bonded imino group in the isocyanides is replaced by two singly bonded amino groups, one obtains the carbene in question; the carbene should be more stable than the isocyanides, which can be characterized by two limiting structures, since it can be described by three limiting structures.



However, the mere fact that tetraaminoethylenes, unlike diisocyanides, actually exist shows that simple considerations of this type are not enough. Furthermore, contrary to earlier assumptions [6], a number of investigations have shown that the presence even of traces of the diaminocarbene in equilibrium with TAE can be ruled out.

Evidence against the dissociation of TDAE into bis(dimethylamino)carbene includes the mass spectrum [38], the ^{1}H-NMR spectrum [9], and chemical investigations in which attempts were made to remove the carbene from the equilibrium with TDAE by means of acceptors such as oxidizing agents or acids [62, 77]. Moreover, if traces of carbene were present in equilibrium with a tetraaminoethylene, an unsymmetrically substituted tetraaminoethylene *(26)* should be formed on reaction of two symmetrically substituted ethylenes *(24)* and *(25)*.

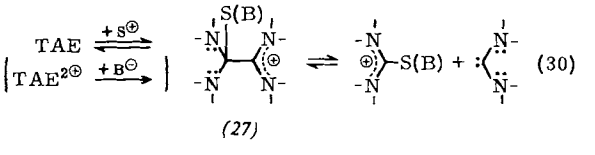

(29)

No unsymmetrical product could be detected even after reaction of TDAE and *(1a)* for one hour at 175 °C.

Attempts to obtain unsymmetrical products from *(1a)* and 1,1′,3,3′-tetra-*p*-tolylbiimidazolidinylidene [97] and from 1,1′,3,3′-tetraethyl- and 1,1′,3,3′-tetrabutyl-2,2′-biimidazolidinylidenes [12] were also unsuccessful.

An answer to the question of dissociation of TAE into carbenes can be estimated by a simple HMO examination [34]. The resonance energy of two molecules $[(CH_3)_2N]_2C$ is about 40 kcal/mole greater than that of TDAE if the Coulomb integral of the carbene carbon is taken to be approximately equal to that of the ethylenic carbon. It can also be shown by a simple HMO calculation that the resonance energy of two molecules of CF_2 is about 10 kcal/mole greater than that of $F_2C{=}CF_2$. Thus the cleavage of TDAE into carbenes is about 30 kcal/mole easier than the corresponding cleavage of tetrafluoroethylene if it is assumed as an approximation that the energy changes in the σ bond region associated with the cleavage are similar for C_2F_4 and for TDAE. Since 70 kcal/mole are required for the dissociation of C_2F_4 [98], the cleavage of TDAE into two carbenes requires about 40 cal/mole.

The formation of carbenes in the reaction of TAE with acids S^+ (Section 3.2.3) or of TAE^{2+} with bases B^- (Section 3.1.1) in accordance with reaction (30)


(30)

(27)

should, on the other hand, be energetically possible, since a new CS(B) bond is formed per CC bond broken [99].

The formation of TAE from aminals $(R_2N)_2CHX$ (cf. reaction (2)) could proceed according to

$$(R_2N)_2CHX \rightleftharpoons (R_2N)_2C + HX \qquad (31)$$

via a carbene, which could then react further in a reversal of reaction (30) or with dimerization to form TAE [100].

However, detailed studies will be required to determine whether carbenes are formed as such in reaction (30) or (31)

[97] *D. M. Lemal, R. A. Lovald,* and *K. I. Kawano,* J. Amer. chem. Soc. *86*, 2518 (1964).

[98] *J. P. Simons,* Nature (London) *205*, 1308 (1965).

[99] Cf. also [85].

[100] Cf. also *N. Wiberg* and *J. W. Buchler,* Z. Naturforsch. *19b*, 953 (1964).

or are only "transferred" in a transition complex. Evidence against the formation of free carbene in the reaction of TAE^{2+} with strong alkali is provided by the unsuccessful attempt to convert a mixture of the dibromide of TDAE and tetramorpholinoethylene into an unsymmetrical reaction product, 1,1-bis(dimethylamino)-2,2-morpholinoethylene by the action of sodium hydroxide solution [cf. reaction (8)] [101].

Though diaminocarbenes have considerable resonance stabilization, it is not sufficient for the cleavage of TAE into two carbenes. Stable carbenes are evidently formed only if both the electron vacancy and the free electron pair on the carbene carbon are chemically saturated [102]:

However, it is not yet certain whether compounds of this type (*e.g.* $R_2N^{\oplus}=C=B^{\ominus}R_2$, $R_3P=C=PR_3$, $R_2C=C=CR_2$) can still be regarded as carbenes [103].

6. Outlook

Tetraaminoethylenes are still a relatively new topic. While many surprising results for ethylene chemistry have appeared in the past six years, further surprises may be expected from these reactive compounds in the future. Apart from the practical interest that the tetraaminoethylenes deserve (*e.g.* for the qualitative and quantitative detection of oxygen and of electron acceptors with TDAE, the generation of electricity with TDAE, *etc.*), a detailed investigation of the electronic structure of TAE, TAE^{+}, TAE^{2+}, and TAE*, as well as of electron donor-acceptor complexes of tetraaminoethylene, should be of great value to the theory of π systems. However, the chemistry of tetraaminoethylenes is only a small part of the chemistry of peramino compounds of carbon. The preparation or investigation of compounds such as $(R_2N)_2C$, $(R_2N)_4C$ [105], $(R_2N)_3C-C(NR_2)_3$, and $(R_2N)C\equiv C(NR_2)$ [65] may be eagerly awaited.

I am indebted to A. N. Flechter, C. A. Heller, D. Lemal, and H. E. Winberg for valuable exchanges of information and for the communication of unpublished results. I should also like to express my gratitude to J. W. Buchler for his cooperation.

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German version: Angew. Chem. *80*, 809 (1968)
Translated by Express Translation Service, London

[101] *W. Carpenter*, unpublished

[102] Cf. also *R. A. Olofson* and *J. M. Landesberg*, J. Amer. chem. Soc. *88*, 4263 (1966).

[103] In the case of the ethylene $(C_6H_5S)_2C=C(SC_6H_5)_2$, *Seebach* [104] recently observed cleavage to a carbene.

[104] *D. Seebach*, Angew. Chem. *79*, 469 (1967); Angew. Chem. internat. Edit. *6*, 443 (1967).

[105] *H. Weingarten*, J. Amer. chem. Soc. *88*, 2885 (1966).

Memory Effects and Stereochemistry in Multiple Carbonium Ion Rearrangements [**]

BY J. A. BERSON [*]

The stereochemical configuration at the initial site of heterolysis in a carbonium ion process in solution controls the specificity of migration two steps later in many sequential multiple rearrangements. These "memory effects" are attributable to the presence on the potential energy surface of small, hitherto undetectable minima. A variety of structural, stereochemical, and isotopic marking techniques are used to demonstrate that memory effects are a general feature of the ring-expansion route to bicyclic carbonium ions. The intermediates formed in these reactions, although necessarily symmetrical or quasi-symmetrical at equilibrium, act unsymmetrically. The memory effect uses the rate of an intramolecular carbonium ion rearrangement as a calibration with which to compare the rate of symmetrization. In this way, the system functions as a sensor of sub-species.

1. Introduction

Much of our understanding of organic reaction mechanism derives historically from the search for solutions to intriguing puzzles of stereochemistry. The study of the phenomena we call "memory effects" is now at the point where experiment has progressed well beyond existing theory, and new principles therefore must emerge.

Stereochemistry controls the course of reaction not only when bond-making and bond-breaking are confined to a single carbon atomic center as, for example, in the familiar inversions that accompany nucleo-

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[**] Part of this material was presented in a lecture at the Second EUCHEM Conference on Stereochemistry (Bürgenstock, Switzerland, May 1966).

philic substitution[1], but also when the process involves a center vicinal to that at which bond-breaking is initiated, as in the neighboring group effect[2].

In multiple carbonium ion rearrangements, such control can be exercised over sites of reaction even more remote. We call these phenomena *memory effects* and recognize their existence whenever two requirements are met: (i) a bond to a configurationally specifiable center of the reactant is broken, initiating a sequence of migrations, and (ii) the configuration of this center determines which of the potential migrating groups actually moves at each stage of the multi-step process. Superficially, the specificity of migration seems to be based on "memory" in that the set of instructions (or to pursue the biological parallel, the "engram") embodied in the original configuration guides the sequence even after one of the bonds at the initiating site no longer exists.

From the purely descriptive point of view, the study of these effects opens up a broad field of new rearrangements and intriguing stereochemical phenomena. But ultimately we are concerned with mechanism, that is, with the intimate structure of the energy-reaction coordinate surface. Memory effects serve as probes for the detection of small potential energy pockets which are impalpable by other means. The structures of the subspecies that occupy these energy minima and the precise way in which the original stereochemical "engram" is processed are subjects that have not yet passed much beyond the phenomenological stage. Before examining these questions, however, we may find it useful to discuss the bases for the characteristic stereochemical phenomena of three-center displacements and neighboring group effects. Then, after a description of several experiments demonstrating memory effects, their fundamental origin can be speculated upon.

2. Theoretical Basis of Stereochemical Control in Three-Center Displacements and Neighboring Group Displacements

Bimolecular nucleophilic (S_N2) displacement occurs with Walden inversion[3], even in the face of strongly countervailing electrostatic forces as in onium salt decompositions, where an anionic nucleophile attacks a cationic substrate[4]. In sharp contrast, electrophilic substitutions, including some specifically believed to be bimolecular (S_E2)[7], frequently give retention of configuration[5, 6]. This extraordinary pattern seems to correlate with the number of electrons involved in the reacting bonds. One therefore is stimulated to seek a common quantum-mechanical basis for the two kinds of result. A treatment of the transition state by molecular orbital methods[8] provides a simple theoretical picture[9, 10].

The substitution reaction can be approached naively as a three-orbital problem; the reacting centers form an array in which the central atom (B) and its two attached groups – the substituting agent (A) and the leaving group (C) – either are disposed linearly (A–B–C) or else form an acute angle. These correspond to the transition states of reactions giving, respectively, configurational inversion or retention at B. Regardless of what orbitals are chosen for the basis set, the idealized case will be one with equal bond integrals (β) between B and both A and C. For the linear, inversion-producing relationship of these centers, one can assume a zero A–C integral, which leads to an allyl-like set of energy levels: one bonding, one non-bonding, and one anti-bonding[1b, 11].

It is not obvious why this arrangement is so favorable in the nucleophilic case (S_N2) except by comparison with the set derived from the alternative geometry, in which the A–B–C angle is acute, corresponding to front-side substitution. This inevitably will produce a non-zero bond integral ($k\beta$) between A and C. Inclusion of this off-diagonal element in the secular determinant produces a cyclopropenyl-like arrangement of energy levels, one bonding and two anti-bonding. For any given value of k, the energy of the bonding orbital of the primitive linear case is lowered by an increment Δm_b, but that of the non-bonding level is raised (to anti-bonding, see Fig. 1) by a greater amount Δm_n. Therefore, the two-electron (electrophilic) system, in which only the bonding level is occupied, will prefer the triangular geometry. In the four-electron (nucleophilic) case, the stabilization of the bonding level produced by the finite A–C interaction in the triangular system is overbalanced because the anti-bonding level is doubly occupied. The linear, inversion-producing geometry therefore is preferred for nucleophilic displacement[12]. Of course,

[1] For historical and critical reviews, see a) *C. K. Ingold*: Structure and Mechanism in Organic Chemistry. Cornell University Press, Ithaca 1953; b) *A. Streitwieser jr.*: Solvolytic Displacement Reactions. McGraw-Hill, New York 1962.

[2] For a review, see *S. Winstein*, Bull. Soc. chim. France (5) *18*, 55C (1951).

[3] *C. K. Ingold*: Structure and Mechanism in Organic Chemistry. Cornell University Press, Ithaca 1953, p. 380.

[4] a) *S. H. Harvey, P. A. T. Hoye, E. D. Hughes*, and *Sir Christopher Ingold*, J. chem. Soc. (London) *1960*, 800; b) *H. R. Snyder* and *J. H. Brewster*, J. Amer. chem. Soc. *71*, 29 (1949); c) *J. Read* and *J. Walker*, J. chem. Soc. (London) *1934*, 308; d) Inversion also occurs in onium salt formation, *S. Siegel* and *A. F. Graefe*, J. Amer. chem. Soc. *75*, 4521 (1953).

[5] *F. R. Jensen, L. D. Whipple, D. K. Wedegaertner*, and *J. A. Landgrebe*, J. Amer. chem. Soc. *81*, 1262 (1959).

[6] a) *S. Winstein* and *T. G. Traylor*, J. Amer. chem. Soc. *78*, 2597 (1956); b) *S. Winstein, T. G. Traylor*, and *C. S. Garner*, *ibid. 77*, 3741 (1955).

[7] a) *Sir Christopher Ingold*, Rec. chem. Progress (Kresge-Hooker Sci. Lib.) *25*, 145 (1964); Helv. chim. Acta *47*, 1191 (1964); b) see also *H. B. Charman, E. D. Hughes*, and *Sir Christopher Ingold*, J. chem. Soc. (London) *1959*, 2523, 2530.

[8] The argument given here is an expansion of one briefly presented elsewhere [9, 10].

[9] *E. L. Eliel, N. L. Allinger, S. J. Angyal*, and *G. A. Morrison*: Conformational Analysis. Interscience, New York 1965, p. 483.

[10] See also *J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick*, and *D. Houston*, J. Amer. chem. Soc. *89*, 2590 (1967).

[11] *H. Jaffe*, J. chem. Physics *21*, 1618 (1953).

[12] This treatment predicts that free-radical three-center displacements should show a rather low degree of stereospecificity, since the difference in energy between the linear and triangular systems in the three-electron case is small.

factors such as electrostatic forces, steric repulsions, and solvation effects, which are not taken into account by the simple LCAO approach, may dominate in some situations, but the basic quantum mechanical influences always will be at work.

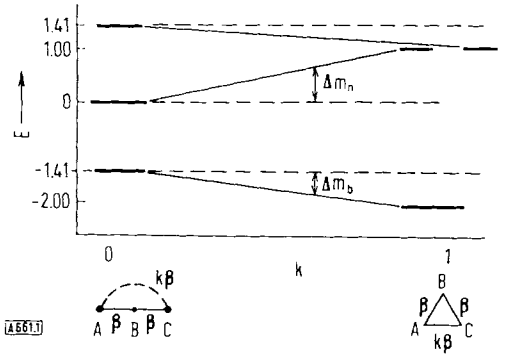
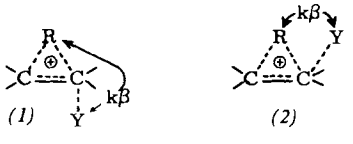


Fig. 1. Energy levels in units of β of the three-center system A—B—C as a function of the bond integral ($k\beta$) between A and C. In general, $|\Delta m_n| > |\Delta m_b|$.

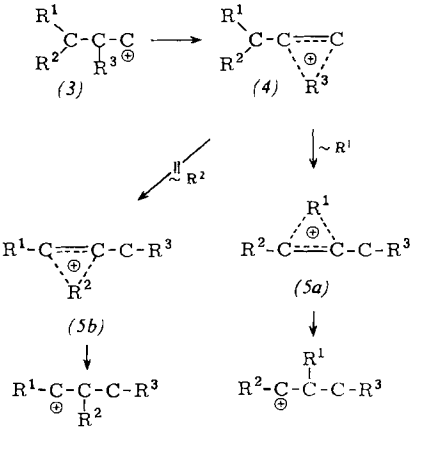
The same destabilizing effect of a front-side interaction occurs in the case of nucleophilic attack on a nonclassical carbonium ion or on the bridged intermediates responsible for the characteristic stereochemistry of neighboring group effects. These may be treated [10] as four-electron, four-center systems in which the nucleophile (Y) displaces the bridging atom (R) from a terminus of the bridge with either inversion [as in *(1)*] or retention [as in *(2)*].

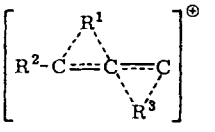


The bond integral ($k\beta$) in case *(2)* will be greater than in case *(1)*, and just as in the three-center system, the destabilization of the lowest anti-bonding level is greater than the stabilization of the bonding level.

3. Multiple Rearrangements

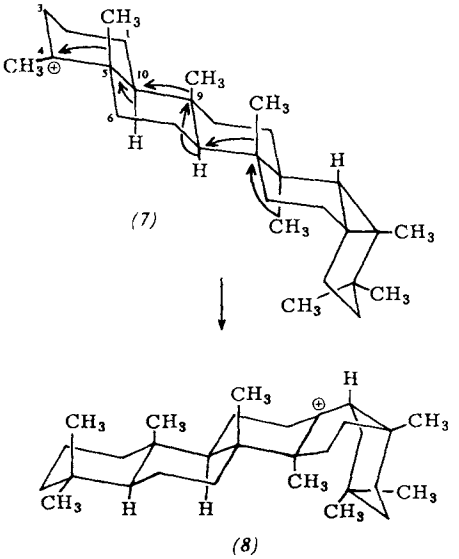
The role of Y in nucleophilic attack on bridged ions can be assumed, in a formal sense, by some internal nucleophile, such as a migrating hydrogen or alkyl group. As is borne out [10] by simple LCAO considerations, the preference for rear-side attack shown by external nucleophiles also should extend to such cases. This predicts that in the multiple rearrangement of *(3)*, shift of R^3 would be followed (or accompanied) by shift of the farther (R^1) rather than that of the nearer (R^2) group. The preference would hold regardless of whether R^1 and R^3 moved in discrete steps [with *(4)* as an intermediate] or simultaneously [one five-center transition state with structure *(6)*].





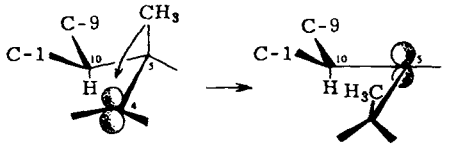
Even when nonclassical bonding is absent and hence front-side migration can occur readily, other influences may still enforce strong rear-side selectivity in the rearrangement steps that follow the initiating one. Conformational effects are potent factors of this kind and may well be influential in the remarkable multistep "backbone" rearrangements of polycyclic terpenoids [13], in which only the extra-annular groups migrate.

An example involving several such steps is that of the friedelanyl cation *(7)*, which rearranges to a cation *(8)* of the β-amyrin series. The selectivity of these transformations does not necessarily signify a "synchronous" or "concerted" multiple migration *via* a single transition state *(6)* or a step-wise process *via* discrete nonclassical intermediates *(4)*, but may also result from a series of classical ions. At each stage of such a process, the extra-annular group (H or CH_3) at the position vicinal to the electron-deficient center is bound by an orbital whose axis is nearly parallel to, and hence in excellent position to interact with, that of the empty p-orbital, whereas the corresponding orbital binding a ring carbon is badly displaced from this favorable orientation. These relationships are shown in *(9)*, which is an excision of part of the "backbone" of *(7)*. Migration of CH_3 from C-5 to C-4 leaves the C-10 hydrogen in a more favorable posi-



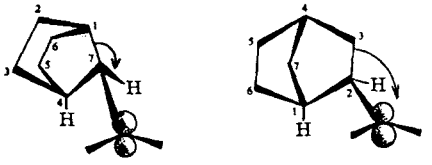
[13] For a review, see *inter alia J. F. King* and *P. de Mayo* in *P. de Mayo*: Molecular Rearrangements. Interscience, New York 1963, Part Two, Chapter 13.

tion than either C-1 or C-9 for a subsequent migration. The rearrangements of the extra-annular groups therefore are expected to be preferred, regardless of whether the intermediates are classical or nonclassical, and the observed memory effects are explicable without recourse to any special theoretical formulation. The truly novel aspects of memory effects emerge only when the commonplace stereoelectronic and conformational features are absent.



(9)

4. Forced Migration of Improperly Situated Groups

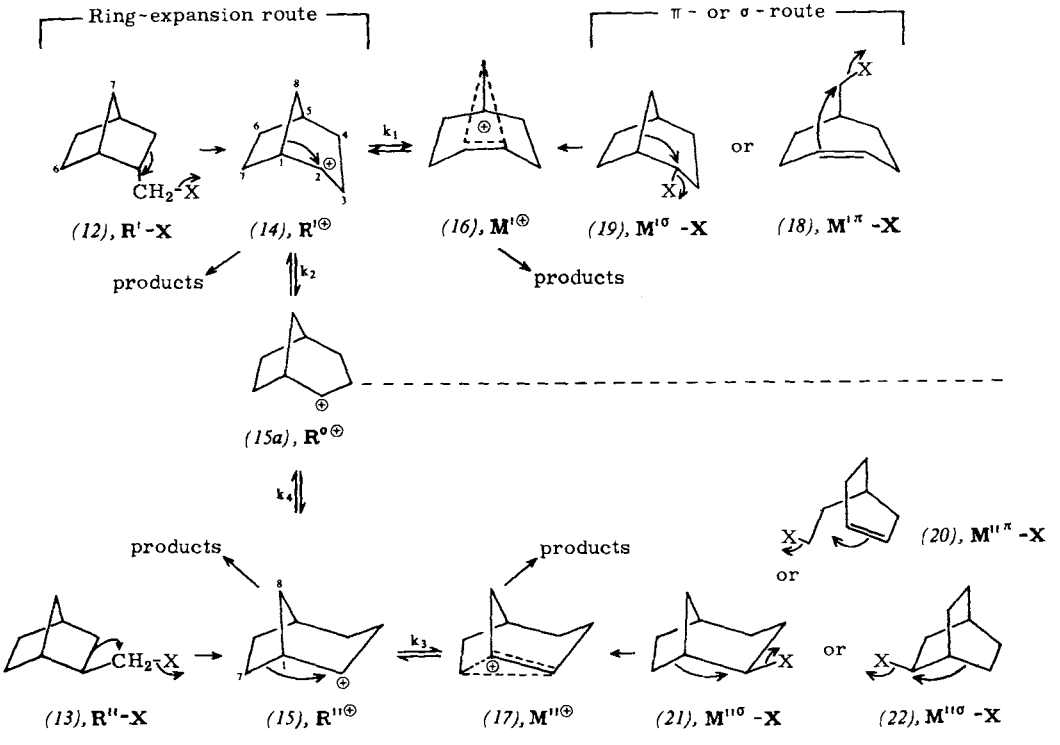


(10) *(11)*

Incorporation of the fragment *(9)* in a bridged bicyclic system, *e.g.*, *(10)* or *(11)*, prohibits migration of the bridgehead hydrogen [at C-4 of *(10)* and C-1 of *(11)*, which correspond stereoelectronically to the most favorable group, the C-10 hydrogen of *(9)*] because of the inability of the bridgehead carbon to assume a trigonal configuration. One of the ring carbons thereby is forced to migrate in the second step of the multiple rearrangement. Neither of these is in a good position to interact with the p-orbital left vacant if the first ring-expanding rearrangement leads to a classical cation, nor can either readily attack the rear side of a mesomeric bridged ion if the ring-expansion leads to a nonclassical intermediate. Such systems therefore put forward a new problem: Is memory preserved despite the attenuation of the normally dominant stereoelectronic factors? The following examples show that it is.

5. Ring-Expansions of 2-Norbornylmethyl Derivatives

The geometric restrictions embodied in structure *(11)* are met in 2-*endo*- and 2-*exo*-norbornylmethyl systems [*(12)* and *(13)*]. Studies by *Alder* and his coworkers [14] show that the deaminative ring-expansion of the *endo*-amine gives a different set of products than that obtained from the *exo*-amine. Later work on the deaminations and on solvolyses of arenesulfonates elucidates further mechanistic details and leads to a formulation [15,16] which is shown in Scheme 1. The systems derived from *(12)* and *(13)* are prototypes of a number of other examples. Scheme 2 summarizes the common phenomena of memory effects in sym-



(a), X = $N_2^{\oplus}$; *(b)*, X = OSO_2-C_6H_4-Br *(p)*

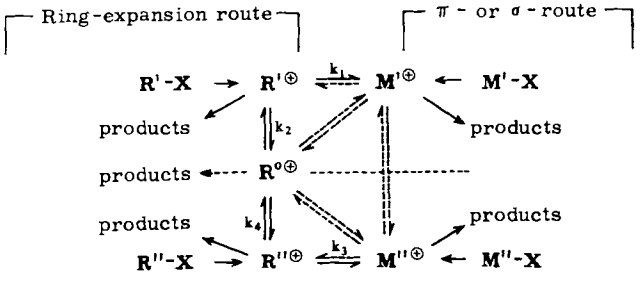
Scheme 1. A specific example of memory effect.

[14] a) *K. Alder* and *E. Windemuth*, Ber. dtsch. chem. Ges. *71*, 2404 (1938); b) *K. Alder*, *H. Krieger*, and *H. Weiss*, Chem. Ber. *88*, 144 (1955); c) *K. Alder* and *R. Reubke*, *ibid.* *91*, 1525 (1958).

[15] *J. A. Berson* and *P. Reynolds-Warnhoff*, J. Amer. chem. Soc. *84*, 682 (1962); *86*, 595 (1964).

[16] *J. A. Berson* and *D. Willner*, J. Amer. chem. Soc. *84*, 575 (1962); *86*, 609 (1964).

bolic form. The dashed arrows represent reactions observed in some but not all of the systems studied. To aid in comparisons, the reactants and unstable entities of Scheme 1 are labeled both with ordinal numbers and with boldface letters, which are also used in Scheme 2.



Scheme 2. Generalized scheme of memory effects.

The first cationic intermediate *(14)* from the *endo* ring expansion has a chair cyclohexane ring, whereas the cation *(15)* from the *exo* has a boat. If conformational interconversion of *(14)* and *(15)* were fast, crossover between the two systems would occur, and the products would be the same or nearly so from either *endo* or *exo* starting material [*(12)* and *(13)* respectively]. In fact, however, crossover is not extensive, and the conformationally isomeric cations *(14)* and *(15)* are trapped, both by external nucleophiles and by further intramolecular bond rearrangements [*(14)* → *(16)* and *(15)* → *(17)*].

The specificities of the second rearrangement steps constitute memory effects. Although the stereoelectronic alignments of the potential migrating bonds, (C-1)–(C-8) and (C-1)–(C-7), are not particularly good in either *(14)* or *(15)*, models suggest that the (C-1)–(C-8) bond in *(14)* and the (C-1)–(C-7) bond in *(15)* would be favored for further rearrangement [15,16], in accord with the observations.

Two kinds of access into the Schemes 1 and 2 may be recognized. From the right one forms cationic intermediates by interaction of the electron-deficient center with a nearby π- or σ-system. This mode of entry provides no opportunity for a memory effect to operate, since only one rearrangement or bond-delocalization step is involved, but it permits the generation by "conventional" routes of the cations ($M'^{\oplus}$ and $M''^{\oplus}$) which are the products of the *two-step* path in the ring-expansion route. The behavior of the cations formed by the π- or σ-routes serves as a standard of comparison for those formed by the ring-expansion route. For example, in Scheme 1, *(16)* is generated from 4-cycloheptenylmethyl or 2-*endo*-bicyclo[3.2.1]octyl precursors [*(18)* [17] or *(19)* [18]], and *(17)* from 3-cyclohexenylethyl, 2-*exo*-bicyclo[3.2.1]-octyl, or 2-bicyclo[2.2.2]octyl precursors [*(20)* [20], *(21)* [18], or *(22)* [18,19]].

From the left in Schemes 1 and 2, the entry is by ring-expansion. In the specific case of Scheme 1, the first-formed ring-expanded cations *(15)* and *(14)* are conveniently represented as boat-chair conformational isomers which interconvert by way of a transition state *(15a)* $R^{0\oplus}$. In other cases, however, $R^{0\oplus}$ is a quasisymmetric or truly symmetric intermediate from which products may be formed directly. This path is indicated in Scheme 2. In the generalized scheme, transformations of $R'^{\oplus}$ to $M'^{\oplus}$ and of $R''^{\oplus}$ to $M''^{\oplus}$ occur by second rearrangements or bond delocalization processes, which compete with crossover (interconversion of $R'^{\oplus}$ and $R''^{\oplus}$).

The competition between intramolecular trapping and crossover, measured by the ratio of rates of the reactions $R'^{\oplus} \rightarrow M'^{\oplus}$ (k_1) and $R'^{\oplus} \rightarrow R^{0\oplus}$ (k_2) gives a quantitative estimate of the magnitude of the memory effect, that is, the efficiency with which the system follows the "instructions" embodied in the specific stereochemistry R′–X. Ideally, one would prefer that the only crossover occur at the stage of the first-formed ring-expanded cations $R'^{\oplus}$ and $R''^{\oplus}$. Then the desired ratio of rates can be deduced from the product distribution data. In this kind of system, those cations which have suffered two successive rearrangements remain on a given side of the dotted line, that is, $M'^{\oplus} \rightleftharpoons M''^{\oplus}$ interconversion is negligible, and all of the selectivity inherent in the ratio of rates k_1/k_2 remains in the observed products.

The conditions for the ideal situation are that $R'^{\oplus} \rightarrow M''^{\oplus}$ be essentially irreversible and that direct as well as indirect interconversion of $M'^{\oplus}$ and $M''^{\oplus}$ be very slow relative to capture of the cations as final products. Although a few systems meet the ideal requirements, many of them form doubly rearranged cations ($M'^{\oplus}$, $M''^{\oplus}$) that drift across the barrier to some extent. The product ratios then give too pessimistic an estimate of the memory effect. This is not an insuperable difficulty, and corrections for it can be made from independent studies of the properties of $M'^{\oplus}$ and $M''^{\oplus}$ generated in the π- or σ-route entry (from the right side of Scheme 2).

The characteristic stereochemical feature of the memory effect is not given by the symbolism of Scheme 2 and must be stated separately. In all cases, the preferred migrating group in the second rearrangement step is the one that was originally remote from the site of the leaving group in the starting material [*e.g.*, C-7 rather than C-6 in the *endo*-norbornylmethyl-system *(12)*].

6. Persistence of the Memory Effect in a System of Low Conformational Stability

If the memory effect were solely caused by a conformational barrier inhibiting rapid interconversion of the isomeric cations $R'^{\oplus}$ and $R''^{\oplus}$ (Scheme 1), it should diminish greatly or completely disappear in systems so rigid that "conformations" represent very shallow

[17] *G. Le Ny*, C. R. hebd. Séances Acad. Sci. *251*, 1526 (1960).

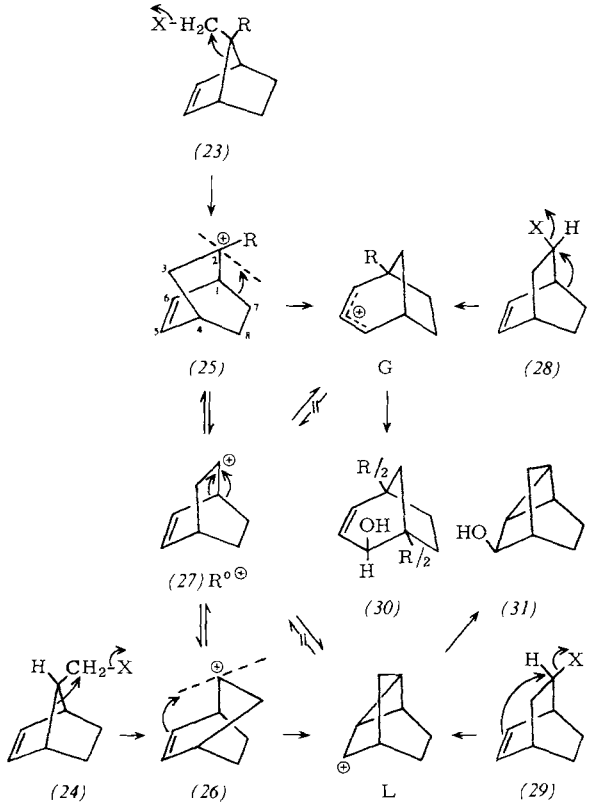
[18] a) *H. L. Goering* and *M. F. Sloan*, J. Amer. chem. Soc. *85*, 1397 (1963); b) *H. L. Goering* and *G. Fickes*, unpublished work; *G. Fickes*, Ph.D. Dissertation, University of Wisconsin, 1964.

[19] a) *A. A. Youssef*, *M. E. Baum*, and *H. M. Walborsky*, J. Amer. chem. Soc. *81*, 4709 (1959); b) *ibid. 83*, 988 (1961); c) *H. M. Walborsky*, *J. Webb*, and *C. G. Pitt*, J. org. Chemistry *28*, 3214 (1964).

[20] *S. Winstein* and *P. Carter*, J. Amer. chem. Soc. *83*, 4485 (1961).

energy minima. The cations *(25)* and *(26)* produced in the ring-expansions of *syn-* and *anti*-norbornenylmethyl derivatives [21, 22] *(23)* and *(24)* are drawn here in "twisted" representations merely as a graphic device to distinguish them from the quasi-symmetric cation *(27)* $R^{0\oplus}$. Although physical evidence on the conformations of bicyclo[2.2.2]octenes is sparse, molecular models of this ring system are rather resistant to twisting distortions, and it seems unlikely that there can be a large barrier separating the two cations from each other or from the quasi-symmetric cation *(27)*. Nevertheless, memory is preserved.

The products in this system are derived from cations G (R = H) and L, which do not interconvert appreciably under the conditions and thus constitute an ideal pair for the preservation of whatever memory inheres in *(25)* and *(26)*. Cations G and L already had been encountered in solvolyses, G from *endo-* and L from *exo*-2-bicyclo[2.2.2]oct-5-en-2-yl substrate [*(28)* [23] and *(29)* [24]]. Cation G generated from optically active *(28)* gives largely the completely racemic alcohol bicyclo[3.2.1]oct-3-en-2-ol *(30)* derived from attack at equal rates at both sites of the symmetrical allylic cation system *(27)* [23]. That the product-forming cation from the ring-expansion starting with *(23)* is also G is demonstrated in the deamination of *syn*-[7-D]-7-



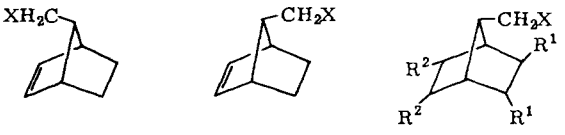
[21] *J. A. Berson* and *J. J. Gajewski*, J. Amer. chem. Soc. *86*, 5020 (1964).

[22] Cf. also *R. K. Bly* and *R. S. Bly*, J. org. Chemistry *31*, 1577 (1966).

[23] *H. L. Goering* and *M. F. Sloan*, J. Amer. chem. Soc. *83*, 1992 (1961); *H. L. Goering*, *R. W. Greiner*, and *M. F. Sloan*, *ibid. 83*, 1391 (1961); *H. L. Goering* and *D. L. Towns*, *ibid. 85*, 2295 (1963).

[24] a) *N. A. Le Bel* and *J. E. Huber*, J. Amer. chem. Soc. *85*, 3193 (1963); b) cf. *R. R. Fraser* and *S. O'Farrell*, Tetrahedron Letters *1962*, 1143.

Table 1. Some memory effect selectivities [o].



A B *(32)*

A. Cations generated from *syn*-7-norbornenyl substrates

X	T (°C)	Solvent	Other reagents (mole/l)	G/L [b, d]	Excess G (%) [c, d]
ONs[p]	125	HOAc	NaOAc, 0.068	3.7	58
ONs[p]	125	HOAc	NaOAc, 0.068 + $LiClO_4$, 0.100	4.6	64
Br	125	HOAc	$AgClO_4$, 0.123 + urea, 0.14	4.5	64
ONs[p]	100	H_2O/ Dioxane [a]	NaOAc, 0.055	3.7	57
ONs[p]	100	H_2O/ Dioxane [a]	NaOAc, 0.055 + $LiClO_4$, 0.100	2.8	47
Br	100	HOAc	$AgClO_4$, 0.123 + urea, 0.14	3.1	51
Br	75	HOAc	$AgClO_4$, 0.123 + urea, 0.14	2.0	33
NH_2	25	HOAc	$NaNO_2$, excess	2.7	46

B. Cations generated from *anti*-7-norbornenyl substrates

X	T (°C)	Solvent	Other reagents (mole/l)	L/G [d, e]	Excess L (%) [d, f]
ONs[p]	125	HOAc	NaOAc, 0.068	3.6 [g]	57
ONs[p]	125	HOAc	NaOAc, 0.069 + $LiClO_4$, 0.100	4.5 [g]	64
ONs[p]	125	HOAc	NaOAc, 0.068 + $LiClO_4$, 0.250	3.5 [g]	56
Br	125	HOAc	$AgClO_4$, 0.122 + urea, 0.14	14	82
Br	75	HOAc	$AgClO_4$, 0.122 + urea, 0.14	42	96
NH_2	25	HOAc	$NaNO_2$, excess	45	96

C. Cations generated from 7-norbornylmethyl substrates

X	R^1	R^2	T (°C)	Solvent	Other reagents (mole/l)	Selectivity (R^2/R^1) [h]
OBs[q]	D	H	120	HOAc	NaOAc, 0.06	2.0, 2.0 [d, i]
OBs[q]	H	R	120	HOAc	NaOAc, 0.06	2.3 [d]
OBs[q]	H	D	120	HOAc/ PVA [k]	none	2.0 [j]
OBs[q]	H	D	100	HCO_2H/ Py [l]	none	2.5 [j]
NH_2	D	H	25	HOAc/ H_2O [m]	$NaNO_2$, excess	6.6 [j]
NH_2	H	D	25	HOAc/ H_2O [m]	$NaNO_2$, excess	5.7 [j]
NH_2	D	H	25	HOAc	$NaNO_2$, excess	1.6, 1.9 [n, j]

[a] 40 % water, 60 % dioxane (v/v). [b] Ratio of products of the G-series to those of the L. [c] 100 (G − L)/(G + L). [d] Corrected for drift (see text). [e] Ratio of products of the L-series to those of the G. [f] 100 (L − G)/(L + G). [g] This value may be as much as 0.5 unit too low because of difficulty in analysis for a minor L-component. [h] Ratio of products derived from migration of the R_2 *vs* R_1-labeled bridges. [i] Duplicate runs. [j] A correction for drift is not yet available for this result, which is therefore a minimum measure of the true selectivity. [k] PVA = polyvinyl acetate sufficient to cause a 15-fold increase in viscosity. [l] 90 % formic acid, 10 % pyridine (v/v). [m] 94 % water, 6 % acetic acid (v/v). [n] Duplicate combustion and falling drop analyses for deuterium. [o] Data for parts A and B of Table are from refs. [21, 25], and *D. Donald*, unpublished observations. For part C. ref. [26] and *W. J. Libbey*, unpublished observations. [p] Ns = *p*-NO_2-$C_6H_4SO_2$. [q] Bs = *p*-Br—$C_6H_4SO_2$.

norbornenylamine *(23)*, R = D, X = NH_2, which gives[25] product from G (R = D), in which exactly half the deuterium is at each bridgehead [*(30)*, R = D]. Similarly, the product distribution from L generated from *(24)* is essentially the same[21,25] as that generated from *(29)*[24], where the major product is the tricyclic alcohol *(31)*.

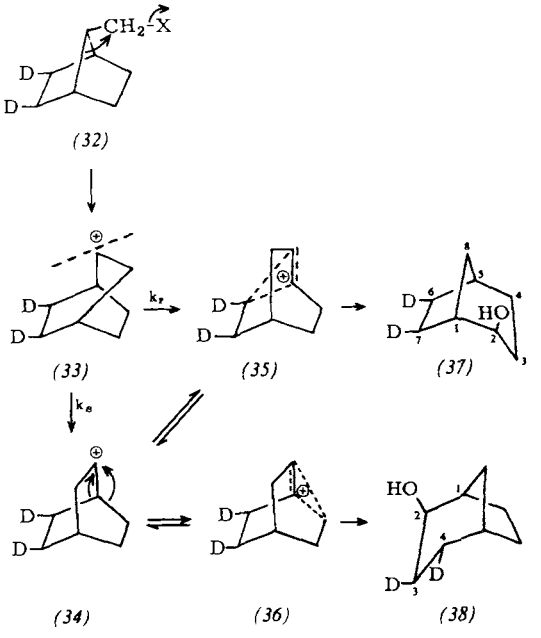
Table 1 shows that in all cases, the ratio (G/L) of products from the two cations is higher from the *syn* starting material *(23)* than from the *anti (24)*.

The ratio G/L has a range of about 200, from 5:1 in the *syn* series to 1:40 in the *anti*. In a formal conformational representation these results fall into the same pattern observed in *(12)* and *(13)*, where chair-boat isomers, the ring-expanded cations *(14)* and *(15)*, are imaginable. The specificities of the follow-up rearrangements would be plausible if *(25)* and *(26)* were twisted in the sense shown, since the p-orbital axis (dotted line) at C-2 in each then would point toward the (C-1)–(C-7) σ-bond in *(25)* and toward the π-bond in *(26)*. Which cation [*(25)* or *(26)*] is the more selective in the second rearrangement step is difficult to ascertain, since the quasi-symmetric cation *(27)* itself has an intrinsic but unknown selectivity for further bond delocalization to G or L. The observed product distribution from, for example, the *syn* substrate *(23)* therefore results not only from the competition that measures the memory effect [the relative rates of *(25)* → G and *(25)* → *(27)*] but also from the "natural" ratio that determines the distribution of the quasi-symmetric cation [the relative rates of *(27)* → G and *(27)* → L].

7. Crossover *via* a Truly Symmetrical Cation. Ring-Expansions of 7-Norbornylmethyl Derivatives

The two ethylene bridges of a 2-bicyclo[2.2.2]octyl cation can be distinguished from each other with an isotopic label, which permits the examination of memory effects in the saturated 7-norbornylmethyl system *(32)*. The unsymmetrical cation, shown here as a twisted species *(33)* for explication, can preserve the distinction between the labeled and unlabeled bridges if migration of one of them occurs at a rate that is not very much slower than conversion to the symmetrical cation *(34)*.

The "natural" partition ratio for *(34)* is unity because the follow-up rearrangements *(34)* → *(35)* and *(34)* → *(36)* necessarily proceed at the same rate (except for a small secondary isotope effect). Therefore, after correction for the drift that partially interconverts their precursor cations *(35)* and *(36)*[16,18,19] the excess of 6,7-labeled 2-bicyclo[3.2.1]octyl product *(37)* over the 3,4-labeled counterpart *(38)* represents the preference for migration of the bridge that was *anti* to the leaving group in the starting material and thereby directly measures the memory effect.



Rearrangements of *anti*-labeled substrates *(32)* (X = NH_2 or arenesulfonate) and of the corresponding *syn*-labeled series[26] (Table 1) show that memory is preserved[27a]. In the acetolysis of the *p*-bromobenzenesulfonate *(32)*, for example, the experimental ratio *(37)*/*(38)* of 1.4 leads, after correction for drift, to a competition ratio $k_s/k_r = 2$. That is, about one-third of the twisted cations *(33)* are trapped by bond rearrangement, and the remainder achieve the symmetrical condition[27b].

8. The Nature of the "Twisted" Cations

So far we have resorted to a purely phenomenological description of the species responsible for memory effects. From the results of further studies of the systems already mentioned[28,29] and those of additional ring-expansions in the nortricyclylmethyl[30], 1-methyl-2,3-

[25] *J. J. Gajewski*, Ph. D. Dissertation, University of Wisconsin, 1965.

[26] a) *J. A. Berson* and *M. S. Poonian*, J. Amer. chem. Soc. *88*, 170 (1966); b) *M. S. Poonian*, Ph. D. Dissertation, University of Wisconsin, 1966.

[27a] This is not a consequence of a secondary isotope effect, since the migratory aptitude of a *syn*- or *anti*-$C_2D_2H_2$ bridge is observed to be virtually the same as that of a *syn*- or *anti*-C_2H_4 bridge, respectively [26].

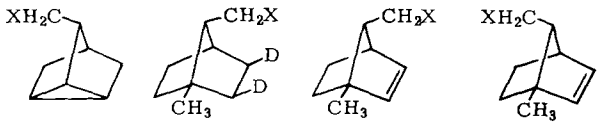
[27b] The 33% efficiency of preservation of memory is derived on the assumption that bond rearrangement *(33)* → *(35)* is completely stereospecific. To the extent that some direct trapping in the opposite stereochemical sense occurs [*(33)* → *(36)*], the calculation overestimates the importance of the symmetrization path *(33)* → *(34)*.

[28] *W. J. Libbey*, unpublished observations.

[29] *D. Donald*, unpublished observations.

[30] a) *J. A. Berson*, *R. G. Bergman*, *G. M. Clarke*, and *D. Wege*, J. Amer. chem. Soc. *90*, 3236 (1968); b) *J. A. Berson*, *G. M. Clarke*, *D. Wege*, and *R. G. Bergman*, *ibid. 90*, 3238 (1968); c) *J. A. Berson*, *D. Wege*, *G. M. Clarke*, and *R. G. Bergman*, *ibid. 90*, 3240 (1968).

dideuterio-*syn*-7-norbornylmethyl[31] and 1-methyl-2-norbornenyl-*syn* and *anti*-7-methyl[32] systems [*(39)*, *(40)*, *(41)*, and *(42)*], we have concluded that the multiple rearrangements are most readily formulated as step-wise rather than concerted processes. The "twisted" cations therefore are true metastable intermediates, occupying minima in the potential energy surface of the reaction. The evidence for this conclusion comes from experiments on extramolecular capture and from the influence of methyl substitution on the memory effect.



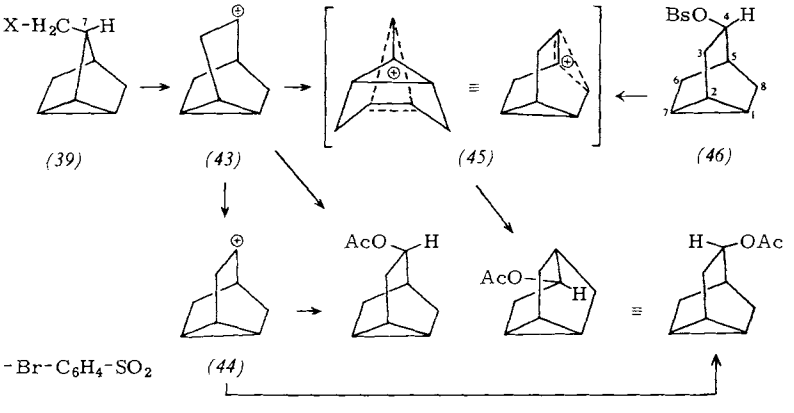
(39) *(40)* *(41)* *(42)*

8.1. Capture of the Once-Rearranged "Twisted" Species by External Nucleophiles

Scheme 2 shows a path providing for formation of product by nucleophilic capture of the first-formed, once-rearranged cation (*e.g.*, $R'^{\oplus}$) in the ring-expansion route. Evidence for the occurrence of this reaction at a rate competitive with that of the second rearrangement step (intramolecular trapping) is available from the chemistry of the chair 2-bicyclo[3.2.1]octyl cation *(14)*. Although a substantial fraction of these cations elude capture by external nucleophile and rearrange to the symmetrical nonclassical ion *(16)*, some of them are trapped before the bond delocalization step. The ring-expansion of optically active *(12)* thus leads to only partially rather than completely racemized *endo*-bicyclo[3.2.1]octyl product [*e.g.* *(14a)*][15]. However, the second rearrangement step apparently is fast enough to outstrip nucleophilic capture in some cases. For example, in the *syn*- and *anti*-7-norbornenylmethyl systems, the amount of bicyclo[2.2.2]oct-5-en-2-yl product is not observably greater when the "twisted" cationic intermediates *(25)* and *(26)* are generated by ring-expansion[21,25] than when the system is entered by conventional solvolyses of the *endo*-[23] and *exo*-bicyclo[2.2.2]oct-5-en-2-yl[24a] substrates *(28)* and *(29)*.

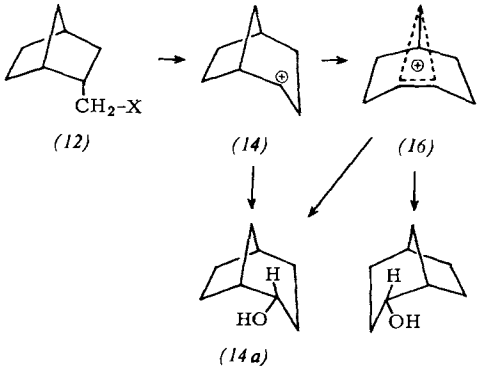
In the analogous saturated system, 7-norbornylmethyl *(32)*, the mixture of 2-bicyclo[2.2.2]- and 2-bicyclo[3.2.1]octyl derivatives formed in the ring-expansion contains a proportion of 2-bicyclo[2.2.2]-octyl product only slightly greater than that obtained[18–20] in solvolysis by conventional π- or σ-routes[26,28].

External nucleophilic capture of the cationic intermediate after one rearrangement step is also detectable in the ring-expansion of optically active 3-nortricyclylmethyl derivatives *(39)*[30,33].



(39) *(43)* *(45)* *(46)* *(44)*

Bs = *p*-Br-C_6H_4-SO_2



(12) *(14)* *(16)* *(14a)*

Rearrangement of one of the two nonequivalent ring members from C-7 to the methylene side chain produces a twisted tricyclo[3.2.1.$0^{2,7}$]octyl cation *(43)* which can lose optical activity either by conversion to the symmetrical ion *(44)* or by bond delocalization, which converts it into optically inactive non-classical ion *(45)*, an intermediate or transition state for the second rearrangement step. This second step occurs readily when the cations are generated by conventional solvolyses of tricyclo[3.2.1.$0^{2,7}$]octyl derivatives *(46)*, as is shown by the equilibration of a deuterium label equally between C-4 and C-5 in the product from [4D]-*(46)*[30b,33b]. The tricyclo[3.2.1.$0^{2,7}$]octyl product from optically active tricyclo[3.2.1.$0^{2,7}$]octyl substrate *(46)* is virtually completely racemized[30b], yet that from the ring-expansion retains about 24 % of

[31] *J. Foley*, unpublished observations.

[32] *J. M. McKenna*, unpublished observations.

[33] Previous studies on this and related systems have been carried out in the racemic series by a) *K. B. Wiberg* and *G. Wenzinger*, J. org. Chemistry *30*, 2278 (1965); b) *R. R. Sauers*, *J. A. Beisler*, and *H. Feilich*, *ibid. 32*, 569 (1967); c) *A. K. Colter* and *R. C. Musso*, *ibid. 30*, 2462 (1965).

its optical purity in arenesulfonate acetolysis or in deamination. From the absolute configurations of the starting nortricyclylmethyl substrate[30a] and tricyclo[3.2.1.$0^{2,7}$]octyl product[30b], it is established that the nucleophilic trapping of the twisted cation *(43)* occurs from the same side as the departure of X ($OSO_2-C_6H_4-Br(p)$ or $N_2^{\oplus}$) from *(39)*.

8.2. "Twisted" Cations as True Metastable Intermediates

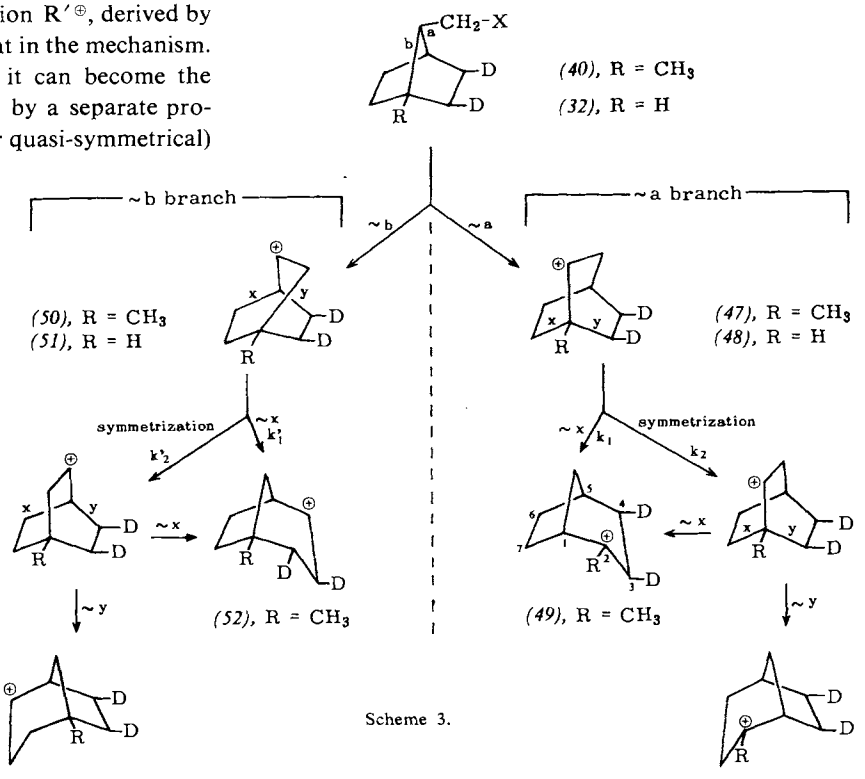
Scheme 2 shows the "twisted" cation $R'^{\oplus}$, derived by ring expansion, as a branching point in the mechanism. By a second rearrangement step, it can become the twice-rearranged cation $M'^{\oplus}$, and by a separate process, it can become symmetrical (or quasi-symmetrical) ion $R^{0\oplus}$.

The question might be raised whether the energy surface could include a small minimum after the transition state of the ring-expansion but that this minimum is by-passed by points descending from the transition state with more than enough excess vibrational energy to overcome the small second barrier. $R'^{\oplus}$ might then be considered to be a vibrationally excited form of the symmetrical cation $R^{0\oplus}$. It will seldom if ever be necessary, however, to consider explicitly such vibrationally excited entities in solution. Collisions with solvent molecules will deactivate the excited $R'^{\oplus}$ by energy transfer at a rate that is within an order of magnitude of a molecular vibration. A reaction of $R'^{\oplus}$ competing with collisional deactivation (*e.g.*, the second rearrangement step $R'^{\oplus} \rightarrow M'^{\oplus}$) therefore would have to have an activation energy not much greater than RT (<1 kcal/mole even at 100 °C). The small second barrier in question would become no obstacle, and the reaction would have, for all practical purposes, only one transition state.

9. Unsymmetrically Substituted Systems. Change in the Competition Ratio

If $R'^{\oplus}$ is an energy minimum, the rearrangement from R′–X to $M'^{\oplus}$ proceeds in two discrete steps, the second of which competes with symmetrization to $R^{0\ominus}$. If the second rearrangement step is initiated before the first is completed, the rearrangement of R′–X to $M'^{\oplus}$ then is a concerted double migration passing over only a single transition state and competing with processes $R'-X \rightarrow R^{0\oplus}$ and/or $R'-X \rightarrow M''^{\oplus}$. Recent evidence on the behavior of unsymmetrically substituted systems strongly favors the first of these possibilities.

In the ring-expansion of the *syn*-[2,3-D_2]-1-methyl-7-norbornylmethyl derivative *(40)*, the unsymmetrically placed bridgehead substituent renders nonequivalent the bonds a and b available for the first rearrangement step. Migrations of a or b lead to the corresponding



Scheme 3.

"twisted" cations *(47)* and *(50)*. The distribution of starting material between these two branches is not of great concern in the present context, as long as some of the reaction goes by each path. The mechanistically significant branching points occur at the next rearrangement stage. If the "twisted" cations are true intermediates and their stereochemical behavior is controlled by Scheme 3, then competition occurs between intramolecular entrapment by a second rearrangement (k_1 and k_1') and symmetrization by some process (k_2 and k_2').

Although the nature of the symmetrization step remains to be discussed, it seems reasonable to suppose that these rates (k_2 and k_2'), whether they involve a conformational change or some kind of extramolecular process (see Section 11), should not be sensitive to methyl substitution. On the other hand, the rates of the second migration step (k_1 and k_1') should be very sensitive.

The second step (~x) in the path initiated by ~b involves conversion of a secondary cation *(50)* to a rearranged secondary cation *(52)*. The methyl substituent is at a remote position and should exert only a feeble effect. Therefore, the ~x step should proceed at

a rate k_1' not greatly different from that in the "twisted" cation *(51)* lacking the methyl group. In the second rearrangement step (~x) of the path initiated by ~a, the "twisted" secondary cation *(47)* is converted into a rearranged tertiary cation *(49)*. The methyl group is directly attached to the site of developing positive charge and provides a large kinetic driving force. One would predict, therefore, that k_1/k_2 in *(47)* should be greater than k_1'/k_2' in *(50)*; that is, the selectivity for

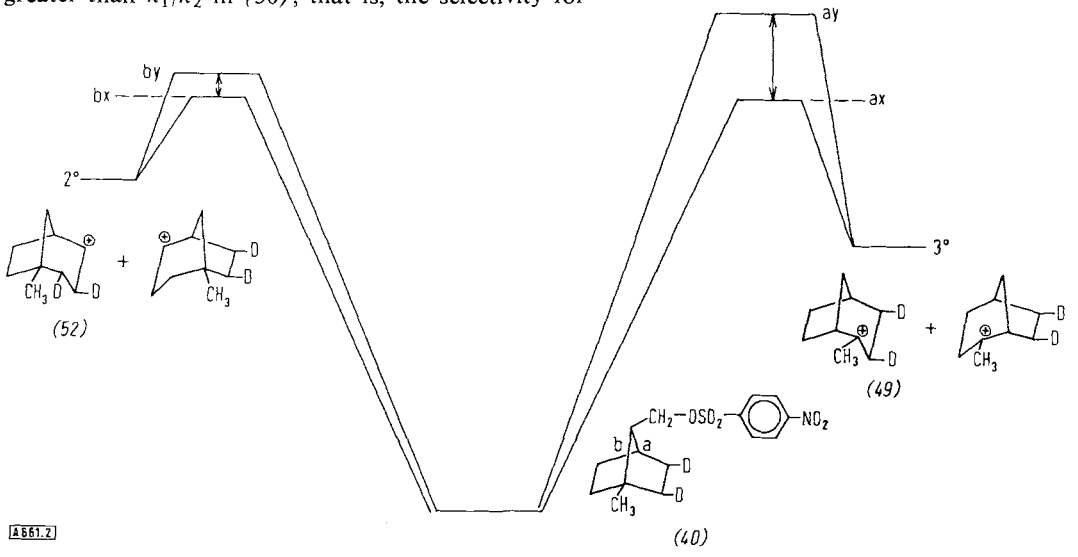


Fig. 2. Energy surface for the acetolysis of [2,3-D_2]-*syn*-1-methyl-7-norbornylmethyl *p*-nitrobenzenesulfonate *(40)* by a double rearrangement mechanism.

total amounts of products derived from the ~a and ~b branches are about equal, but whereas the part derived from the ~b branch shows [34] a selectivity (k_1'/k_2') that is nearly the same as that observed [26] in the unsubstituted series *(32)* the selectivity in the ~a branch is substantially higher [34].

These results are difficult to reconcile with a concerted double rearrangement mechanism having an energy surface like Fig. 2, where the two rearrangement steps in each branch are telescoped into one. In the ~a branch, leading to tertiary doubly rearranged cation *(49)* or its [6,7-D_2]-isomer, the reactants would pass over either single transition state ax or

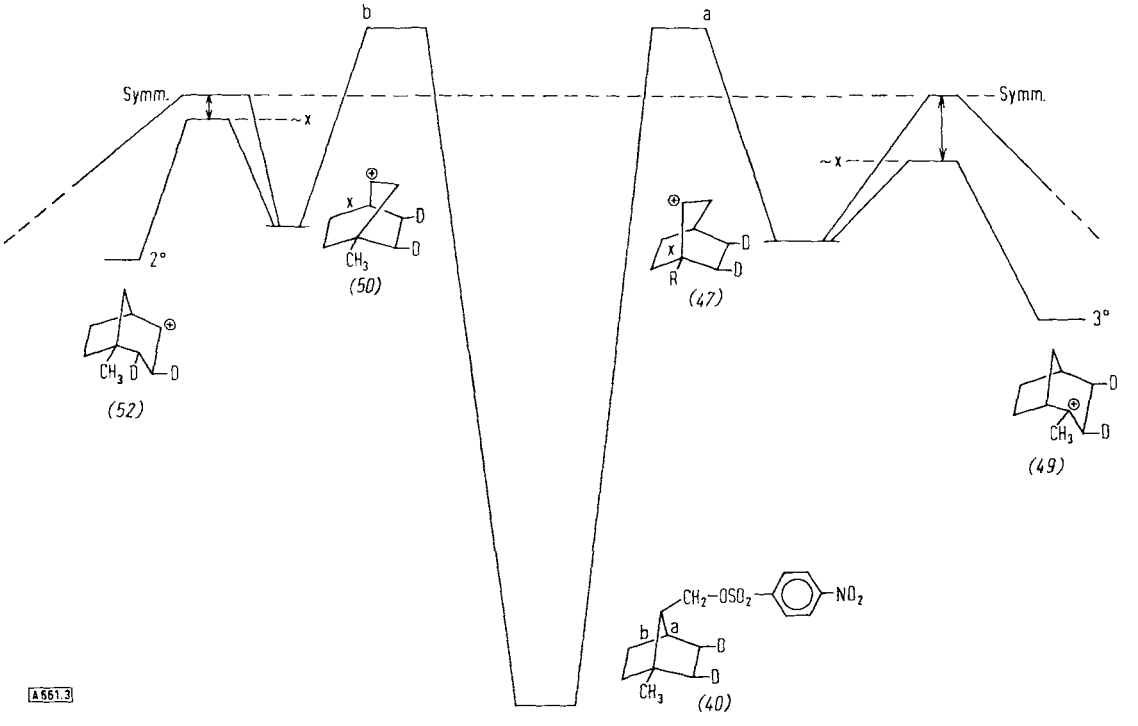


Fig. 3. Energy surface for the acetolysis of [2,3-D_2]-*syn*-1-methyl-7-bornylmethyl *p*-nitrobenzenesulfonate *(40)* by a stepwise mechanism. Symm. = symmetrization.

stereospecific migration of x in the branch of the ring expansion of *(40)* initiated by ~b should be about the same as that in *(32)*, but this selectivity in the ~a branch should be substantially higher.

These predictions are confirmed in the acetolysis of [2,3-D_2]-*syn*-1-methyl-7-norbornylmethyl-*p*-nitrobenzenesulfonate *(40)*, X = $OSO_2-C_6H_4-NO_2(p)$. The

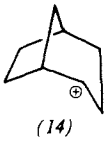
[34] a) *J. Foley*, unpublished observations; b) Similar investigations are under way in the unsaturated series 1-methyl-*syn*- and 1-methyl-*anti*-7-norbornenyl derivatives (*J. M. McKenna*, unpublished observations); c) The selectivity in the second stage of ring expansion of a 1-methyl-2-*endo*-norbornylmethyl derivative is considerably higher than in the case of the unsubstituted compound (*H. Junge*, unpublished).

single transition state ay. In the ~b branch, leading to secondary doubly rearranged cation *(52)* or its [6,7-D_2]-isomer, reactants would pass over single transition states bx or by. The selectivities in each branch would be determined by the differences $F_{ay} - F_{ax}$ and $F_{by} - F_{bx}$. The experimental facts given would have to be interpreted as being caused by a much larger difference between the competing transition states in the ~a branch than in the ~b branch ($F_{ay} - F_{ax} > F_{by} - F_{bx}$). The difficulty with this interpretation is that it is not obvious why one of the four transition states should be so much higher in energy than the other three.

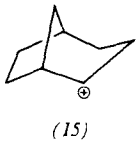
On the other hand, a very natural explanation for the observed behavior emerges from the step-wise mechanism (Fig. 3). Once the first barrier a or b is passed in the ring-expansion step, intermediate once-rearranged secondary cations [*(47)* and *(50)*] of very nearly equal energies result. The relative heights of the a and b barriers for this first step are not readily predicted, but it would not be surprising if they were nearly the same and if, consequently, the starting material were about evenly divided between the ~a and ~b branches, as is observed. The major point, however, concerns the second step. There the further partitioning of the individual once-rearranged "twisted" cations so as to favor ~x *vs.* symmetrization *specifically in the a branch* is clearly to be expected. The "twisted" cations $R'^{\oplus}$ are thus most simply formulated as true intermediates. They are unsymmetrical and can be trapped intramolecularly or intermolecularly before symmetrization. The major remaining problem concerns the source of their asymmetry.

10. Possible Intramolecular Origins of Memory Effects

In the earliest examples of the memory effect [ring-expansion of the 2-norbornylmethyl derivatives *(12)* and *(13)*], the first-formed cations *(14)* and *(15)* were



(14)

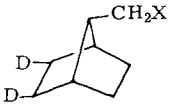


(15)

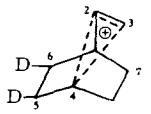
(33)

thought to be conformational isomers of the chair-boat cyclohexane type. Although it is easy to visualize an energy barrier for interconversion of these cations, and such a barrier may well contribute to the observed mechanistic insulation from each other of the 2-*endo* and 2-*exo*-norbornylmethyl systems, it is clear that cyclohexane-type conformational isomerism is not a requirement for the operation of the memory effect. In the case of 2-bicyclo[2.2.2]octyl cation, molecular models suggest that any barrier between the twisted form *(33)* and its enantiomer must be very small. Further, although one perhaps might not be surprised if bicyclo[2.2.2]octane preferred to exist in a slightly twisted conformation so that the vicinal hydrogen-hydrogen repulsions of the symmetrical eclipsed form would be relieved[35], large departures from the eclipsed form would not be expected[36f, 36g]. The weight of physical evidence from X-ray crystallography and infrared-Raman spectroscopy on the parent hydrocarbon and some of its derivatives is compatible with the eclipsed or almost eclipsed structure[36]. It seems likely that any conformational barrier separating twisted and eclipsed forms or enantiomeric twisted forms must be small. Introduction of a double bond into the bicyclo[2.2.2]octyl cation system to give bicyclo[2.2.2]octenyl cation results in an even stiffer structure. If one, nevertheless, insists upon a conformational rationalization of the observed behavior in these cases, the memory effect then constitutes a very sensitive probe for small conformational minima.

Nonclassical bonding might be another imaginable intramolecular source of asymmetry. Thus, in the ring-expansion of 7-norbornylmethyl derivatives *(32)*, the "twisted" cation might be assigned the nonclassical structure *(53)*, in which partial bonding of C-4



(32)



(53)

to C-2 and C-3 makes the two faces of C-2 nonequivalent. This explanation is not very satisfactory, since opening of the mesomeric bridge should occur with inversion, whereas neither C-6 nor C-7 is in a favorable position to accomplish this. The reason for the observed specificity C-6 > C-7 in the second rearrangement step therefore is not immediately evident. A possible explanation comes from consideration of a model which shows that the (C-1)–(C-7) bond axis lies almost in the nodal plane of the (C-2)–(C-3) π system. The (C-1)–(C-7) σ electrons therefore cannot interact with the π system. In contrast, the (C-1)–(C-6) bond axis assumes an angle of about 60° to the π nodal plane. The (C-1)–(C-6) σ electrons cannot approach from the preferred rear side of the π system, but if bond migration does take place in spite of this, then the only bond interaction possible is that between the (C-1)–(C-6) σ electrons and the front side of the π system. If this interpretation is correct, the memory effect is a much more sensitive test for nonclassical intermediates than any previously used technique.

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[35] a) *R. B. Turner*, *W. R. Meador*, and *R. E. Winkler*, J. Amer. chem. Soc. *79*, 4116 (1957); b) In any case, since this type of repulsion is absent from the (C-2)–(C-3) bridge of the symmetrical 2-bicyclo[2.2.2]octyl cation, it is not obvious that the hydrocarbon is a good model.

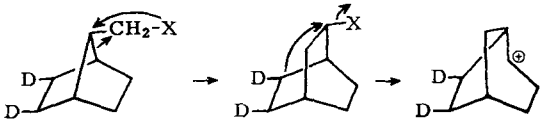
[36] a) *A. H. Nethercot, jr.* and *A. Javan*, J. chem. Physics *21*, 363 (1953); b) *J. J. McFarlane* and *I. G. Ross*, J. chem. Soc. (London) *1960*, 4169; c) *T. Wada*, *E. Kishida*, *Y. Tomia*, *H. Suga*, *S. Seki*, and *I. Nitta*, Bull. chem. Soc. Japan *33*, 1317 (1960); d) *G. S. Weiss*, *A. S. Parkes*, *E. R. Nixon*, and *R. E. Hughes*, J. chem. Physics *41*, 3759 (1964); e) *M. P. Marzocchi*, *G. Sbrana*, and *G. Zerbi*, J. Amer. chem. Soc. *87*, 1429 (1965); f) *A. F. Cameron*, *G. Ferguson*, and *D. G. Morris*, Chem. Commun. *1968*, 316, have found by X-ray analysis a (C-1)–(C-2) *vs.* (C-3)–(C-4) dihedral angle of 3° in the *p*-bromobenzenesulfonate of bicyclo[2.2.2]-octyl-1-methanol; g) The X-ray structure analysis of bicyclo-[2.2.2]octane-1,4-dicarboxylic acid carried out by *O. Ermer* and *J. D. Dunitz*, Chem. Commun. *1968*, 567, gave a dihedral angle of 0°.

11. Possible Extramolecular Origin of Memory Effects

Since the intermediates in these rearrangements are formed in solution, any temporarily asymmetric arrangement of this extramolecular environment might persist long enough to evoke a correspondingly asymmetric response, even from a cation of intrinsically symmetrical constitution. Several potential sources of such effects might be imagined.

Perhaps the most obvious of these is ion-pair return. In the case of 7-norbornylmethyl arenesulfonate solvolysis, for example, stereospecific ion-pair return from *(32)*, X = $SO_2-C_6H_4-Br(p)$ to [5,6-D_2]-bicyclo-[2.2.2]octyl-2-*exo*-*p*-bromobenzenesulfonate *(54)* followed by anchimerically assisted solvolysis of the latter would produce qualitatively the observed pattern of the memory effect, that is, preferred migration of the *anti* bridge in the second rearrangement step.

In detail, however, this process cannot be responsible for all of the memory effect, which occurs not only in solvolysis but also with equal or greater selectivity in deamination *e.g.* of



(32) *(54)*

(32), X = $N_2^{\oplus}$. The return process in deamination would involve molecular nitrogen, which if it traps the once rearranged cation at all, should do so with much lower efficiency than *p*-bromobenzenesulfonate. Further, even in solvolysis not all of the rearrangement can pass through the ion-pair return product *(54)*, since independently synthesized *(54)* rearranges with considerably higher selectivity than does *(32)* [26b]. There must then be some mechanism for symmetrization on the path between *(32)* and *(54)*, which in the ion-pair context would be ascribed most simply to separation of the ions into independently solvated species. This separation process should be extremely sensitive to solvent, as has been observed with other ion-pair → solvated-ion reactions. For example, ion-pair return, which is pronounced in the acetic acid solvolysis of 3-*p*-anisyl-2-butyl derivatives, is almost completely obliterated in the more proficient ion-solvating solvent, formic acid [37]. If the memory effects observed with *(32)* were caused by ion-pair return, they should be drastically diminished by similar changes of solvent, but they do not show this response. Especially striking is the behavior of the *syn*-7-norbornenylmethyl series *(23)* (Table 1). Although there seems to be a small temperature effect, the selectivity is nearly invariant over a large range of solvents, leaving groups, and electrophilic catalysts [21, 25, 38].

The same results argue against a variant of the ion-pair return hypothesis in which the counter-ion, instead of capturing the cation covalently, merely remains in its vicinity but stays predominantly on one side of it.

Starting from a purely electrostatic point of view, one might develop a more general hypothesis of the origin of memory effects. The positive charge in a carbonium ion interacts with all the other ionic charges in the solution to produce an equilibrium distribution of surrounding ions. For a uni-univalent electrolyte in aqueous solution at 25 °C and a concentration of 0.05 M, the mean radius of this ionic atmosphere of a given ion is about 13 Å [39].

A Wagner-Meerwein rearrangement of the carbonium ion would displace the central charge by a distance of about 1.5 Å. If this rearrangement were fast relative to the rate at which the ionic atmosphere could adapt itself to the new location of positive charge, there would exist a finite time during which a non-equilibrium state prevailed. Even a symmetrical cation (*e.g.*, 2-bicyclo[2.2.2]octyl) when formed by rearrangement would have a temporarily asymmetric ionic atmosphere and in principle could behave in an asymmetric manner.

How fast must the characteristic second rearrangement step be in order to compete with relaxation of the ionic atmosphere to the normal, symmetrical condition? The relaxation time τ for a model electrolyte, tetraethylammonium acetate, in aqueous solution can be calculated [39] to be approximately $10^{-10}/c$ sec, where c is the molar concentration of ions. At 0.05 M, $\tau \approx 2\times10^{-9}$ sec.

The second rearrangement step thus would have to be an extremely fast reaction with a rate only a few thousand times slower than that of a molecular vibration. Since not much is known about the absolute rates of such rearrangements, one has no strong basis *a priori* upon which to evaluate the hypothesis. Fortunately, however, the whole matter is subject to experimental test, since the relaxation time and thereby the memory effect should decrease with increasing total ionic concentration. The experimental results [38] with 7-norbornenylmethyl solvolyses show that the selectivities are unaffected by a three-fold increase in ionic concentration. Therefore, the memory effect in this system (and, by implication, in the others) does not originate in an asymmetric ionic atmosphere. Although the asymmetric atmosphere may well exist temporarily around the newly-formed cation, it either relaxes much more rapidly than the second rearrangement can occur, or else its contribution to the asymmetric behavior of the cation is negligibly small.

A superficially similar but more readily defensible argument can be constructed in terms of the intimate details of the solvation shell of the freshly-formed rearranged ion. Little is known about the relaxation rates of solvent structures, but it seems likely that the necessary reorganization in hydroxylic media must involve readjustments of hydrogen-bonded aggregates or networks in the immediate vicinity of the cation. These processes should be rather insensitive to the macroscopic viscosity, since long-range diffusion is not a major contributor. The evidence is at least consistent with this picture. The memory effect (selectivity) in the 7-norbornylmethyl arenesulfonate solvolysis system is hardly affected by the fifteen-fold change in macroscopic viscosity resulting from a change of pure

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[38] *D. Donald*, unpublished observations.

[39] Cf. *H. S. Harned* and *B. B. Owen*: Physical Chemistry of Electrolytic Solutions. Reinhold Publishing Company, Inc., New York 1953.

acetic acid to an acetic acid-polyvinyl acetate solution [26b].

A guess at a reasonable upper limit for the solvent reorganization rate derives from the study of the dissociation of ε-aminocaprolactam dimers, which occurs at a rate between 10^9 and 10^{10} sec^{-1} in various solvents [40, 41]. Since the reorganization of solvent clusters under consideration in connection with memory effects would require several such elementary steps, the rate would be substantially lower than this limit.

12. Conclusions

Although it is plausible to attribute some of the memory effects to the occurrence of conformationally isomeric cations, there are many cases in which the conformational barriers between the "twisted" and symmetrical forms are so low that non-classical or extramolecular causes for the observed effects must be considered.

The systems exhibiting memory effects provide uniquely suitable devices for revealing the existence of subspecies. The problem of defining the nature of these intermediates is at the heart of carbonium ion chemistry. We hope that the observations reported here will provide some stimulus to the more intensive study of the microscopic structure of solutions, which may provide the key to an understanding of the extramolecular group of memory effects.

The physical phenomena underlying memory effects are very probably present whenever carbonium ions are formed in solution. In the most general terms, one can conclude that a description of the "structure" of a carbonium ion in solvolytic medium is incomplete without a specification of the means by which it is generated.

This work has been supported in part by the National Institute of Arthritis and Metabolic Diseases (Grant AM 07505), the Petroleum Research Fund, the Wisconsin Alumni Research Foundation, and the National Science Foundation, to whom we are grateful. All of the experimental observations and many of the concepts have been contributed by the dedicated and enthusiastic group of collaborators whose names are given in the text references. To work with them has been both challenge and reward.

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German version: Angew. Chem. *80*, 765 (1968)

Dehydration of Alcohols on Aluminum Oxide

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The dehydration of alcohols on γ-aluminum oxide, which yields water, olefins, and/or ethers, was studied with the aid of kinetic methods and IR spectroscopy. The unimolecular olefin formation probably proceeds via a surface compound, in which an alcohol molecule is joined by two angular H-bonds to an OH group and an oxygen ion on the surface. The ether formation (bimolecular reaction), on the other hand, requires OH groups and oxygen and aluminum ions on the surface. The ether is formed from a surface alkoxide group and molecularly adsorbed alcohol.

1. Introduction

The heterogeneous alumina-catalyzed dehydration of alcohols has been known since the end of the 18th century. Nevertheless, it is only recently that efforts have been made to explain the elementary processes in heterogeneously catalyzed eliminations, whereas the elucidation of reaction mechanisms in the liquid phase has reached a much more advanced stage [1]. In the dehydration on aluminum oxide (which has been mainly studied with ethanol as the alcohol), efforts have often been made to find analogies with the reaction in the liquid phase. An excellent review of developments up to 1960 has been published by *Winfield* [2].

Widely differing views are still held concerning the mechanism of the heterogeneously catalyzed dehydration of alcohols on aluminum oxide. In the case of aliphatic and some other alcohols the situation is complicated, particularly by the simultaneous occurrence of a bimolecular reaction leading to ether formation.

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[1] *D. V. Banthorpe*: Elimination Reactions. Elsevier, Amsterdam 1963.

[2] *M. E. Winfield* in *P. H. Emmett*: Catalysis. Reinhold, New York 1960, Vol. VII, p.93.

Kinetic studies are then meaningful only if the reaction scheme is known.

An oxonium-carbonium ion mechanism similar to that assumed for the liquid-phase reaction in acidic media is also supported by several authors [3–6] for the dehydration of alcohols on solid surfaces. A proton from the surface is assumed to add to the alcohol in the adsorption step. This process can be explained by the formation of more or less strongly polarized H-bonds [2]. Taking into account the surface properties of aluminum oxide, *Pines* and *Haag* [7] showed that this mechanism is also valid for the dehydration of 2-butanol (cf. however, [8]). The participation of surface protons or OH groups is supported by the need for water to be present at the contact surface [9, 10]; however, there appears to be no unambiguous relationship between the dehydrating activity and the acidity of the surface [7]. For an oxonium ion to be formed by proton addition, the surface of the aluminum oxide must contain acid centers of the Brønsted type; *Parry* [11], however, found only centers of the Lewis type in IR studies on aluminum oxide with adsorbed pyridine. Any Brønsted acids present are certainly only weakly acidic [12], so that ionic addition of protons to alcohols is not very likely.

On the basis of the need for water to be present at the catalyst surface [9, 10], and taking into account the principle of the least structural change, *Eucken* and *Wicke* [10, 13, 14] derived a hydrogen exchange mechanism, in which the substrate molecule is adsorbed in such a way that it already approximates as closely as possibly to the structure of the product molecule. In an oxonium-carbonium ion mechanism and in some other mechanisms, hydrogen must be exchanged with the catalyst surface.

In opposition to ionic mechanisms, a covalently bound adsorption complex in the form of a surface alkoxide has been postulated for the dehydration of ethanol [15–17]. The dissociation of this surface compound yields ethylene, whereas the condensation of two adjacent alkoxide groups leads to ether formation. *Topchieva et al.* [17] believe the active centers to be the surface OH groups. Though alkoxide structures have been detected in the IR spectra of some alcohols adsorbed on aluminum oxide [18, 19], this does not provide conclusive proof of the mechanism described.

Heiba and *Landis* [20] compared the products obtained in the dehydration of alcohols with those obtained on pyrolysis of the corresponding alkoxides. However, since the authors certainly did not obtain the primary products above 300 °C, the results cannot be taken as conclusive proof of a given mechanism.

Vasserberg [21] suggested a free-radical mechanism, and free radicals of compounds having extremely strong electron donor properties have in fact been detected on aluminum oxide surfaces by visible and UV adsorption spectroscopy and by ESR studies [22–25]. These donor properties are not so pronounced in alcohols as in the aromatic compounds studied. Moreover, since free-radical mechanisms proceed preferentially in apolar media, whereas the surfaces of metal oxides must be regarded as polar [26], this route is rather unlikely.

Some authors regarded the dehydration (and the dehydrogenation) of alcohols as electron donor-acceptor reactions in the electronic theory of heterogeneous catalysis. Thus *Wolkenstein* [27, 28] and *Garner* [29] postulate a rate-determining electron acceptor step for the dehydrogenation and a rate-determining donor step for the dehydration. *Hauffe* [30], on the other hand, regards the rate-determining step in the dehydrogenation of ethanol as a donor step, *i.e.* the desorption of acetone. It seems very doubtful, however, whether the dehydration of alcohols is a donor-acceptor reaction, since it presumably involves the displacement, not of single electrons, but of electron pairs. Thus *Meye* [31] showed that neither p- nor n-doping of α-Al_2O_3 had any definite effect on the rate and activation energy of the dehydration of methanol to dimethyl ether.

Different conclusions were reached by *Pines et al.*, who studied the effect of the structure of the substrate on the distribution of the primary products. Secondary isomerization of the primary products, which generally

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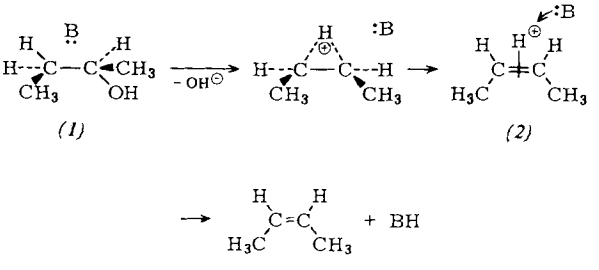
occurs on pure aluminum oxide[32], was suppressed by modification of the catalysts with ammonia, pyridine, or piperidine.

Pines and *Pillai*[33] found preferential *trans*-elimination in the dehydration of menthol and neomenthol. To explain this, they suggested neighboring-group effects and reaction at preferred sites on the catalyst, *e.g.* on steps or in sufficiently narrow pores and cracks; this view had already been advanced by Schwab[34]. The heterogeneously catalyzed dehydrochlorination of menthyl and neomenthyl chlorides also proceeds by *trans*-elimination[35]. The principal product in the dehydration of 2-*endo*- and 2-*exo*-bornanol is camphene. *Pines et al.*[36] interpret this reaction as resulting from a synchronous *trans*-elimination in which the hydroxyl group is attracted by an acidic surface center (A) and the proton by a basic center (B). They also reached the same conclusion for the dehydration of *endo*- and *exo*-norbornanol, which is assumed to proceed in pores of a suitable size. *Pines et al.* also assume that *trans*-elimination is preferred in the dehydration of primary aliphatic alcohols. This conclusion is based on the distribution of primary products in the dehydration of 1-butanol[7], isobutanol, and 2-phenyl-1-propanol[37] with and without ^{14}C-labeling[8], the effects of neighboring groups also being taken into account. The authors rule out an oxonium-carbonium ion mechanism in these cases.

To clarify the question of the order in which the elementary steps take place, the dehydration of primary and secondary alcohols was compared with that of tertiary alcohols. *Pines et al.* concluded from this comparison that the dehydration of *tert*-pentyl alcohol proceeds by a carbonium ion mechanism, whereas the hydroxyl group and the γ-proton are removed simultaneously from the primary neopentyl alcohol[38]. *trans*-Elimination is also claimed for the pairs 3,3-dimethyl-2-butanol and 2,3-dimethyl-2-butanol[38] and 3,3-dimethyl-2-pentanol and 2,3-dimethyl-2-pentanol[38], the secondary alcohol being preferentially dehydrated by a synchronous mechanism, while the tertiary alcohols react *via* a carbonium ion. Neighboring-group effects leading to reorientation of the carbon skeleton are also possible, particularly in the case of alcohols of the neopentyl type. On dehydration of 2-butanol *(1)* and of 2- and 3-pentanol, 1- and *cis*- and *trans*-2-alkenes were obtained as primary products[7,38]. This *cis*-alkene is always favored in relation to the *trans*-alkene to a greater degree than that corresponding to thermal equilibrium. *Pines et al.* explain this result by a synchronous *trans*-elimination.

The intermediate proton-olefin complex *(2)* is thought to be responsible for the unusually high *cis*:*trans* ratio.



(1) *(2)*

Pines and *Manassen*[8] concluded that acidic and basic centers take part in the dehydration of alcohols on aluminum oxide. A carbonium ion mechanism appears to be favored in the dehydration of tertiary alcohols and a synchronous mechanism in the case of primary or secondary alcohols. If possible, the reaction proceeds as a simple 1,2-*trans*-elimination. Neighboring-group effects can lead to the migration of methyl groups. The reaction is thought to take place preferentially on steps, in pores, and in cracks in the oxide. Thus the aluminum oxide must surround the alcohol molecule in such a way that the acidic centers can act as proton donors (electron acceptors) and the basic centers as proton acceptors (electron donors). The catalyst is therefore regarded as a pseudosolvent, and the strong analogy with eliminations in the liquid phase is stressed.

Using these views as a basis, *Jain* and *Pillai*[39] proposed a mechanism (adsorbed phase substitution-elimination mechanism) that also embraces the ether formation.

If the aluminum oxide is assumed to have electrophilic (A) and nucleophilic (B) sites on its surface, there should also be two types of adsorbed alcohol molecules, *i.e.* carbonium ions *(3)* and alkoxide ions *(4)*. A nucleophilic attack by *(4)* on the positively charged C atom of *(3)* leads to ether formation (cf. homogeneous S_N2 reactions), while the abstraction of a β proton from the carbonium ion *(3)* by the alkoxide *(4)* (or by the basic site on the surface, as is now assumed) leads to the olefin. According to this view, therefore, the catalyst gives the reacting molecules the required polarity and fixes them in the correct arrangement. The adsorbed phase thus resembles a polar medium in which nucleophilic substitution and elimination compete with each other.

(3) *(4)*

The simultaneous dehydration of phenol and aliphatic alcohols, as well as poisoning experiments, carried out by the same authors[39a] lends support to the concept of two different species taking part in ether formation.

2. The Reaction Scheme in the Dehydration of Alcohols

The dehydration of simple alcohols on aluminum oxide leads mainly to ethers, olefins, and water, which may be formed in successive or parallel steps or else simultaneously. For the dehydration of methanol and ethanol up to about 200 °C, *Balaceanu* and *Jungers*[40] assume primary ether formation with possible equilibrium. In the dehydration of ethanol, ethylene is formed as a secondary product with re-formation of ethanol; it is also formed directly at higher temper-

[32] *H. Pines* and *W. O. Haag*, J. Amer. chem. Soc. *82*, 2471 (1960).

[33] *H. Pines* and *C. N. Pillai*, J. Amer. chem. Soc. *83*, 3270 (1961).

[34] *G.-M. Schwab* and *E. Schwab-Agallidis*, J. Amer. chem. Soc. *71*, 1806 (1949).

[35] *P. Sndréu*, *E. Bussmann*, *H. Noller*, and *S. K. Sim*, Z. Elektrochem., Ber. Bunsenges. physik. Chem. *66*, 739 (1962).

[36] *K. Watanabe*, *C. N. Pillai*, and *H. Pines*, J. Amer. chem. Soc. *84*, 3934 (1962).

[37] *J. Herling* and *H. Pines*, Chem. and Ind. *1963*, 984.

[38] *C. N. Pillai* and *H. Pines*, J. Amer. chem. Soc. *83*, 3274 (1963).

[39] *J. R. Jain* and *C. N. Pillai*, Tetrahedron Letters *11*, 675 (1965).

[39a] *J. R. Jain* and *C. N. Pillai*, J. Catalysis *9*, 322 (1967).

[40] *J. C. Balaceanu* and *J. C. Jungers*, Bull. Soc. chim. belges *60*, 476 (1951).

atures. *Isagulyants et al.* [41, 42] reached the same conclusions on the basis of investigations on [^{14}C]-ethanol but assumed that the olefin is formed as a secondary product by the dehydration of ethers. *Stauffer* and *Kranich* [43], on the other hand, assumed that the primary aliphatic alcohols up to *n*-hexanol are dehydrated to the ether and the olefin in independent parallel steps. The results obtainable for other alcohols are not very extensive.

A good method for the determination of the reaction schemes of complex reactions is the study of the product distribution as a function of the catalyst temperature and the contact time. We used this method to study the reaction scheme for the dehydration of some unbranched and branched aliphatic alcohols [44, 45]. γ-Al_2O_3 was used as the catalyst for all the kinetic studies described.

Since the dehydration of methanol up to 320 °C yields only ether by the bimolecular reaction

$$2\,CH_3OH \rightleftarrows (CH_3)_2O + H_2O$$

with possible equilibration, the reaction scheme will be discussed for the case of ethanol. Figure 1 shows the partial pressures of the components occurring as a function of

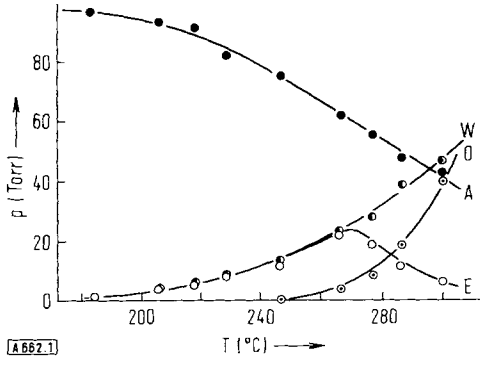


Fig. 1. Product distribution in the dehydration of ethanol on γ-Al_2O_3 as a function of the temperature [45].

A = alcohol, E = ether, O = olefin, W = water.

temperature. At low temperatures, only equimolar quantities of ether and water are obtained; the reaction therefore proceeds in accordance with:

$$2\,C_2H_5OH \underset{-1}{\overset{1}{\rightleftarrows}} (C_2H_5)_2O + H_2O \qquad (1)$$

Ethylene is formed only above 240 °C. The maximum in the ether-concentration curve points to secondary decomposition of the ether. Since ethylene formation begins in the immediate vicinity of the point of inflection in the ether curve, ethylene should be formed by the secondary decomposition of the ether. Diethyl ether on this catalyst does in fact give ethanol and ethylene (cf. Fig. 2). Both diagrams show that the secondary decomposition of ether on γ-Al_2O_3 begins

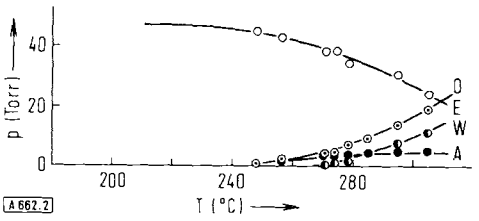


Fig. 2. Product distribution in the decomposition of diethyl ether on γ-Al_2O_3 as a function of the temperature [45].

A = alcohol, E = ether, O = olefin, W = water.

between 240 and 250 °C. The quantities of ethanol and ethylene in Figure 2 are initially equimolar

$$(C_2H_5)_2O \xrightarrow{2} C_2H_5OH + C_2H_4 \qquad (2)$$

Above 260 °C, the ethylene concentration increases more rapidly than the ethanol concentration, and at the same time water begins to appear as a result of secondary dehydration of ethanol in accordance with

$$(C_2H_5)_2O \xrightarrow{3} 2\,C_2H_4 + H_2O \qquad (3)$$

Even with long contact times, no ethylene is observed below 240 °C, while small concentrations that increase with the contact time appear at 256 °C (Fig. 3).

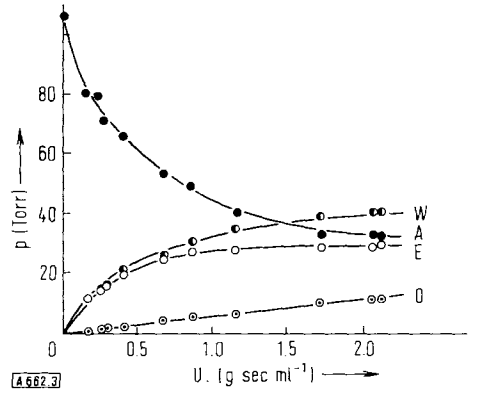


Fig. 3. Reaction isotherms for the dehydration of ethanol on γ-Al_2O_3 at 256 °C [45].

A = alcohol, E = ether, O = olefin, W = water, U = conversion.

Since the ethylene concentration does not exhibit the induction period (convex curvature with respect to the abscissa) characteristic of pure secondary reactions, direct olefin formation from ethanol must be superimposed on the

$$C_2H_5OH \xrightarrow{4} C_2H_4 + H_2O \qquad (4)$$

secondary ethylene formation from the ether. Two steps (3) and (4) leading to ethylene thus evidently proceed simultaneously and begin on γ-Al_2O_3 in approximately the same temperature range (240–250 °C).

At about 300 °C and above, the ethanol is not only dehydrated, but also dehydrogenated to acetaldehyde and hydrogen [45].

The unbranched primary alcohols up to *n*-hexanol behave in exactly the same manner. However, the temperature range for pure ether formation decreases as the number of carbon atoms increases, so that even for *n*-butanol, the reactions start almost simultaneously. Direct kinetic studies cannot therefore be carried out on any of these reactions for primary alcohols higher than *n*-propanol.

In the case of the higher homologs of the primary alcohols, isomerizations also occur in the initially formed 1-olefins. In agreement with *Pines* and *Haag* [7], we found isomeriza-

[41] *G. W. Isagulyants, A. A. Balandin, E. J. Popow* and *Yu. J., Derbenzew*, Ž. fiz. Chim. *38*, 20 (1964).

[42] *G. W. Isagulyants* and *A. A. Balandin* in: Radioisotopes in the Physical Sciences and Industry. Intern. Atomic Energy Agency, Vienna 1962, p. 245.

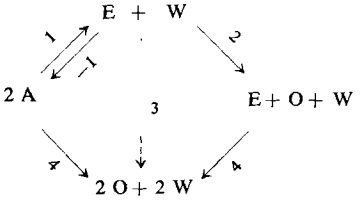
[43] *J. E. Stauffer* and *W. L. Kranich*, Ind. Engng. Chem., Fundamentals *1*, 107 (1962).

[44] *H. Knözinger* and *R. Köhne*, J. Catalysis *3*, 559 (1964).

[45] *H. Knözinger* and *R. Köhne*, J. Catalysis *5*, 264 (1966).

tion of 1-butene to *cis*- and *trans*-2-butene (with a clear preference for the *cis* product) in the dehydration of *n*-butanol, though no skeletal isomerization was detected [45].

Thus the steps corresponding to reactions (1) to (4) are observed for the primary alcohols containing two to six carbon atoms, and the ether formation can be clearly isolated for ethanol and *n*-propanol at low temperatures. As the temperature is raised, the primary olefin formation from alcohol and the secondary olefin formation from ether start in the same temperature range and steadily become more important. It is not certain whether the secondary olefin formation proceeds with regeneration of alcohol in accordance with step (2) or with dehydration of the ether in accordance with step (3). Step (2) should however be favored at low temperatures at least, since it is known from experience that the probability of the simultaneous participation of several bonds in the reacting molecule is very small. On the other hand, step (3) cannot be ruled out at about 300 °C (cf. [17]). The possible reaction directions for primary aliphatic alcohols are shown in Scheme 1, which is in agreement with the results obtained by *Balaceanu* and *Jungers* [40] as well as by *Bliss, Butt et al.* [46, 47, 47a]



Scheme 1.

Isopropanol, 2-butanol, isobutanol, and *tert*-butanol have also been investigated [44, 45]. The dehydration of isopropanol leads to the formation of propylene, and yields only small quantities of isopropyl ether. The dehydration of 2-butanol yields 1-butene and *cis*- and *trans*-2-butene, which, according to *Pines* and *Haag* [32] are formed as primary products in parallel steps. Isobutanol and *tert*-butanol give isobutylene in yields of more than 95 % (based on reacted alcohol).

Benzyl alcohol gives only dibenzyl ether up to 200 °C [48], while cyclohexanol gives cyclohexene [7, 49, 94]. A slow secondary skeletal isomerization of cyclohexene into methylcyclopentene was observed by *Pines* and *Haag* [7] only above 300 °C on strongly acidic oxides.

The alcohols suitable for kinetic studies are those in whose dehydration individual primary steps can be definitely isolated at least in narrow temperature ranges. Methanol, ethanol, *n*-propanol, and benzyl alcohol can be used as representative examples for the study of ether formation, and *tert*-butanol, isobutanol, and cyclohexanol for the study of olefin formation. Since the catalytic activity of a surface is strongly dependent on its structure and properties as well as on the surface compounds of the substrates and reaction products, the γ-Al_2O_3 surface and the adsorption structures of alcohols and their dehydration products will be considered before the kinetic studies are described.

3. The Surface Structure of γ-Al_2O_3

In the simplest model, the surface centers of aluminum oxide are regarded as incompletely coordinated aluminum and oxygen ions, the surface being assumed to be completely free from OH groups. Other models take into account cation defects and strained sites, which result from the dehydration of the originally hydrated surface [50, 51]. By investigation of the water-absorption and analysis of the IR spectra of water adsorbed on γ-Al_2O_3, *Peri* [52] developed a more detailed model based on the following considerations (cf. Fig. 4a).

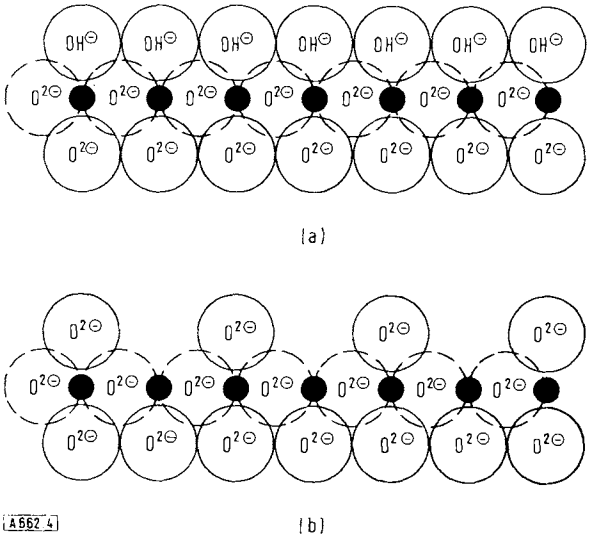


Fig. 4. Vertical section through an ideal γ-Al_2O_3 surface.
(a) hydrated surface, (b) dehydrated surface, ● = Al (after [52]).

The oxide is in the form of a defect lattice of the spinel type. Ionic surfaces are generally bounded by anions, which are more readily polarizable than cations. Though many authors (*e.g.* [53]) believe the [111] face of the oxygen sublattice to be energetically favored, *Peri* concludes that γ-Al_2O_3 is bounded by the [100] face. To reduce the surface energy, oxides of this type characteristically adsorb water, which leads whenever possible to the formation of OH groups. The liberation of water from a hydrated surface by condensation of two OH groups must expose oxygen ions. The re-

[46] *J. B. Butt, H. Bliss,* and *C. A. Walker,* A. I. Ch. E. Journal *8,* 42 (1962).

[47] *H. J. Solomon, H. Bliss,* and *J. B. Butt,* Ind. Engng. Chem., Fundamentals *6,* 325 (1967).

[47a] *R. Mezaki* and *J. B. Butt,* Ind. Engng. Chem., Fundamentals *7,* 120 (1968).

[48] *P. Sabatier* and *P. Mailhe,* Ann. Chim. physique [8] *20,* 298 (1910).

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[50] *E. B. Cornelius, T. H. Milliken, G. A. Mills,* and *A. G. Oblad,* J. physic. Chem. *59,* 809 (1955).

[51] *S. G. Hindin* and *S. W. Weller,* Advances Catalysis related Subjects *9,* 70 (1957).

[52] *J. B. Peri,* J. physic. Chem. *69,* 211, 220 (1965).

[53] *J. H. de Boer, G. M. M. Houben, B. C. Lippens, W. H. Meijs* and *W. K. A. Walrave,* J. Catalysis *1,* 1 (1962).

maining OH groups acquire different properties, which *Peri* explains by the change in their immediate surroundings. At the same time, aluminum ions in the second atomic position lose their full coordination and become accessible from the surface through oxygen vacancies (cf. Fig. 4b).

Aluminum oxide retains a part of its unimolecular surface coating of water even on dehydration for several hours under vacuum, the proportion retained depending on the heating temperature [54, 55]. This retained water is described as irreversibly adsorbed, and is partly in the molecular state and partly in the form of OH groups [52, 54, 56]. Adsorption isobars for a water partial pressure of zero, *i.e.* for the irreversibly adsorbed water, show that pure water does not give a unimolecular coating of OH groups in the temperature range for the catalytic dehydration of alcohols [55]. According to the Peri model, OH groups and oxygen ions as well as incompletely coordinated aluminum ions will therefore be accessible at the surface in this range. Since alcohols are also irreversibly adsorbed [57, 58], the distribution of these three types of centers will be modified by the adsorption of the alcohol.

It has been shown by gas chromatography that irreversibly adsorbed water on aluminum oxide is partly displaced by ethanol, and irreversibly adsorbed ethanol by water [59]. The aluminum ions whose coordination is disturbed by the condensation of two OH groups with formation and desorption of water may be regarded as acidic centers of the Lewis type [60, 61], which can be very selectively poisoned by organic bases [11, 12]. The OH groups are extremely weakly acidic Brønsted centers [11, 62]. Protons in cation vacancies have also been suggested as proton donors, but these would become effective only at temperatures above 400 °C because of their low activation energy [63].

4. IR Studies on the Adsorption Structures

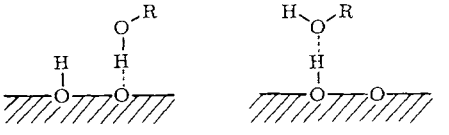
4.1. Adsorption of Alcohols

On adsorption of alcohols, particularly ethanol, IR studies showed three surface compounds:

1. molecular alcohol adsorbed *via* H bonds [67, 70];
2. alkoxide groups formed by dissociative adsorption [18, 19, 64–67, 75, 76];
3. carboxylate groups formed by oxidation of the alcohol [18, 19, 67, 76, 80, 81].

4.1.1. Molecular Adsorption of Alcohols

Whereas *Babushkin et al.* [64, 65] and *Boreskov et al.* [66] thought that they could still detect molecularly adsorbed ethanol even at high desorption temperatures, *Greenler* [18] (methanol and ethanol), *Treibmann* and *Simon* [19] (ethanol, *n*-propanol, and isopropanol) and *Kagel* [67] (*n*-propanol and *n*-butanol) found that alcohols are readily desorbed, even at room temperature. NMR studies showed that the hydroxyl group of the alcohols interacts directly with the oxide surface [68, 69]; it must therefore be assumed that H bonds are formed. *Kagel* [67] assumes without direct spectroscopic evidence, that the structures *(5)* and *(6)* are both present, *i.e.* that the alcohol forms both active and passive H bonds.



(5) *(6)*

However, the temperature dependence of the OH stretching bands on adsorption of methanol, ethanol, *tert*-butanol, isobutanol, cyclohexanol, and benzyl alcohol also indicates the presence of structures with two angular H bonds per alcohol molecule [70].

The absorption of the free OH groups of alcohols should be expected to appear at 3600 to 3650 cm^{-1}; the OH stretching vibrations of the chain associates formed by linear H bonds in the liquid phase occurs at 3350 cm^{-1} for all the alcohols in question. The shift of the OH stretching band is a measure of the strength of the H bonds. Linear H bonds are always stronger than angular bonds [71]. The pronounced frequency shift in liquid alcohols is thus explained by the formation of linear H bonds. All adsorbed alcohols give strong OH stretching bands centered around 3500 cm^{-1}. At low temperatures the bands are asymmetric, with a shallow gradient on the low wave-number side. As the temperature is raised, the bands decrease in intensity, starting at lower wave numbers, though the center still remains at 3500 cm^{-1}.

Thus at low temperatures there must be adsorption structures with relatively strong, probably substantially linear H bonds as well as weaker angular bonds, since the OH stretching band extends down to 3200 cm^{-1}. As the temperature is raised, the strong hydrogen bonds are broken while the weak-

[54] *J. B. Peri* and *R. B. Hannan*, J. physic. Chem. *64*, 1526 (1960).

[55] *H. Spannheimer* and *H. Knözinger*, Ber. Bunsenges. physik. Chem. *70*, 570 (1966).

[56] *J. H. de Boer*, *J. H. M. Fortuin*, *B. C. Lippens*, and *W. H. Meijs*, J. Catalysis *2*, 1 (1963).

[57] *J. J. Kipling* and *D. B. Peakall*, J. chem. Soc. (London) *1957*, 834.

[58] *H. Knözinger* and *H. Stolz*, Kolloid-Z., Z. Polymere *223*, 42 (1968).

[59] *H. Knözinger*, *H. Spannheimer*, and *G. Kinshofer*, unpublished.

[60] *J. B. Peri*, J. physic. Chem. *69*, 231 (1965).

[61] *J. B. Peri*, Actes Congr. intern. Catalyse, 2e, Paris 1960, Vol. 1, p. 1333.

[62] *E. Koberstein*, Z. Elektrochem., Ber. Bunsenges. physik. Chem. *64*, 906 (1960).

[63] *S. E. Tung* and *E. McIninch*, J. Catalysis *3*, 229 (1964).

[64] *A. A. Babushkin*, *A. V. Uvarov*, and *L. A. Ignateva*, Materialien des X. Allunionskongresses über Spektroskopie 1957, p. 161.

[65] *A. A. Babushkin* and *A. V. Uvarov*, Doklady Akad. Nauk SSSR *110*, 581 (1956).

[66] *G. K. Boreskov*, *Yu. M. Shtschekotschichin*, *A. D. Makarov*, and *V. N. Filimonov*, Doklady Akad. Nauk SSSR *156*, 901 (1964).

[67] *R. O. Kagel*, J. physic. Chem. *71*, 844 (1967).

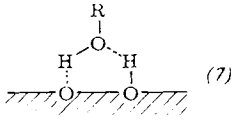
[68] *G. De la Hardrouyere*, Arch. Sci. *13*, 1 (1960).

[69] *D. Geschke* and *H. Pfeifer*, Z. physik. Chem. *232*, 127 (1966).

[70] *H. Knözinger*, *E. Ress*, and *H. Bühl*, Naturwissenschaften *54*, 516 (1967).

[71] *W. Luck*, Naturwissenschaften *52*, 25, 49 (1965).

er bonds (absorption at 3500 cm^{-1}) remain intact. Since the absorption band of cyclic alcohol dimers with two non-linear H bonds in dilute solutions[72] and in N_2 matrices[73] was localized at 3500 cm^{-1} similar structures, such as *(7)* should be favored on adsorption of alcohols on aluminum oxide.



(7)

A structure such as *(7)* will be more stable and more heat-resistant than the singly H-bonded structures *(5)* and *(6)* if the energy of formation of each of the two angular H bonds is greater than half the energy of formation of singly H-bonded structures. Such energy relations have been found for the cyclic dimers of alcohols in dilute solution[74]. In the adsorption of alcohols on surfaces, steric factors must also be taken into account since, owing to the geometry of the alcohol molecules, the formation of a linear active H bond brings the alkyl group closer to the surface, this effect being particularly pronounced in the case of *tert*-butanol. The steric factors thus favor the formation of adsorption complexes of structure *(7)*, in which the alkyl groups are pushed farther away from the surface.

An adsorption *via* two passive H bonds to the surface by way of the two free electron pairs of the hydroxy oxygen atom cannot be dismissed categorically. In this case, the frequency of the free OH vibration of the alcohol should occur; however, this absorption would hardly be recognizable in the steep high-frequency flank of the band due to the perturbed OH-groups.

4.1.2. Alkoxide Structures

A comparison of the IR-spectra of adsorbed phases with those of solid alkoxides shows the presence of surface alkoxide groups on adsorption of methanol[18], ethanol[18,19,64–66,75], *n*-propanol[19,67], isopropanol[19], *n*-butanol[67], and benzyl alcohol[76]. In the Peri model of the aluminum oxide surface, there are two possible routes for the formation of alkoxide by dissociative adsorption:

1. A hydroxyl proton may be split off to form a surface OH group, while the alkoxide residue occupies an oxygen vacancy in the surface (Lewis center);

2. The C–O bond of the alcohol may be broken, the resulting hydroxyl group filling an oxygen vacancy on the surface, while the alkyl residue adds to an adjacent oxygen ion.

Though the somewhat lower energy of rupture of the C–O bond in the free alcohol[77] favors the second possibility, the lattice energy liberated on incorporation of the alkoxide or hydroxyl group decides in favor of the rupture of the O–H bond. *Treibmann* and *Simon*[19] concluded from displacement reactions that the alkoxide formation involves incompletely coordinated aluminum ions; *Kagel*[67] reached the same conclusion on the basis of mass-spectroscopic residual gas analyses after adsorption.

While dissociative adsorption with formation of a surface alkoxide has been substantially verified for the alcohols discussed so far, no analogous surface compound has been detected on adsorption of *tert*-butanol, isobutanol, and cyclohexanol[75,76]. This can be explained on the basis of the thermal stability of the corresponding alkoxides. The thermal stability of zirconium alkoxides decreases in the order $Zr(OC_2H_5)_4 \gg Zr[OCH(CH_3)_2]_4 > Zr[OC(CH_3)_3]_4 \approx Zr[OC(CH_3)_2C_2H_5]_4$[78]. The methoxides of aluminum and zirconium are stable up to 240 and 280 °C respectively, whereas *tert*-butoxides have an extremely poor thermal stability[79]. All the alcohols studied so far that can form a surface alkoxide give ethers on dehydration on aluminum oxide at low temperatures, while the others tend toward olefin formation.

4.1.3. Carboxylate Structures

Oxidation of the alcohols during adsorption or aluminum oxide above about 170 °C to give carboxylate structures with the aid of the oxygen ions on the surface has been observed for methanol[18], ethanol[18,19,75], *n*-propanol, and *n*-butanol[67,80]. Corresponding surface compounds have recently also been found on adsorption of isobutanol and benzyl alcohol on aluminum oxide above about 120 °C[81]. *Treibmann* and *Simon*[19] concluded from the occurrence of an acetate structure on adsorption of isopropanol that the carbon skeleton of the molecule is broken down. These carboxylate structures are observed up to 400 °C; the adsorption of water does not change their adsorption bands. In view of its high stability, this structure could hardly be important as an intermediate in surface reactions up to 250 °C. However, the dehydrogenation of ethanol observed above about 300 °C could proceed *via* an acetate structure[82].

4.2. Adsorption of Water

The adsorption of alcohols in the catalytic temperature range is always accompanied by the appearance of a band at about 1600 cm^{-1}, the intensity of which increases with rising temperature, and which is not due to the alcohol or any of its surface compounds[85].

Using the N_2 matrix technique, *van Thiel, Becker* and *Pimentel*[83] were able to show that the water molecules in the H-bonded clusters have a deformation band at 1633 cm^{-1},

[72] *L. P. Kuhn*, J. Amer. chem. Soc. *74*, 2492 (1952).

[73] *M. van Thiel. E. D. Becker*, and *G. C. Pimentel*, J. chem. Physics *27*, 95 (1957).

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[75] *H. Knözinger*, Habilitationsschrift, Universität München 1967.

[76] *H. Knözinger, H. Bühl*, and *E. Ress*, J. Catalysis, in press.

[77] *H. Preuss*: Quantentheoretische Chemie Bibliographisches Institut, Mannheim 1863.

[78] *D. C. Bradley* and *M. M. Faktor*, J. appl. Chem. *9*, 435 (1959); Trans. Faraday Soc. *55*, 2117 (1959).

[79] *D. C. Bradley* and *M. M. Faktor*, Nature (London) *184*, 55 (1959).

[80] *V. Corso*, C. R. hebd. Séances Acad. Sci. *259*, 1413 (1964).

[81] *H. Knözinger* and *H. Bühl*, unpublished.

[82] *H. Knözinger*, Z. physik. Chem. N.F. *48*, 151 (1966).

[83] *M. van Thiel, E. D. Becker*, and *G. C. Pimentel*, J. chem. Physics *27*, 486 (1957).

while the corresponding band for the free monomeric molecule occurs at 1600 cm^{-1}. Since the surface of aluminum oxide contains OH groups and oxygen ions, it must be assumed that molecular water is adsorbed by means of H bonds. The deformation band is a particularly suitable aid to the detection of such H bonds, as was shown by *Glemser* and *Hartert* [84] for the adsorption of water on aluminum oxide at room temperature. The temperature-dependence of the intensity and position of this band provides information about the structure of the H bonds [85].

Figure 5 shows the region around 1600 cm^{-1} for the rehydration of a sample of γ-Al_2O_3 that has been heated under vacuum at 520 °C. This oxide initially shows no absorption

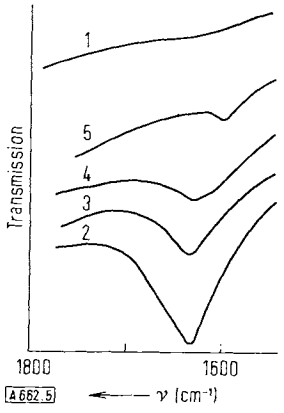
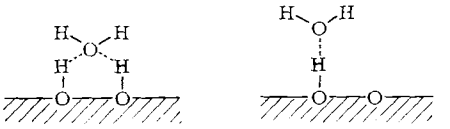


Fig. 5. Deformation bands of water adsorbed on γ-Al_2O_3.
1: after evacuation for 60 min at 520 °C/10^{-3} torr, spectrum recorded at 80 °C, 2: water adsorbed at 80 °C, 3: at 130 °C, 4: at 168 °C, 5: water desorbed at 168 °C, evacuation for 70 min at 10^{-3} torr.

between 1630 and 1600 cm^{-1}. On rehydration (55 torr of water vapor), a strong band due to polymeric water associates with strong, substantially linear H bonds develops at 1630 cm^{-1}. It is conceivable that multilayer adsorption occurs, with incipient formation of liquid water in the form of cluster-like regions, at least in pores and cracks. With rising temperature and hence decreasing surface concentration, the intensity of the band at 1630 cm^{-1} decreases, while a band simultaneously develops at 1600 cm^{-1}; this latter band is assigned to the deformation vibration in quasimonomeric water molecules. (Molecules that are only passively involved in H bonds *via* free pairs of electrons exhibit the vibration frequencies of the free molecule [86, 87].) The band observed at 1600 cm^{-1} on adsorption of alcohols after catalytic dehydration has started must therefore be the deformation vibration of water molecules that are adsorbed on surface OH groups by passive H bonds and which do not undergo any further interactions. *Yates* [88] found a band at 1605 cm^{-1}, which he interpreted in a similar manner, on adsorption of water on titanium dioxide.

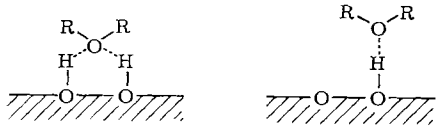
It is generally assumed that molecules containing oxygen and having two free pairs of electrons are preferentially adsorbed *via* two passive H bonds as in *(8)* [89]. This is thought to be the case in the adsorption of water on silanol groups [90]. This type of adsorption bonding *via* two H bonds requires two immediately adjacent OH groups on the surface, a condition that should be satisfied for the adsorption of pure water on aluminum oxide between 80 and 170 °C since up to 200 °C the surface of γ-Al_2O_3 still has a 50–80 % covering of OH groups [52, 55]. However, adsorption on isolated OH groups as in *(9)* should also be possible, at least when two adjacent OH groups are not available. This case is particularly probable when water is adsorbed in the presence of excess alcohol, *i.e.* under conditions that lead to the development of the band at 1600 cm^{-1} on adsorption of alcohol in the catalytic temperature range.



(8) *(9)*

4.3. Adsorption of Diethyl Ether

Diethyl ether is similar to the water molecule in that the oxygen atom has two free pairs of electrons, though ether cannot act as a proton donor and form active H bonds. However, the H-bond acceptor properties of the two molecules on adsorption on oxide surfaces having OH groups should be qualitatively similar. IR investigation of the adsorption of diethyl ether on aluminum oxide [85] shows that up to about 170 °C, it is bound only in a readily desorbable form. By analogy with the adsorption structures proposed for silicon dioxide [90–92] and the structures *(8)* and *(9)* for the adsorption of water on γ-Al_2O_3, it is assumed that diethyl ether is present in one of the forms *(10)* and *(11)*, depending on the surface concentration of OH groups.



(10) *(11)*

Bands indicating the formation of a surface ethoxide appear in the spectrum only above 200 °C [85]. This compound may be formed directly by dissociative adsorption of the ether or by secondary adsorption of the ethanol resulting from catalytic decomposition [*].

[84] *O. Glemser* and *E. Hartert*, Z. anorg. allg. Chem. *297*, 175 (1958).

[85] *H. Knözinger* and *E. Ress*, Z. physik. Chem. N.F. *59*, 49 (1968).

[86] *L. P. Kuhn*, J. Amer. chem. Soc. *74*, 2492 (1952).

[87] *D. P. Stevenson*, J. physic. Chem. *69*, 2145 (1965).

[88] *D. J. C. Yates*, J. physic. Chem. *65*, 746 (1961).

[89] *L. H. Little*: Infrared Spectra of Adsorbed Species. Academic Press, New York 1966, p. 263.

[90] *M. M. Egorov, W. I. Kvilividze, A. V. Kizelev*, and *K. G. Krassilnikov*, Kolloid-Z., Z. Polymere *212*, 126 (1966).

[91] *A. V. Kizelev* and *V. I. Lygin*, Usp. Chim. *31*, 351 (1962).

[*] *Note added in proof* (Sept. 19, 1968): In contrast to the results discussed here [85] no great shift of the OH stretching high-frequency bands of the surface hydroxyl groups after desorption of diethyl ether was observed by *Arai, Saito*, and *Yoneda* [92a]. The authors therefore rule out adsorption *via* H bonds. However, this conclusion does not necessarily apply when ether is also present in the vapor phase. On comparison of the desorption spectra with spectra of the $(C_2H_5)_2O$–$AlCl_3$ complex, the authors conclude that a coordinative adsorption bond is formed between ether and incompletely coordinated aluminum ions below 100 °C. This complex undergoes thermal decomposition to ethanol, diethyl ether, and ethylene. A surface ethoxide is observed at temperatures above 130 °C.

[92] *V. Y. Davidov, A. V. Kizelev*, and *V. I. Lygin*, Kolloidnyj Ž. *25*, 152 (1963).

[92a] *H. Arai, Y. Saito*, and *Y. Yoneda*, J. Catalysis *10*, 128 (1968).

5. Kinetics and Mechanism of the Dehydration of Alcohols

Only a few intensive studies have been carried out on the kinetics of the dehydration of alcohols. The test reaction used in most cases was the formation of ethylene from ethanol at relatively high temperatures. However, the product distribution (cf. Section 2) shows no definite reaction steps. *Topchieva* and *Romanovskii* [93] described the kinetics of the formation of ethylene from ethanol by a simple Langmuir formula containing an inhibition term for water. According to *Kochloefl et al.* [94] the formation of olefins from some aliphatic and alicyclic alcohols at about 200 °C and at alcohol pressures of 70 to 80 torr is a zeroth order reaction. On the basis of kinetic data for the dehydration of 2-butanol and *n*-hexanol, *Kittrell* and *Mezaki* [95] proposed the participation of two types of centers. The same conclusion was reached by *de Mourges et al.* [96] for the dehydration of isopropanol, and by *Carrà et al.* for the dehydration of cyclohexanol [96a]. From the kinetic analysis of reaction isotherms for the dehydration of ethanol, on the other hand, *Solomon, Bliss*, and *Butt* [47, 47a] postulated a one-center mechanism, in which the simultaneous formation of ethylene and ether is assumed to take place *via* a common intermediate. The kinetics of the formation of olefins from *tert*-butanol, isobutanol, and cyclohexanol and of the bimolecular ether formation on dehydration of methanol, ethanol, *n*-propanol, and benzyl alcohol, *i.e.* of clearly isolable reaction steps, will now be discussed.

5.1. Olefin Formation

Under the conditions chosen for the measurements, *tert*-butanol [97] and cyclohexanol [76] are dehydrated above about 130 °C, whereas the reaction begins only above 160 °C in the case of isobutanol.

5.1.1. Influence of the Alcohol Pressure

At low conversions (<3 %), *i.e.* at low partial pressures of water, the reaction rate is independent of the alcohol pressure over a wide range; the reaction is thus zeroth order under the following conditions: Isobutanol up to 240 °C above 80 torr, *tert*-butanol up to 180 °C above 150 torr, and cyclohexanol up to 180 °C above 80 torr.

5.1.2. Influence of the Products

No decrease in the reaction rate due to the olefins formed could be observed in the cases of isobutanol, *tert*-butanol, and cyclohexanol, whereas water strongly inhibits dehydration to the olefin. Inhibition by water has also been observed in the formation of olefins from ethanol [93] and isopropanol [96]. The influence of water always decreases with increasing alcohol partial pressure and with rising temperature. The experimental results cannot be quantitatively described by the usual Langmuir formula for unimolecular decompositions with product inhibition. On the other hand, the reaction rates found can be excellently reproduced over the entire measuring range up to a water:alcohol concentration ratio of 15:85 at all temperatures by the empirical equation

$$r = r_0\Theta_A = \sqrt{p_A} \;/\; (\sqrt{p_A} + bp_W) \qquad (5)$$

(r = reaction rate, r_0 = reaction rate for zeroth order, both in mole/sec per g of catalyst, p_A, p_W = partial pressures of alcohol and water, b = constant). In linear form, equation (5) becomes:

$$r_0/r = 1 + bp_W \;/\; \sqrt{p_A} \qquad (6)$$

The validity of equation (6) is confirmed by Figure 6 for the formation of olefin from cyclohexanol. It has also been checked in the same way for *tert*-butanol [97] and isobutanol [76].

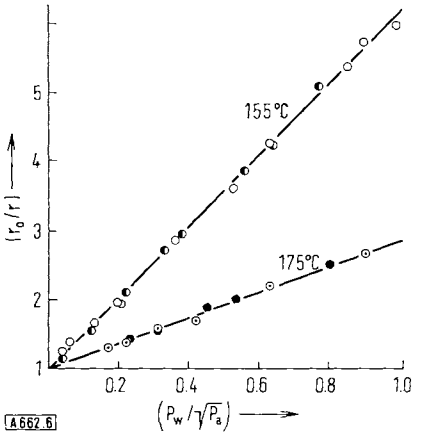


Fig. 6. Kinetics of olefin formation from cyclohexanol at alcohol pressures of 115 (○) and 155 torr (◐) (155 °C in each case), and 100 (●) and 160 torr (○) (175 °C in each case).

The expression Θ_A in equation (5) may be regarded as an adsorption isotherm. Θ_A then represents the relative coverage of the surface with alcohol in the presence of water. A similar equation with the pressure at powers less than one was derived by *Sips* [97a] for one-component adsorption exhibiting saturation properties at energetically heterogeneous surfaces; the validity of this equation has been established experimentally for a number of systems [97b, 97c]. The

[93] *K. V. Topchieva* and *B. V. Romanovskii*, Kinetika i Kataliz *6*, 279 (1965).

[94] *K. Kochloefl, M. Kraus, Chon Chin-Shen, L. Beránek*, and *V. Bažant*, Collect. czechoslov. chem. Commun. *27*, 1199 (1962).

[95] *J. R. Kittrell* and *R. Mezaki*, Ind. Engng. Chem. *59*, 28 (1967).

[96] *L. de Mourges, F. Peyron, Y. Trambouze*, and *M. Prettre*, J. Catalysis *7*, 117 (1967).

[96a] *S. Carrà, S. Santangelo*, and *A. Fusi*, Chim. e Ind. (Milano) *48*, 229 (1966).

[97] *H. Knözinger* and *H. Bühl*, Ber. Bunsenges. physik. Chem. *71*, 73 (1967).

[97a] *R. Sips*, J. chem. Physics *16*, 490 (1948).

[97b] *H. Bradley*, Trans. Faraday Soc. *31*, 1652 (1935).

[97c] *E. O. Wiig* and *S. B. Smith*, J. physic. Chem. *55*, 27 (1951).

IR spectra had shown that under the catalytic conditions, two-point adsorption in accordance with *(7)* is favored for alcohols, whereas a one-center adsorption in accordance with *(9)* must be assumed for water in the presence of an excess of alcohol.

5.1.3. Active Centers

The dehydration activity has repeatedly been found to exhibit an optimum value for a given pretreatment temperature of the aluminum oxide [9, 10, 98]. This optimum shows that a certain surface water content is essential to the reaction, but that other active centers besides OH groups must also be present on the surface. This is suggested by the adsorption structure *(7)*, which requires the presence of oxygen ions. If aluminum hydroxide (bayerite) is used as the catalyst, the dehydration of *tert*-butanol does not begin below 180 °C, *i.e.* about 50 °C higher than on the oxide [82]. Aluminum hydroxide has only OH groups on the surface, and in this form it is evidently inactive for the dehydration of *tert*-butanol. Above about 150 °C, the trihydroxide loses water to form the monohydroxide, with the result that oxygen ions and aluminum ions become accessible on the surface as well as OH groups, and the dehydration of *tert*-butanol can gradually begin.

A decision as to whether oxygen and/or aluminum ions are involved as active centers in the dehydration can be obtained by poisoning the aluminum oxide with pyridine. This strong Lewis base is very selectively adsorbed on the incompletely coordinated aluminum ions at the surface, which are Lewis-acid centers, with formation of an electron donor-acceptor complex [11]. The activity of the catalyst in olefin formation is not affected by modification with pyridine [75, 99, 100]. The (Lewis) acidic aluminum ions in the surface, which are responsible *inter alia* for isomerization [8] and polymerization [99], thus play no part in the formation of olefins from alcohols, and the OH groups and oxygen ions may be regarded as the active centers [*].

5.1.4. Mechanism of Olefin Formation

Olefin formation begins with an adsorption complex *(7)*. The water inhibiting the reaction blocks only the OH groups by a passive H bond. If, in accordance with *Peri* [52], the area required for an oxygen atom in the surface of γ-Al_2O_3 [see structure *(7)*] is assumed to be about 8 Å^2, the H–O···H angle between the H bonds is about 110 °, which is very close to the H–O–H angle in the water molecule. In agreement with the principle of least structural change [101], therefore, the water molecule may already be substantially formed in the adsorption structure *(7)* under the conditions of catalysis.

The further rearrangement could occur in two ways. With strongly polarized H bonds, *(7)* may approximate to an oxonium ion and change by charge migration into a carbonium ion, which allows the formation of an olefin by subsequent transfer of a proton to an adjacent surface oxygen ion. In this form the course of the reaction corresponds to the oxonium-carbonium mechanism of olefin formation [3–5]. However, a concerted E2-type mechanism is also possible, with simultaneous rupture of the C–H and C–O bonds in the alcohol. According to the results obtained by *Pines et al.* [8], it should be assumed that tertiary alcohols, which form relatively stable tertiary carbonium ions, are dehydrated to olefins by an ionic mechanism, and the other aliphatic alcohols by a concerted mechanism. β-Elimination always appears to occur if the molecule contains β-protons [8, 102]. In both mechanisms the water molecule is preformed in the adsorption complex, and the hydrogen exchange with the surface observed by *Eucken* and *Wicke* [10, 13, 14] must necessarily take place.

The rate-determining step can be established by measurement of the kinetic isotope effect. Investigations of this type have so far not been published for the dehydration of *tert*-butanols on γ-Al_2O_3 [103]. No primary isotope effect was observed in the dehydration of $(CH_3)_3COD$, in which heavy water is formed on deuterated surfaces; the rate cannot therefore be determined by the desorption of the water or the cleavage of the RO–H bond. On the other hand, a high primary alcohol effect is found in the dehydration of $(CD_3)_3COD$. Below 200 °C, removal of the β-proton must therefore be the slowest step also with *tert*-butanol.

Only a secondary isotope effect would be expected in the case of a pure carbonium-ion mechanism. An E2-type mechanism must therefore also be assumed for the dehydration of *tert*-butanol at temperatures below 200 °C. The investigations by *Pines* were all conducted at considerably higher temperatures. At low temperatures, olefin formation from aliphatic alcohols over aluminum oxide should therefore proceed fundamentally by an E2-type mechanism, the transition state – determined by the ionization potential of the alkyl group – containing ionic contributions. These ionic contributions should become more important as the temperature increases, so that when the temperature is sufficiently high for olefin formation from

[*] *Note added in proof* (Sept. 19, 1968): The participation of basic centers has recently been established by poisoning experiments with tetracyanoethylene [100a]. Formation of radical ions when this compound is adsorbed on aluminum oxide has been observed by means of electron spin resonance. Modification of aluminum oxide catalysts by tetracyanoethylene causes a considerable inhibition of the formation of not only ethylene but also ether. Since steric effects can be ruled out, active participation of basic centers in dehydration is thus proved.

[98] *K. V. Topchieva, E. N. Rosolovskaja,* and *O. K. Sharajev,* Vestnik Moskovskogo Univ. Ser. Math., Mech., Ast., Physik, Chem. *14*, 217 (1959).

[99] *L. Beránek, M. Kraus, K. Kochloefl,* and *V. Bažant,* Collect. czechoslov. chem. Commun. *25*, 2513 (1960).

[100] *M. Misono, Y. Saito,* and *Y. Yoneda,* Proc. third int. Congr. Catalysis, Amsterdam 1964, Vol. 1, p. 408.

[100a] *F. Figueras Roca, A. Nohl, L. de Mourges,* and *Y. Trambouze,* C. R. hebd. Séances Acad. Sci. *266*, 1123 (1968).

[101] *F. O. Rice* and *E. Teller,* J. chem. Physics *6*, 489 (1938).

[102] *G.-M. Schwab, O. Jenkner,* and *W. Leitenberger,* Z. Elektrochem. Ber. Bunsenges. physik. Chem. *63*, 461 (1959).

[103] *H. Knözinger* and *A. Scheglila,* unpublished.

tertiary alcohols an E1-type transition state will be present, as was observed by *Pines*. This concept is further supported by the strong temperature dependence of the isotope effect.

Olefin formation by dissociation of short-lived alkoxide groups has also been discussed [17]. The alkoxide would be formed by dissociative adsorption of alcohol on incompletely coordinated aluminum ions in the surface [19, 67]. However, since poisoning of these Lewis centers with pyridine does not decrease the activity of the aluminum oxide catalyst in the olefin formation [75, 99, 100], a mechanism of this type must be rejected, at least at low temperatures [*].

5.1.5. Reaction Rates of the Alcohols

Dohse [104] and *Bork* and *Tolstopja-Tova* [105] found a definite relationship between the activation energy for olefin formation on bauxite and the methyl substitution. According to *Dohse*, a methyl group in the α-position decreases the activation energy by 5.5 kcal/mole, in the β position by 2.5 kcal/mole, and in the γ position by 0.5 kcal/mole. *Stauffer* and *Kranich* [43] report a constant activation energy of 30.8 kcal/mole for the formation of olefins from linear alcohols from ethanol to *n*-hexanol on γ-Al_2O_3. *Kraus*, *Kochloefl et al.* [49, 94] showed that steric effects are much more important than electronic effects in the dehydration of aliphatic and cyclic secondary alcohols and of stereoisomeric alkylcyclohexanols on aluminum oxide. The authors conclude that the rate of reaction of organic compounds in heterogeneously catalyzed reactions is determined mainly by the steric arrangement of the reacting molecule and particularly of the chemisorbed species.

Kraus and *Kochloefl* [106] also detected electronic effects in the rate of dehydration of *meta*- and *para*-substituted phenylethanols. However, these effects are less important than the steric effects. Since the styrenes formed do not polymerize, the authors rule out the possibility of an ionic dehydration mechanism. A Hammett relationship between the logarithm of the rate constant and the σ* constant can be verified for these reactions (Fig. 7).

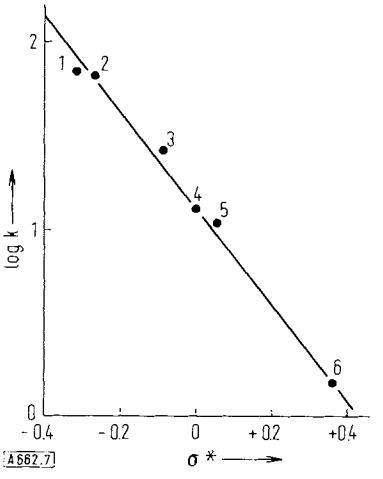


Fig. 7. Correlation of the rate constants (200 °C) for the dehydration of substituted phenylethanols with the Hammett equation (after [106]). 1: 2-(*p*-tolyl)-ethanol, 2: 2-(*p*-tert-butylphenyl)ethanol, 3: 2-(*p*-fluorophenyl)ethanol, 4: 2-phenylethanol, 5: 2-(*m*-methoxyphenyl)ethanol, 6: 2-(*m*-fluorophenyl)ethanol.

The "true activation energies" for the dehydration of aliphatic alcohols to olefins show a marked dependence on structure [106a] in the series $q_{primary} > q_{sec} > q_{tert.}$ If the E2-type mechanism represented in Section 5.1.4 is assumed to be valid, this order can be interpreted in terms of the structurally dependent ionic contributions to the transition state and of the inductive effect of the alkyl groups adjacent to the β-C atom. A comparison of the dehydration of *tert*-butanol (q = 25.5 kcal/mole [97]) and that of isobutanol (q = 30 kcal/mole [76]) may be cited as an example. The ionic contributions to the transition state are low for isobutanol compared to *tert*-butanol. Furthermore, the partial positive charge on C_β in isobutanol is compensated to some extent by the inductive effect of the two methyl groups in the γ position. Consequently, in the transition state the acidity of the β protons in isobutanol is much lower than in *tert*-butanol, so that the activation energies for dehydration fall as the acidity of the β protons increases. Comparison of the activation energies for the different possible reactions of alcohols that afford a number of olefinic products on dehydration clearly shows that not only the inductive effect but also an inductometric effect must come into play. On dehydration, 3-methyl-2-butanol and 2-methyl-2-butanol yield comparable amounts of "Hofmann" and "Saytzeff" products. If the inductive effect alone were to operate, the lower activation energy would be expected for the "Hofmann" product. In fact, however, the activation energy for the formation of this product from 3-methyl-2-butanol and from 2-methyl-2-butanol is lower by 2.5 kcal/mole and about 1 kcal/mole, respectively, than for the forma-

[*] *Note added in proof* (Sept. 19, 1968): Confirmation of the alkoxide mechanism has recently been attempted by investigations of the thermal desorption of ethanol [103a] and diethyl ether [92a] adsorbed on aluminum oxide. In this case olefin formation is desribed as a concerted decomposition of the alkoxide-type surface species, whereas ether formation is regarded as proceeding *via* condensation of two neighboring alkoxide groups. Using the same experimental technique, *Makarov* and *Shtschekotshichin* [103b] arrived at similar results. However, these authors assume direct or indirect participation of the surface carboxylate (cf. 4.1.3) in olefin formation. In view of the high stability of these surface compounds, such a route seems questionable, particularly since *tert*-butanol does not form a compound of this kind. Moreover, it does not appear certain whether conclusions regarding the mechanism of heterogeneously catalyzed dehydration of alcohols from the gaseous phase can be drawn from investigations of thermal desorption, since the experimental conditions differ greatly. In the reaction from the gaseous phase, molecules are necessarily also present that are physically adsorbed *via* H bonds; such molecules can also play a role in the reaction.

[103a] *H. Arai, J.-I. Take, Y. Saito*, and *Y. Yoneda*, J. Catalysis *9*, 146 (1967).

[103b] *A. D. Makarov* and *Yu. M. Shtschekotschichin*, Metody Issled. Katal. Reakts., Akad. Nauk SSSR, Sib. Otd., Inst. Katal. *1*, 20 (1965); Chem. Abstr. *66*, 53400 (1967).

[104] *H. Dohse*, Z. physik. Chem. Abt. B, Bodenstein-Festband *1931*, 533.

[105] *A. Bork* and *A. Tolstopjatova*, Acta physicochim. URSS *8*, 603 (1938).

[106] *M. Kraus* and *K. Kochloefl*, Collect. czechoslov. chem. Commun. *32*, 2320 (1967).

[106a] *H. Knözinger* and *H. Bühl*, unpublished.

tion of the "Saytzeff" product. The relatively low differences in the true activation energies are nevertheless well outside the limits of experimental accuracy. Nor can they be due to lateral interactions in the adsorbed phase, since in each case two possible reactions of one alcohol, and not of substrates having different structures, are being compared. This result is in accord with the assumption of an E2-type mechanism, because inductometric effects can only play a role when the double bond of the incipient olefin is already present in the transition state; this is the case with transition states of the E2 type but not with those of the E1 type.

5.2. Ether Formation

The bimolecular ether formation from methanol [107], ethanol [108], *n*-propanol [75, 76], and benzyl alcohol [76] begins on γ-Al_2O_3 at about 130–140 °C. In the reaction

$$2\,ROH \underset{-1}{\overset{1}{\rightleftarrows}} ROR + H_2O \qquad (1)$$

the equilibration is fundamentally possible. However, since the equilibrium lies on the side of ether and water, the rate of the reverse reaction r_{-1} at low product concentrations, *i.e.* at low conversions in the dehydration, will be low in relation to the rate of ether formation r_1. This can be confirmed by thermodynamic estimations and by measurement of the rate of reformation of the alcohol (–1) [75, 107, 108]. Thus the ether formation from the four alcohols in question can be followed kinetically at low conversions independently of the equilibrium reaction.

5.2.1. Effect of Alcohol Pressure

The rate of the ether formation from methanol, ethanol, *n*-propanol, and benzyl alcohol becomes independent of pressure above about 160 torr at the highest measuring temperatures (about 200 °C), *i.e.* the bimolecular ether formation is a zeroth order reaction in the limiting case of high partial pressures of alcohol [76, 107, 108]. This behavior must be expected if the Langmuir-Hinshelwood mechanism is valid. The ethers should thus be formed from alcohols over aluminum oxide in a bimolecular reaction from the adsorbed phase, since a reaction oder of 1 should be obtained in the limiting case of high substrate partial pressures if the Eley-Rideal mechanism were valid. *Balaceanu* and *Jungers* [40] reached the same conclusion on the basis of kinetic studies. *de Boer et al.* [109, 110], on the other hand, propose the superposition of two independent mechanisms for the formation of ether from ethanol, the principal mechanism being an Eley-Rideal mechanism, with a smaller contribution by a Langmuir-Hinshelwood mechanism. However, these authors worked at conversions of up to 20 % and temperatures at which the secondary decomposition of the ether and the olefin formation probably cannot be neglected. Moreover, at the high conversions and relatively low alcohol partial pressures used, the inhibition of the reaction by the water formed may be appreciable, and the equilibrium reaction may falsify the rate of formation of the ether.

5.2.2. Influence of the Products

No inhibition of the reactions by the ethers formed has been observed in any case, whereas the ether formation is strongly inhibited by water. The inhibiting action of water decreases with rising temperature and increasing alcohol partial pressure [76, 107, 108]. As in the formation of olefins, the rate of ether formation can be satisfactorily described by the empirical equation (5) (in the form (6)) (Fig. 8). The quotient Θ_A may again be interpreted as an adsorption isotherm, which

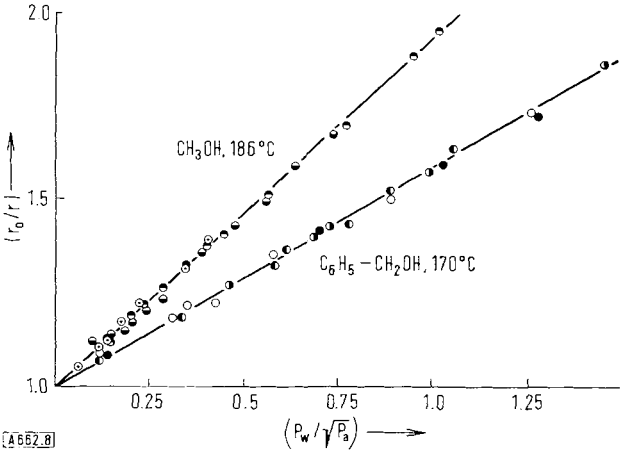


Fig. 8. Kinetics of ether formation from methanol at 109 (◓), 180 (◒), and 225 torr (○) (186 °C in each case) and from benzyl alcohol at 25 (●), 40 (◑), 50 (◐), and 78 torr (○) (170 °C in each case).

expresses the relative coverage of the surface with alcohol in the presence of the inhibiting water. Alcohol is molecularly adsorbed in the structure *(7)*, while water blocks only one surface OH group [structure *(9)*]. A limiting form of equation (5) for low surface coverages and negligible inhibition

$$r = r_0 \sqrt{p_A} \qquad (7)$$

was also found by *Meye* [31] for the formation of ether from methanol on γ-Al_2O_3. It is unusual for an equation (5) having the typical form of the kinetic equation of a unimolecular decomposition to be valid for a bimolecular reaction. For the ether formation one would expect an expression containing the square of the surface concentration of the alcohol. At least one reactive surface compound having a finite life must be assumed for ether formation [82], since the probability of a bimolecular surface reaction would otherwise be extremely small. Since a surface alkoxide has been de-

[107] *D. Kalló* and *H. Knözinger*, Chemie-Ing.-Techn. 39, 676 (1967).

[108] *H. Knözinger* and *E. Ress*, Z. physik. Chem. N.F. *54*, 136 (1967).

[109] *J. H. de Boer* and *R. B. Fahim*, Proc. Kon. nederl. Akad. Wetensch., Ser. B *67*, 127 (1964).

[110] *J. H. de Boer, R. B. Fahim, B. G. Linsen, W. J. Visseren*, and *W. F. N. M. de Vleesschauwer*, J. Catalysis *7*, 163 (1967).

tected in the catalytic temperature range for all the ether-forming alcohols that have been studied spectroscopically (cf. Section 4.1.2), this species must be regarded as the intermediate in question. The rate constant for the reaction is proportional to the surface concentration of the ethoxide [110a]. Because of its finite life and its relatively high stability, its concentration may be assumed to remain constant during the reaction. The rate equation therefore only explicitly contains the concentration of a second reactant Θ_A, *i.e.* an alcohol molecule adsorbed as such by means of two nonlinear H-bonds. The rate equation for the bimolecular ether formation must consequently be of the same form as that for the unimolecular olefin formation.

5.2.3. Active Centers

As in the olefin formation (cf. Section 5.1.3), it can be shown that OH groups are also necessary as active centers for the ether formation. Activity measurements on aluminum hydroxide, on the other hand, show that the catalytic activity is not due to OH groups alone, since aluminum hydroxide is at first totally inactive for ether formation. The ether formation begins with increasing conversion of the trihydroxide into monohydroxide, though only at higher temperatures than on γ-Al_2O_3 [75, 82]. In the Peri model of the oxide surface, therefore, oxygen ions and/or incompletely coordinated aluminum ions must take part in the reaction as well as OH groups. On blockage of the Lewis centers with pyridine, in contrast to the olefin formation, formation of ether from ethanol is strongly retarded. Figure 9 shows a plot of the relative rate of ether formation on a catalyst modified with pyridine at 320 °C with respect to the rate on pure γ-Al_2O_3 against the reaction time.

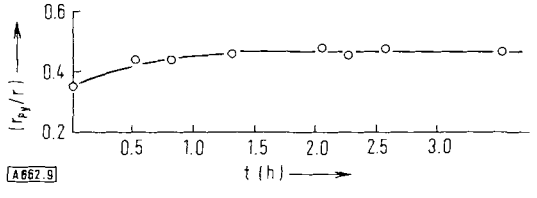


Fig. 9. Blockage of the surface of γ-Al_2O_3 in the formation of ether from ethanol. r_{Py}/r = relative reaction rate of a γ-Al_2O_3 catalyst modified with pyridine at 320 °C.

After a build-up period of about 70 minutes, the relative activity remains constant. As a result of the poisoning by pyridine, however, the rate of ether formation decreases by more than 50 %, and the activity does not regain its original value even after several hours. This shows that the ether formation, unlike the olefin formation, involves the active participation of Lewis centers. The oxygen ions must also be concluded to be involved on the basis of the structure *(7)* assumed for the adsorption of molecular alcohol, so that three types of centers, *i.e.* OH groups, oxygen ions, and incompletely coordinated aluminum ions, are necessary for ether formation (cf. also the note added in proof, p. 800).

5.2.4. Mechanism of Ether Formation

The formation of ethers from alcohols is assumed to result from the reaction of surface alkoxide groups with molecularly adsorbed alcohol molecules. A mechanism of this type is suggested by the fact that all the ether-forming alcohols examined so far can form a surface alkoxide that can be detected by IR spectroscopy, whereas no analogous surface compound is found for the olefin-forming alcohols. Since the alkoxides of the ether-forming alcohols are thermally more stable than those of the olefin-forming alcohols [78, 79], the direction followed by the reaction may be determined by the thermal stability of the alkoxide. The temperature range for the undisturbed ether formation thus becomes narrower with decreasing thermal stability of the alkoxide (cf. Section 2). Thus for isopropanol and *n*-butanol, olefin and ether formation and secondary decomposition of the ether begin at roughly the same temperature.

This naturally does not conclusively prove the active participation of surface alkoxides in the ether formation and the special reaction-directing effect of this group. However, since no opposing evidence has yet been found, a course of this type may be assumed, particularly since these views are indirectly reinforced by the form of the kinetic equation and the active participation of the Lewis centers, on which the alkoxide formation must occur [19, 67]. Ether formation by condensation of two adjacent alkoxide groups has been discussed by *Topchieva, Yun-Pin*, and *Smirnova* [17], but this would not explain the active participation of the three types of centers (cf. also the note added in proof, p. 801).

The rate determining step in the ether formation could in principle be the desorption of the water formed. However, since the formation of ether from deuteriomethanols on a deuterated oxide surface, which yields heavy water, shows no primary isotope effect [111], the rate cannot be determined by the desorption of water. There are two routes by which the reaction could proceed, but no definite decision as to which is actually followed is possible at present:

1. The R–OH bond of the molecularly adsorbed alcohol and the RO–Al bond in the alkoxide group are broken. No primary isotope effect is to be expected in this case, in agreement with the experimental observations [111]. The rate of ether formation may be determined by the cleavage of one of these two bonds, though it is not known which. Since the separation energies for homolysis are much lower than those for heterolysis [112, 113], the reaction would have to be assumed to be substantially nonionic.

2. Alternatively, the RO–H bond in the alcohol molecule and the R–OAl- bond in the alkoxide group

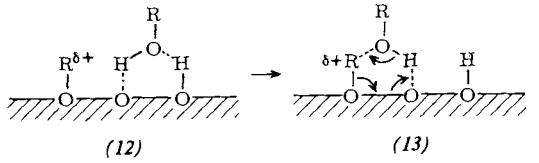
[110a] *H. Knözinger* and *H. Stolz*, unpublished.

[111] *H. Knözinger, A. Scheglila*, and *A. M. Watson*, J. physic. Chem. *72*, 2770 (1968).

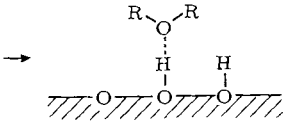
[112] *Landolt-Börnstein*: Zahlenwerte und Funktionen, Vol. 1: Atom- und Molekularphysik, Part 2: Molekeln I. Springer-Verlag, Heidelberg 1951, p. 36.

[113] *V. J. Vedeneyev, L. V. Gurvich, V. N. Kondratyev, V. A. Medvedev*, and *Ye. L. Frankevich*: Bond Energies, Ionization Potentials and Electron Affinities. Arnold Publ. Comp., London 1966.

may be broken. This route could be favored on steric grounds. The α-C atom in the alkoxide group may be positively charged because of the electron-attracting action of the aluminum, and, as an electrophile, attack the hydroxyl oxygen of the alcohol. This will cleave the passive H-bond between the hydroxyl oxygen of the alcohol and the surface proton. Rearrangement of the molecule then leads readily to a structure *(14)*



(12) *(13)*



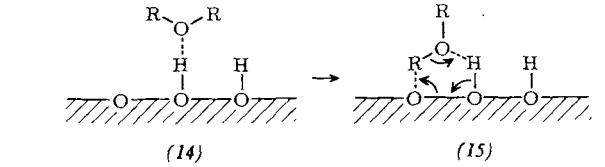
(14)

postulated on the basis of spectroscopic observations for the physically adsorbed ether [85]. The second reaction product, water, must be formed in this case by condensation of two adjacent surface OH groups. Thus hydrogen exchange with the surface must also occur in the ether formation.

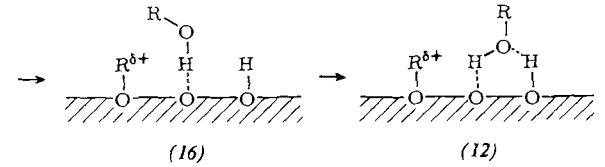
These views on mechanism can also be used to describe the equilibrium reaction (−1), *i.e.* the hydration of ethers

$$ROR + H_2O \xrightarrow{-1} 2\,ROH \qquad (-1)$$

while obeying the principle of microscopic reversibility. Starting with a surface area in which two adjacent OH groups have been formed by dissociative adsorption of a water molecule (*i.e.* reversal of the desorption of water during dehydration), the reaction can be schematically rerpesented as proceeding *via* the stages *(14)*, *(15)*, *(16)*, and *(12)*.



(14) *(15)*



(16) *(12)*

This brings us to the starting state *(12)* chosen in the dehydration of alcohols. In the following, final step, the second alcohol molecule must be formed by condensation of an alkoxide group with an OH group. This act of desorption corresponds, in the sense of microscopic reversibility, to the dissociative adsorption of alcohol with formation of the required surface alkoxide. According to these views, different intermediates would be required for the formation of ethers and of olefins.

Brey and *Krieger* [4], on the other hand, proposed the same intermediate, *i.e.* a carbonium ion, for both reactions. *Topchieva, Yun-Pin,* and *Smirnova* [17] deduced the same scheme, but replaced the common ionic intermediate by an alkoxide, as did *Solomon, Bliss,* and *Butt* [47].

If the second mechanism is correct, the cleavage of the RO–H bond may be ruled out as the rate-determining step for the ether formation, since no primary isotope effect is observed [111]. The slowest step in the ether formation should therefore be the cleavage of the AlO–R bond. The rate could in principle also be determined by the combination of the two groups to form the ether molecule, but this is unlikely in view of the high separation energies of the bonds to be broken.

5.2.5. Rate of Reaction of the Alcohols

The "true" activation energies for the formation of ethers from methanol, ethanol, *n*-propanyl, and benzyl alcohol are given with their maximum errors in Table 1.

Table 1. Reaction rates r_0 and "true" activation energies of some alcohols in ether formation on γ-Al_2O_3.

	q (kcal/mole)	$r_0 \cdot 10^7$ (mole/g sec) at 183 °C
Methanol [107]	25.9 ± 0.6	3.8
Ethanol [108]	25.9 ± 0.6	2.6
n-Propanol [76]	25.1 ± 0.6	1.5
Benzyl alcohol [76]	25.5 ± 0.6	17.2

To within the limits of accuracy, the true activation energies are the same, irrespective of the substrate alcohol. The zeroth order rates of formation r_0 of the ether decreases from methanol to *n*-propanol, while the ether formation from benzyl alcohol is 4.5 times as fast as from methanol. These observations can be explained by the reaction of a surface alkoxide group with a molecularly adsorbed alcohol molecule, with cleavage of the AlO–R bond as the rate-determining step. No data are available for the separation energy of this bond; the separation energy of the homolysis of the C–O bond in alcohols is independent of the alkyl residue R [77, 112, 113]. The separation energy of the Ti–O bond in titanium alkoxides is also substantially independent of the alkyl group [114]. It may therefore be assumed that a similar state of affairs exists for the separation energy of the C–O bond in aluminum alkoxides; this would explain the constancy of the activation energy. The rates of ether formation, on the other hand, vary with the substrate. The relative reaction rates based on that for methanol are plotted in Fig. 10 against the Taft constant σ*. They exhibit good agreement with the Taft equation. The differences in rate must therefore be due to inductive effects of

[114] *D. C. Bradley* and *M. J. Hillyer*, Trans. Faraday Soc. *62*, 2374 (1966).

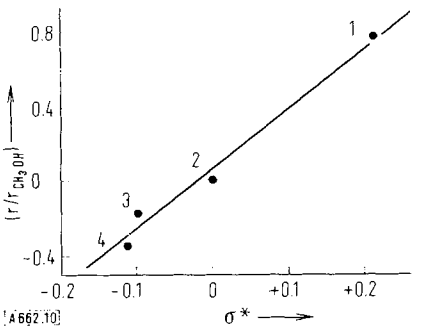


Fig. 10. Correlation of the relative rates of ether formation with the Taft equation.
1: benzyl alcohol, 2: methanol, 3: ethanol, 4: *n*-propanol.

the alkyl residues R. The straight line in Figure 10 has a positive gradient, *i.e.* the reaction constant ρ^* of the Taft equation is positive. Since this quantity becomes increasingly negative with increasing ionic character of the transition state[115], the transition state in the proposed ether formation mechanism (electrophilic substitution) must be assumed to be only weakly ionic.

I am grateful to my colleagues Dr. H. Bühl, G. Clement, G. Kinshofer, R. Köhne, W. Meye, E. Ress, A. Scheglila, Dr. H. Spannheimer, and H. Stolz for their enthusiastic cooperation, and to Prof. Dr. G.-M. Schwab for his interest in and encouragement of our work. Special thanks are due to the Deutsche Forschungsgemeinschaft and the Stiftung Volkswagenwerk for their generous support.

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Translated by Express Translation Service, London

[115] *K. Kochloefl*, Advances Catalysis related Subjects *17*, 75 (1967).

COMMUNICATIONS

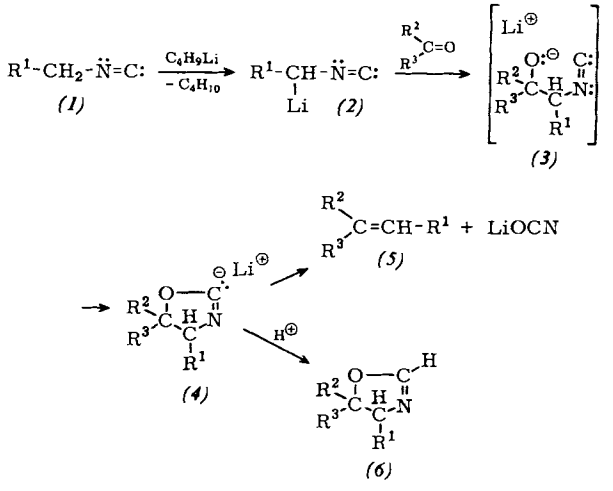
Carbonyl Olefination with α-Metalated Isocyanides

By *U. Schöllkopf* and *F. Gerhart*[*]

Dedicated to Professor H. Brockmann on the occasion of his 65th birthday

As is shown by the success of the Wittig reaction[1], the organic chemist is in urgent need of a process for the positionally specific conversion of carbonyl compounds into olefins.

We have now found that the reaction of α-metalated isocyanides *(2)* with aldehydes and ketones yields olefins *(5)* with their double bond in the position originally occupied by the carbonyl group. The olefination reagents *(2)* are obtained from isocyanides *(1)*[2] and bases such as butyllithium. The metalated oxazolines *(4)* are important intermediates; they result from the cyclization of the carbonyl adducts *(3)* and fragment to give the olefin *(5)* and metal cyanate. The readiness with which this decomposition occurs depends on the nature of the groups R_1, R_2, and R_3. The intermediates *(4)* and *(3)*, respectively, can be intercepted with protons with formation of the oxazolines *(6)*[3].



R¹	R²	R³	T (°C) [a]	Product	Yield %
H	C_6H_5	C_6H_5	−65	1,1-Diphenylethylene [b]	40
C_6H_5	C_6H_5	C_6H_5	−70	1,1,2-Triphenylethylene [c]	74
H	C_6H_5	CH_3	65	α-Methylstyrene	65
H	C_6H_5–CH=CH	H	65	1-Phenyl-1,3-butadiene [d]	28
CH_2=CH	C_6H_5	C_6H_5	−70	1,1-Diphenyl-1,3-butadiene [e]	38
CH_2=CH	C_6H_5	H	65	1-Phenyl-1,3-butadiene	41
C_6H_5	C_6H_5	CH_3	65	*trans*-α-Methylstilbene	44
C_2H_5	$-(CH_2)_5-$		65	Benzylidenecyclohexane	10

[a] Decomposition of *(4)*; metalation and carbonyl addition at −70C°; tetrahydrofuran as solvent.

[b] Together with 2-(diphenylhydroxymethyl)-5,5-diphenyloxazoline.

[c] Together with small quantities of 2-(diphenylhydroxymethyl)-4,5,5-triphenyloxazoline.

[d] Together with 5-(β-styryl)oxazoline.

[e] Together with 2-(diphenylhydroxymethyl)-5,5-diphenyl-4-vinyloxazoline.

The metalated isocyanides *(2)* are more reactive than the alkylidenetriphenylphosphoranes. For instance, α-lithiobenzhydrylisocyanide reacts even at −70 °C smoothly with benzaldehyde to 1,1,2-triphenylethylene (yield 30%), whereas diphenylmethylenetriphenylphosphorane is unreactive towards aldehydes and ketones[1].

1,1,2-Triphenylethylene:
A solution of 50 mmole of butyllithium in 45 ml of pentane was diluted with 150 ml of dry tetrahydrofuran. A solution of 5.85 g (50 mmole) of benzyl isocyanide in 30 ml of tetrahydrofuran was added dropwise at −70 °C. 9.1 g (50 mmole) of benzophenone dissolved in 50 ml of tetrahydrofuran was then added dropwise to the intensely yellow-red solution at −70 °C. The mixture was allowed to warm up to room temperature and evaporated to dryness under vacuum on a

rotary evaporator. 100 ml of water was added to the residue, the solution was extracted with 400 ml of ether, and the extract was dried over magnesium sulfate. Small quantities of 2-(diphenylhydroxymethyl)-4,5,5-triphenyloxazoline crystallized out on standing, and this was filtered off. Removal of the ether under vacuum left 13.3 g of residue. 3.5 g of this was chromatographed on 300 g of silica gel. 2.5 g (74%) of 1,1,2-triphenylethylene could be eluted with chloroform.

α-Methylstyrene:

Starting from methyl isocyanide and butyllithium, 50 mmole of isocyano-methyllithium was prepared at −70 °C (analogously to the above procedure). To the suspension was added with stirring at −70 °C 6.0 g (50 mmole) of acetophenone. The mixture was refluxed (under nitrogen) for 40 hours and subsequently poured into 600 ml of water. The olefin was extracted five times with 100-ml portions of pentane and dried over magnesium sulfate. The usual workup yielded 3.8 g of α-methylstyrene with b.p. 60–61 °C/18 torr.

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[1] *G. Wittig* and *U. Schöllkopf*, Chem. Ber. *87*, 1318 (1959); for reviews see: *U. Schöllkopf*, Angew. Chem. *71*, 260 (1959); *J. Levisalles*, Bull. Soc. chim. France *1958*, 1021; *S. Tripett*, Advances org. Chem. *1*, 83 (1960); *B. Pelc*, Chem. Listy *53*, 177 (1959); *L. A. Yanovskaya*, Usp. Chim. *30*, 813 (1961); *S. Tripett*, Quart. Rev. chem. Soc. (London) *17*, 406 (1963); *A. Maercker*, Org. Reactions *14*, 270 (1965).

[2] For the synthesis of isocyanides see *I. Ugi*, *U. Fetzer*, *U. Eholzer*, *H. Knupfer*, and *K. Offermann*, Angew. Chem. *77*, 492 (1965); Angew. Chem. internat. Edit. *4*, 472 (1965).

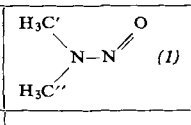
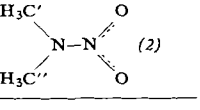
[3] For the synthesis of oxazolines from α-metalated isocyanides, see *U. Schöllkopf* and *F. Gerhart*, Tetrahedron Letters, in press.

Structure of Nitroso- and Nitro-dimethylamine

By *P. Rademacher*[*], *R. Stølevik*[**], and *W. Lüttke*[*]

Dedicated to Professor H. Brockmann on the occasion of his 65th birthday

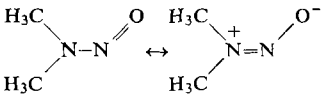
Continuing our systematic study of donor-acceptor molecules D–A, we have determined the structure of molecules of medium size containing an electron donor D linked directly to an electron acceptor A; we have used electron diffraction, IR, Raman, and NMR measurements as well as quantum-mechanical calculations. The structure recently published[1] for dimethylnitrosoaminecopper(II) chloride $(CH_3)_2N{-}NOCuCl_2$ induced us to report our results for the molecular geometry of nitrosodimethylamine *(1)* and nitrodimethylamine *(2)*.

	 *(1)*	 *(2)*
Symmetry	C_s	C_{2v}
Bond lengths (Å):		
N–O	1.235 (2)	1.223 (2)
N–N	1.344 (2)	1.382 (3)
C–N	1.461 (2)	1.460 (3)
C–H	1.129 (3)	1.121 (5)
Bond angles (°):		
N–N–O	113.6 (2)	114.8 (7)
O–N–O		130.4 (1.3)
C′–N–N	120.3 (3)	116.2 (3)
C″–N–N	116.4 (3)	116.2 (3)
N–C–H	109.6 (8)	101.9 (1.9)

Electron diffraction of *(1)* and *(2)* was measured in the usual way[2]. The molecular parameters (bond distances, angles, root mean squares of the vibrational amplitudes, shrinkage parameters) were determined from the scattering intensity curves by the method of least squares. No significant deviation from a planar skeleton was indicated for either molecule; and this finding was supported by quantum-chemical calculations and spectroscopic measurements[3].

The following results (standard deviations in parentheses) were obtained for the molecular geometries:

In a comparison of the structural data for gaseous *(1)* with those for the molecule bound in the $CuCl_2$ complex *(3)*[1] it is remarkable that both have the same C–N bond length, but that the N–N and the N–O bonds of the ligand in the complex are appreciably shorter (by 0.08 and 0.02 Å, respectively) while the N–N–O and the C′–N–N angles are larger (by about 4 °). The greatest shortening from the free molecule *(1)* to *(3)* occurs with the N–N bond length, which indicates an electronic influence of the type



in which the influence of the dimethylamino group on the nitroso group strengthens the complex bonding in the sense that the ligand becomes more firmly attached to the central atom. The compound *(1)* differs sharply from azomethane in this respect, since the molecular dimensions of azomethane are the same in the gaseous state[4] as when a ligand in the $CuCl_2$ complex[5].

The difference in the N–N distances for *(1)* and *(2)* (0.04 Å) can be interpreted as showing that the dimethylamino group is a stronger electron acceptor than the nitro group.

A detailed report of the electron diffraction study will appear elsewhere shortly[6].

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Blindern, Oslo 3 (Norway)

[1] *U. Klement* and *A. Schmidpeter*, Angew. Chem. *80*, 444 (1968); Angew. Chem. internat. Edit. *7*, 470 (1968). In Fig. 1 of the German version of this paper the value of the Cu–O distance was given erroneously as 2.82 instead of 2.28 Å. Editorial correction.

[2] *A. Almenningen*, *O. Bastiansen*, *A. Haaland*, and *H. M. Seip*, Angew. Chem. *77*, 877 (1965); Angew. Chem. internat. Edit. *4*, 819 (1965).

[3] *P. Rademacher* and *W. Lüttke*, unpublished.

[4] *W. West* and *R. Killingworth*, J. chem. Physics *6*, 1 (1938).

[5] *J. D. Brown* and *J. D. Dunitz*, Acta crystallogr. *13*, 28 (1960).

[6] *P. Rademacher* and *R. Stølevik*, Acta chem. scand., in press.

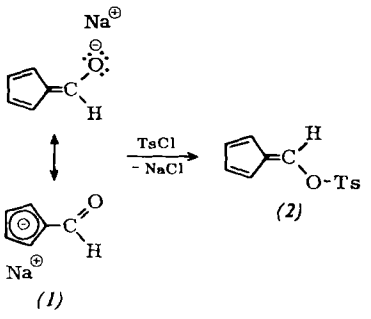
A Simple Synthesis of Substituted Fulvenes from 6-Fulvenyl *p*-Toluenesulfonates

By *K. Hafner*, *W. Bauer*, and *G. Schulz*[*]

6-Dimethylaminofulvene[1] and its derivatives are useful starting materials for the preparation of non-benzenoid, cyclic, conjugated π-electron systems[2]. In the treatment of 6-fulvenyl *p*-toluenesulfonates with nucleophilic reagents we have found a simple process for the introduction of functional groups at the 6-position of the fulvenoid system.

While reaction of sodium formylpentadienide *(1)*[3] with the Vilsmeier complex from dimethylformamide and dimethyl

sulfate[4] or with carbon dioxide affords 6-dimethylaminofulvene-2-carbaldehyde or 6-hydroxyfulvene-2-carboxylic acid, respectively, by *C*-acylation, we observed formation of *O*-acylation products[5] in the reaction with acyl halides. *p*-Toluenesulfonyl chloride and *(1)* in ether at −5 °C give

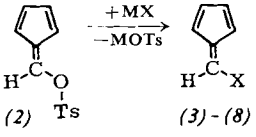


(1) *(2)*

6-fulvenyl *p*-toluenesulfonate *(2)* [yield 60 %; yellow needles (from ether), decomp. 47–48 °C; UV spectrum (*n*-hexane), λ_{max} = 226 nm (log ε = 4.11), 261 (4.34), 358 (2.51); NMR spectrum (CCl_4), τ = 2.25 (2H), d, τ = 2.70 (3H), d, τ = 3.80 (4H), m, τ = 7.64 (3H), s].

Analogously sodium 1-formylindenide and potassium 9-formylfluorenide[6] afford, respectively, 1-indenylidenemethyl *p*-toluenesulfonate (benzofulvenyl *p*-toluenesulfonate) [yield 63 %; pale yellow leaflets (from ethanol), m.p. 97–99 °C; UV spectrum (*n*-hexane), λ_{max} = 227 nm (log ε = 4.53), 305 (3.82), 314 (3.90), 326 (4.79); NMR spectrum ($CDCl_3$), τ = 2.75 (11H), m, τ = 7.67 (3H), s] and 9-fluorenylidenemethyl *p*-toluenesulfonate (dibenzofulvenyl *p*-toluenesulfonate) [yield 50 %; pale yellow crystals (from ethanol), m.p. 103–105 °C; UV spectrum (*n*-hexane), λ_{max} = 223 nm (log ε = 4.69), 228 (4.71), 247 (4.47), 257 (4.72), 274 (4.18), 283 (4.19), 300 (4.12), 313 (4.15); NMR spectrum ($CDCl_3$), τ = 2.4 (13H), m, τ = 7.65 (3H), s[7]].

6-Fulvenyl *p*-toluenesulfonate *(2)* reacts with secondary amines, alkoxides, carbanions, or sodium azide below 0 °C with C–O fission, presumably involving an addition-elimination mechanism, yielding the fulvenes *(3)–(8)* that are substituted at C-6.



(2) *(3)-(8)*

Benzo and dibenzo derivatives of *(2)* react with nucleophilic reagents analogously to the parent compound. 1-Indenylidenemethyl *p*-toluenesulfonate and sodium azide in aqueous methanol, acetonitrile, or acetone affords 1-indenylidenemethyl azide (azidobenzofulvene) [yield 21 %; pale yellow needles (from light petroleum), m.p. 76–78 °C (decomp.); UV spectrum (*n*-hexane), λ_{max} = 236 nm (log ε = 3.97), 274 (4.40), 283 (4.49), 333 (4.25), 346 (4.12)]; and 9-fluorenylidenemethyl *p*-toluenesulfonate affords the corresponding azide (azidodibenzofulvene)[9] [yield 57 %; yellow needles (from light petroleum), m.p. 88–90 °C (decomp.); UV spectrum (*n*-hexane), λ_{max} = 227 nm (log ε = 4.55), 233 (4.60), 246 (4.43), 253 (4.47), 263 (4.59), 280 (3.99), 290 (4.14), 302 (4.22), 325 (4.41), 337 (4.36)].

6-Fulvenyl p-toluenesulfonate (2):

A solution of *p*-toluenesulfonyl chloride (16 g) in ether (150 ml) is added dropwise to a suspension of sodium formylcyclopentadienide *(1)* (11.6 g) in ether (100 ml) at −5 °C with exclusion of oxygen and moisture. After 5 h the insoluble residue is filtered off under nitrogen, and the red ethereal solution is washed with water and dried over previously ignited Na_2SO_4. The solvent is removed under nitrogen at reduced pressure and the red, oily residue is then chromatographed on Al_2O_3 (neutral, activity grade III) with ether, whereupon a yellow zone can be eluted. The eluate is concentrated under nitrogen and cooled to −50 °C. Compound *(2)* (15 g, 60 %) is obtained as yellow needles that are sensitive to heat and to autoxidation and that decompose at 47–48 °C.

6-Fulvenyl azide (8):

A solution of sodium azide (6.5 g) in water (30 ml) is added to a solution of 6-fulvenyl *p*-toluenesulfonate *(2)* (12.8 g) in methanol (120 ml) at 0 °C, and the mixture is stirred for 4 h at −5 °C. After addition of water, the mixture is extracted with ether. The ether is removed under nitrogen at reduced pressure and the red, oily residue is chromatographed on Al_2O_3 (neutral, activity grade III) with light petroleum (40 to 60 °C). A red oil is obtained that affords 6-sulvenyl azide *(8)* (3 g, 50 %), as a yellow-red compound that is crystalline up to about −40 °C, on condensation in a low-temperature trap. *(8)* decomposes at room temperature and is characterized by its photolabile nature and by its sensitivity to air.

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Compound	Metal	X	Yield (%)	M.p. (°C) B.p. (°C/torr)	UV (*n*-hexane) λ_{max} (nm) (log ε)	NMR (τ)
(3)	K	$(C_6H_5)CH_3N$	51	65–66	336 (4.59)	2.45–2.9 (6H), m; 3.27–2.73 (4H), m; 6.38 (3H), s
(4)	K	$(C_6H_5)_2N$	39	95–96	301 (4.04) 351 (4.48)	2.4–2.98(11H) m; 3.6–4.02 (3H), m; 5.0 (1H), m
(5)	K	1-Carbazolyl	28	99–101	236 (4.69) 286 (4.17) 371 (4.37)	1.9–2.92 (9H), m; 3.4–3.72 (4H), m
(6)	K	$(CH_3)_3CO$	20	60/10^{-3}	280 (4.32) 284 (4.32) 349 (2.68)	3.0 (1H), s; 3.48–4.04 (4H), m; 8.6 (9H), s
(7) [8]	Li	C_6H_5				
(8)	Na	N_3	50	*ca.* −40	296 (4.44)	3.4 (1H), s; 3.5–4.0 (4H), m

[2] *K. Hafner, K. H. Häfner, C. König, M. Kreuder, G. Ploss, G. Schulz, E. Sturm,* and *K. H. Vöpel,* Angew. Chem. *75*, 35 (1963); Angew. Chem. internat. Edit. *2*, 123 (1963); *K. Hafner, K. F. Bangert,* and *V. Orfanos,* Angew. Chem. *79*, 414 (1967); Angew. Chem. internat. Edit. *6*, 451 (1967); *U. Müller-Westerhoff* and *K. Hafner,* Tetrahedron Letters *44*, 4341 (1967).

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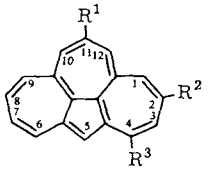
[9] 9-Fluorenylidenemethyl azide was recently prepared by *G. Smolinsky* and *C. A. Pryde* (J. org. Chemistry *33*, 2411 (1968)) from 9-fluorenylidenemethyl bromide and sodium azide.

Azuleno[8,8a,1,2-*def*]heptalene

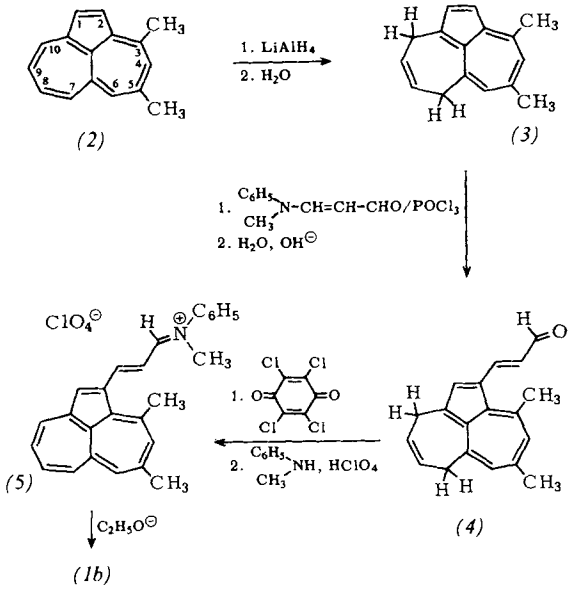
By *K. Hafner, G. Hafner-Schneider,* and *F. Bauer* [*]

Methyl derivatives of the still unknown hydrocarbon *(1a)* azuleno[8,8a,1,2-*def*]heptalene (dicyclohept[*cd-ij*]azulene) can be prepared by a simple process that has already repeatedly proved its value for preparation of polycyclic condensed



(1a), $R^1 = R^2 = R^3 = H$
(1b), $R^1 = CH_3$, $R^2 = R^3 = H$
(1c), $R^1 = R^2 = R^3 = CH_3$

non-benzenoid systems [1]. 11-Methylazuleno[8,8a,1,2-*def*]-heptalene *(1b)* is accessible from 3,5-dimethylaceheptylene *(2)* [2] by base-catalyzed intramolecular cyclization of the aldimmonium perchlorate *(5)*. The salt *(5)* cannot be prepared from *(2)* by the Vilsmeier reaction with 3-(*N*-methylanilino)acrolein and $POCl_3$ [3], since *(2)* is preferentially substituted in the 1- and 4- or 9-, and 6- or 7-positions by electrophiles. It can, however, be obtained by way of 7,10-dihydro-3,5-dimethylaceheptylene *(3)*, which is formed in



(2) *(3)* *(5)* *(4)* *(1b)*

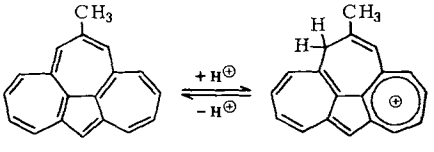
65–70% yield on partial reduction of *(2)* by $LiAlH_4$ in boiling tetrahydrofuran [dark blue crystals of m.p. 74–76 °C (from light petroleum) [4]].

As a derivative of azulene, compound *(3)* is substituted exclusively at C-2 by electrophilic reagents. On reaction with 3-(*N*-methylanilino)acrolein and $POCl_3$ in tetrahydrofuran and subsequent alkaline hydrolysis, *(3)* affords the propenal *(4)* [yield, 81%; dark green needles of m.p. 150 to 151 °C (from ethyl acetate) [5]], dehydrogenation of which by chloranil in boiling benzene gives 3-(3,5-dimethyl-2-aceheptylenyl)acrolein [yield, 68%; reddish-brown needles of m.p. 109–110 °C (from ethyl acetate) [5]]. Treatment with *N*-methylaniline and 70% perchloric acid in tetrahydrofuran leads to a 98% yield of the aldimmonium perchlorate *(5)* (black crystals, decomp. > 230 °C), which in the presence of sodium ethoxide in boiling ethanol condense to the thermally stable hydrocarbon *(1b)* [yield 7%; dark green needles of m.p. 115–116 °C (from light petroleum); trinitrobenzene adduct, black needles of m.p. 182–184 °C (from ethanol)].

Elemental analysis, molecular-weight determination, and UV and NMR spectra prove the constitution of *(1b)*.

The banded electronic spectrum of *(1b)* in *n*-hexane shows absorption maxima at 233 nm (log ε = 4.40), 276 (4.53), 299 (4.88), 337 (3.88), 398 (3.67), 507 (sh) (2.44), 539 (2.27), 583 (2.24), 638 (2.10), 930 (1.64), 1075 (1.74), 1275 (1.72), and 1630 (1.40). The unusually long-wave absorption of this 18 π-electron system accords satisfactorily with the result of an SCF calculation [6]. In the NMR spectrum of *(1b)* in CS_2 the proton signals are at notably high field: as well as the singlet of the five-ring proton H^5 at $\tau = 5.42$, there is the ABCD spectrum of the eight protons of the two unsubstituted seven-rings (H^1–H^4, H^6–H^9) at $\tau = 5.46$, 6.31, 6.04, and 7.12; a broadened singlet at $\tau = 8.02$ is to be ascribed to the two equivalent protons H^{10} and H^{12}, and a triplet at $\tau = 9.68$ (allylic coupling with H^{10} and H^{12}; $J = 0.6$ Hz) to the methyl protons. The positions of the signals indicate a strong paramagnetic ring current in the three seven-membered rings and a weak diamagnetic ring current in the five-membered ring [7].

Compound *(1b)* is strongly basic. The reversible protonation, occurring even in 2N H_2SO_4, leads to the reddish-violet conjugated acid *(6)* [UV spectrum of *(1b)* in CH_2Cl_2/



(1b) *(6)*

CF_3COOH: $\lambda_{max} = 326$ nm (log ε = 4.71) 402 (3.92), 423 (3.91), 551 (4.05), 645 (3.05), and 715 (2.52)], which is formally a combination of the azulene with the heptalenium cation [8]. The NMR spectrum of *(6)* [H^1–H^9, 2 multiplets centered at $\tau = 1.62$ (7H) and $\tau = 0.90$ (2H); H^{12}, broad singlet at $\tau = 2.66$; CH_2 (in position 10), singlet at $\tau = 6.12$; CH_3, doublet at $\tau = 7.32$ (allylic coupling with H^{12}, $J = 1.2$ Hz] confirms the protonation at position 10 (≡ 12), as does the SCF calculation [6] for *(1b)* according to which these positions have the highest electron density.

2,4,11-Trimethylazuleno[8,8a,1,2-*def*]heptalene *(1c)* can be prepared analogously to *(1b)* from 3,5,8,10-tetramethylaceheptylene [9] [yield, 7%; dark green cuboids of m.p. 106 to 107 °C (from light petroleum); trinitrobenzene adduct, black needles, decomp. > 190 °C (from ethanol)] by intramolecular cyclization of the aldimmonium perchlorate corresponding to *(5)* (yield, 97%, bluish-black crystals of m.p. 200 to 202 °C). This product *(1c)* has the same chemical and physical properties as hydrocarbon *(1b)*.

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[1] *K. Hafner*, Angew. Chem. *75*, 1041 (1963); Angew. Chem. internat. Edit. *3*, 165 (1964), where earlier references are cited; *K. Hafner, R. Fleischer*, and *K. Fritz*, Angew. Chem. *77*, 42 (1965); Angew. Chem. internat. Edit. *4*, 69 (1965); *K. Hafner, K. F. Bangert*, and *V. Orfanos*, Angew. Chem. *79*, 414 (1967); Angew. Chem. internat. Edit. *6*, 451 (1967); *R. Kirchlechner* and *Ch. Jutz*, Angew. Chem. *80*, 367 (1968); Angew. Chem. internat. Edit. *7*, 376 (1968). *Kirchlechner* and *Jutz* used this method for preparation of 2-azapyrene.

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[4] *K. Hafner* and *G. Schneider*, Liebigs Ann. Chem. *672*, 194 (1964); on reduction of *(2)* by $LiAlH_4$ the main product *(3)* was accompanied by small amounts of the 7,8- and 9,10-dihydro derivatives.

[5] All the substances described gave correct analytical results.

[6] *R. Zahradnik* and *U. Müller-Westerhoff*, unpublished work.

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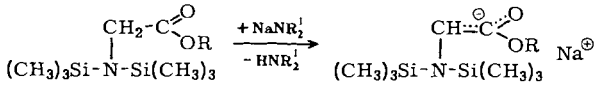
[8] *H. J. Dauben jr.*, and *D. J. Bertelli*, J. Amer. chem. Soc. *83*, 4659 (1961).

[9] *K. Hafner* and *G. Hafner-Schneider*, unpublished work; 4,6,8-trimethylazulene and 4-diethylamino-3-penten-2-one afforded 3,5,8,10-tetramethylaceheptylene in a synthesis analogous to that of *(2)* [2]. This aceheptylene derivative reacts preferentially with substitution in positions 4 and 6 on treatment with 3-*N*-methylanilinoacrolein/$POCl_3$; 3-(3,5,8,10-tetramethylaceheptylen-1-yl)acrolein is formed only as a by-product (25%).

Synthesis of Amino Acids from *N,N*-Bis(trimethylsilyl)glycine Esters[1]

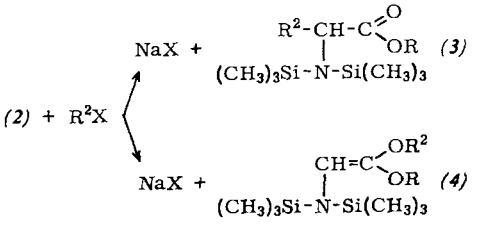
By *K. Rühlmann* and *G. Kuhrt*[*]

During our work on *N,N*-bis(trimethylsilyl)amines[2] we have found a very convenient and general synthesis of amino acids. *N,N*-Bis(trimethylsilyl)glycine esters *(1)* are first converted into the sodio derivatives *(2)* (not isolated) by means of Na bis(trimethylsilyl)amide or another base. The compounds *(2)* can undergo nucleophilic substitution or addition. The



(1a), R = C_2H_5 R^1 = H, $Si(CH_3)_3$ *(2a)*, R = C_2H_5
(1b), R = $Si(CH_3)_3$ *(2b)*, R = $Si(CH_3)_3$

C-substitution products *(3)* are obtained on reaction with alkyl halides, and *O*-substitution products *(4)* on reaction with trimethylsilyl chloride (see Table 1).

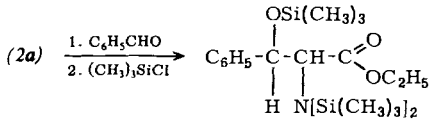


All the Si–O and Si–N bonds in compounds *(3)* and *(4)* are rapidly and completely cleaved by dilute aqueous or ethereal HCl. Thus ethyl amino-ester hydrochlorides are obtained from *(3a)–(3d)*, glycine ethyl ester hydrochloride from *(4a)*, and glycine from *(4b)*.

Table 1. Ethyl *N,N*-bis(trimethylsilyl)amino esters *(3)* and *N,N*-bis(trimethylsilyl)aminoketene acetals *(4)*.

Cpd.	R	R^2	X	B.p. (°C/torr)	n_D^{20}	Yield (%)
(3a)	C_2H_5	CH_3	I	110/111	1.4422	55
(3b)	C_2H_5	C_2H_5	I	115–117/12	1.4460	65
(3c)	C_2H_5	C_6H_5–CH_2	Br	179–181/10	1.4952	70
(3d)	C_2H_5	$(CH_3)_2HSi$–CH_2	I	133–134/10	1.4518	52
(4a)	C_2H_5	$(CH_3)_3Si$	Cl	118/9	1.4430	77
(4b)	$(CH_3)_3Si$	$(CH_3)_3Si$	Cl	122–126/10	1.4397	67

On treatment with aldehydes, *(1a)* loses hexamethyldisiloxane to afford imines, and *(2a)* gives salts of ethyl α-amino esters which can be converted into *N,N,O*-tris(trimethylsilyl) derivatives by trimethylsilyl chloride. As an example we



(5)

report the reaction with benzaldehyde yielding 3-phenyl-*N,N,O*-tris(trimethylsilyl)serine ethyl ester *(5)*, b.p. 115 °C/0.5 torr, n_D^{20} = 1.4703. This product, which is accessible in good yield, is hydrolyzed by dilute HCl to phenylserine ethyl ester hydrochloride, m.p. 170 °C[3].

N,N-Bis(trimethylsilyl)glycine ester (1):
Glycine ethyl ester or glycine is heated with an excess of (trimethylsilyl)diethylamine in the presence of a catalytic amount of $(NH_4)_2SO_4$ at *ca.* 120 °C until no more diethylamine distils off. For purification the residue is distilled in a vacuum. *(1a)*, b.p. 100 °C/10 torr, n_D^{20} = 1.4369, is formed in 75 % yield from glycine ethyl ester, and *(1b)*, b.p. 106–108 °C/10 torr, n_D^{20} = 1.4341, in 90 % yield from glycine.

Ethyl N,N-bis(trimethylsilyl)amino esters (3):
0.055 mole of Na bis(trimethylsilyl)amide in 100 ml of ether is added to 0.05 mole of *(1a)* in 50 ml of ether at −10 ° to 0 °C with stirring and the mixture is kept at room temperature for a short time. 0.05 mole of R^2X is then added dropwise and the whole is heated at the b.p. for 10–15 h, then filtered and distilled. *(4a)* is formed under analogous conditions; the synthesis of *(4b)* is carried out at −60 °C.

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[1] Part 30 of The Si–N Bond. – Part 29: *K.-D. Kaufmann, H. Bormann, K. Rühlmann, G. Engelhardt*, and *H. Kriegsmann*, Chem. Ber. *101*, 984 (1968).

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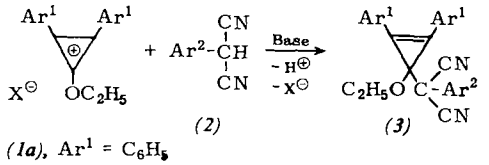
[3] *C. Tanaka* and *N. Saito*, J. pharmac. Soc. Japan (Yakugaku Zasshi) *82*, 136 (1962).

Quinodimethanes from 1,2-Diaryl-3-ethoxycyclopropenylium Ions

By *K. Eiglmeier* and *Th. Eicher*[*]

1,2-Diaryl-3-ethoxycyclopropenylium salts *(1)*[1] (X = BF_4) react with arylmalononitriles *(2)* in the presence of a base, preferably *N*-ethyldiisopropylamine (Hünig base), with formation of 1:1-adducts *(3)*.

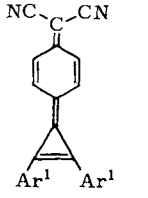
The 3-ethoxy-1-cyclopropene structure of the adducts follows unambiguously from the IR spectra (cyclopropene bands[2] at *ca.* 1800 cm^{-1}) and the NMR spectra [CH_2 quadruplet of an



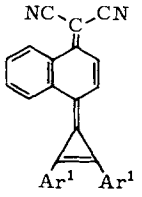
(1a), $Ar^1 = C_6H_5$
(1b), $Ar^1 = p\text{-}CH_3O\text{-}C_6H_4$

Cpd.	Ar^1	Ar^2	Obtained from	*(3)* M.p. (°C)	*(3)* Yield (%)
(3a)	C_6H_5	C_6H_5	*(1a)*	103–104	24
(3b)	C_6H_5	α-Naphthyl	*(1a)*	146–147 (decomp.)	27
(3c)	$p\text{-}CH_3O\text{–}C_6H_4$	β-Naphthyl	*(1b)*	133–135 (decomp.)	74
(3d)	$p\text{-}CH_3O\text{–}C_6H_4$	9-Phenanthryl	*(1b)*	164–165 (decomp.)	62
(3e)	$p\text{-}CH_3O\text{–}C_6H_4$	C_6H_5	*(1b)*	180 (decomp.)	42
(3f)	$p\text{-}CH_3O\text{–}C_6H_4$	α-Naphthyl	*(1b)*	161–162 (decomp.)	78

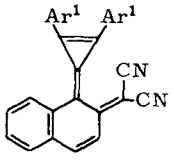
ethoxy group bound to a sp^3-hybridized C atom ($\tau = 6.5 - 6.7$)]. When kept molten, when boiled in acetic acid/acetic anhydride or, for *(3f)* or *(3d)*, when kept in $CHCl_3$ at room temperature with a catalytic amount of acid, the adducts *(3a)*, *(3e)*, *(3b)*, and *(3f)*, are converted with loss of ethanol into the *p*-quinodimethanes *(4a)*, *(4e)*, *(4b)*, and *(4f)*, respectively.



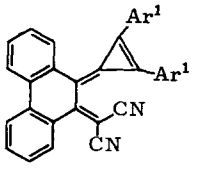
(4a),(4e)



(4b),(4f)



(4c)



(4d)

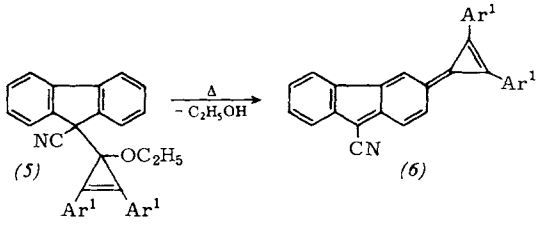
However, the *o*-quinodimethane derivatives *(4c)* and *(4d)* are formed from *(3c)* and *(3d)*, respectively.

Cpd.	Ar^1	M.p. (°C)	λ_{max} (nm) ($\varepsilon \cdot 10^{-4}$) [a]	Yield (%)
(4a)	C_6H_5	200 (decomp.)	503 (3.9) [3]	10
(4b)	C_6H_5	>340	527 (8.1)	26
(4c)	$p\text{-}CH_3O\text{–}C_6H_4$	228–229	533 (1.8)	7
(4d)	$p\text{-}CH_3O\text{–}C_6H_4$	218–219	513 (2.05)	56
(4e)	$p\text{-}CH_3O\text{–}C_6H_4$	240 (decomp.)	504 (7.05)	95
(4f)	$p\text{-}CH_3O\text{–}C_6H_4$	300 (decomp.)	537 (10.5)	72

[a] In CH_2Cl_2.

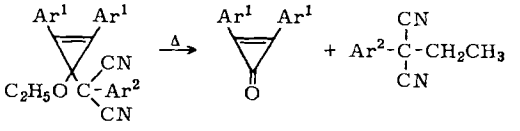
The 1:1 adduct *(5)* from *(1b)* and 9-cyanofluorene, when heated, gives the *p*-quinonoid system *(6)* [*(5)*, m.p. 219 to 220 °C (decomp.), 81 % yield; *(6)*, m.p. >340 °C, 38 % yield, λ_{max} (CH_2Cl_2) = 582 nm, $\varepsilon = 3.0 \cdot 10^4$]. The product *(6)* was obtained pure only as solvate with 1 mole of CH_3COOH of crystallization (from acetic acid/acetic anhydride).

The structure of the quinodimethanes *(4)* is supported by IR and NMR spectroscopic results. The IR spectra show absorption characteristic of the methylenecyclopropene grouping[4] at *ca.* 1850 cm^{-1}, and the NMR spectra show only aromatic protons (where Ar^1 = *p*-methoxyphenyl, also CH_3O). The *p*-quinonoid arrangement in *(4a)* and *(4b)* is favored by the fact that no quinodimethanes, but instead ethylated arylmalononitriles *(7a)* and *(7b)*, are formed when the *p*-position to the malononitrile group is blocked, *i.e.*, from the adducts of 4-methyl-1-naphthyl- *(3g)* and 4-biphenylyl-malononitrile *(3h)*, respectively and *(1a)*. The structure of the products *(7)* was proved by independent syntheses. Ethylation is also the main reaction when *(3c)* is heated.



(5) *(6)*

The *o*-quinonoid structure of *(4c)* and *(4d)* is made most probable by, *inter alia*, the UV-spectroscopic finding that the long-wavelength maxima differ relatively little in position from those of the *p*-quinonoid *(4b)*; so that an "*amphi*-quinonoid" system is improbable in *(4c)*, as is a vinylogous *p*-quinonoid system in *(4d)*.



(3g),(3h) *(7a),(7b)*

2-(1-Ethoxy-2,3-di-p-anisyl-2-cyclopropenyl)-2-phenylmalononitrile (3e):

A solution of diisopropylethylamine (2.60 g ≈ 20 mmole) in 1,2-dichloroethane (5 ml) was added dropwise to a suspension of *(1b)* [1] (20 mmole) and phenylmalononitrile (2.8 g ≈ 20 mmole) in anhydrous 1,2-dichloroethane (35 ml) over a period of 5 min; the mixture became warm, an orange coloration was observed, and the solids dissolved. After 45 min the solvent was removed in a rotary evaporator and the residue was digested with benzene (100 ml); diisopropylethylammonium tetrafluoroborate (4.36 g ≈ 20 mmole) remained behind. After removal of the solvent from the benzene solution, a red oil remained that crystallized on rubbing with ethanol (20 ml): 3.70 g (42%) *(3e)*, m.p. 180 °C (decomp.); pure on thin layer chromatography (benzene).

2-[4-(2,3-Di-p-anisyl-2-cyclopropenylidene)-2,5-cyclohexadienylidene]malononitrile (4e):

(3e) (1.00 g ≈ 2.3 mmole) was heated to 160 °C for 10 min, whereupon the substance turned carmine red and ethanol was evolved. On cooling the product was taken up in ether/CH_2Cl_2 1:1 and chromatographed on a silica gel column (150 g of "Kieselgel Merck", 0.05–0.2 mm). After elution of traces of *(3e)* with ether/CH_2Cl_2 1:1, the red substance remaining at the start was eluted with CH_2Cl_2/methanol 9:1: 0.85 g (95%) *(4e)*, m.p. 230–235 °C; carmine red needles from glycol monomethyl ether, m.p. 240 °C (decomp.).

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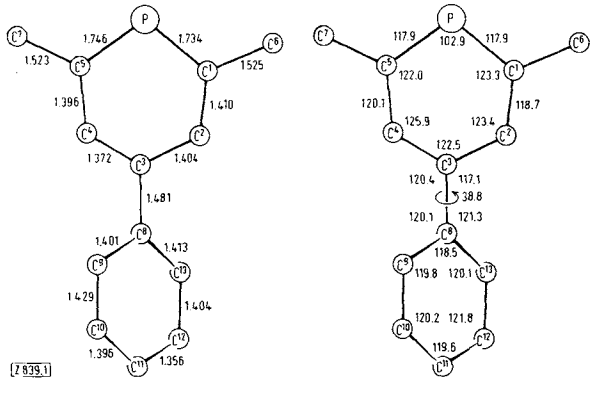
The Structure of 2,6-Dimethyl-4-phenylphosphabenzene

By *J. C. J. Bart* and *J. J. Daly* [*]

Märkl [1] has described an ingenious synthesis of 2,4,6-triphenylphosphabenzene *(1)*. The ^{31}P–NMR spectrum of this compound showed a large chemical shift of $\delta = -178.2$ ppm (in pyridine, $\delta H_3PO_4 = 0$) indicating considerable deshielding of the phosphorus nucleus. The compound is the first containing an apparently aromatic ring with phosphorus as a constituent. A triphenylphosphaindan (1,2,3-triphenyl-1,2,3-triphosphaindan) has been described [3] but its structure [2] shows no short P–C or P–P bonds; the phosphorus valences are not coplanar, so the five-ring system cannot be described as aromatic.

We have now determined the structure of 2,6-dimethyl-4-phenylphosphabenzene [4]. The crystals melt at 62–63 °C and are orthorhombic, space group $P\,2_12_12_1$ with $a = 7.312$, $b = 14.333$, $c = 10.820$ Å. There are four molecules of $C_{13}H_{13}P$ (M.W. = 200.2) in the unit cell. The intensities of the diffracted X-rays were measured on a Hilger and Watts linear diffractometer [5] and reflections with counts not significantly above the background were omitted from the analysis. The structure was solved by three-dimensional Patterson and two-dimensional (0*kl* projection) Fourier methods. The structure was refined by least squares with individual anisotropic temperature factors and the current value of *R* for 925 planes is 0.077. The hydrogen atoms have not yet been included in the analysis.



Projection along *a* of a 2,6-dimethyl-4-phosphabenzene molecule. Left: bond lengths (Å); maximum error ±0.0012 Å. Right: bond angles (°); maximum error ±0.8 °.

The results of the analysis are summarized in the Figure. The molecule possesses the approximate symmetry 2 (C_2), the axis running through the phosphorus atom and C(11). The two six-membered rings are both planar within the limits of error of the analysis. The dihedral angle between the least squares ($w = Z$) planes through these rings is 39 °, close to the value found for biphenyl [6] in the vapor phase (42 °). The CPC angle is quite small (103 °) and may be compared with the values found [7] in $P(C_6H_5)_3$ (103 °) and in a phosphamethinecyanine [8] cation (105 °). A phosphabenzene ring with a CPC angle of 103 ° and the remaining angles of 120 ° would not be planar. The planarity of this ring is achieved by an expansion of the PCC and CCC angles to about 123.3 °. A similar distortion is found in pyridine [9], but there only the NCC angles are greater than 120 °C. The P–C lengths are essentially equal (1.740 Å) and lie between the shorter [10, 11] values given for P=C (1.65 and 1.68 Å) and the length found in $P(C_6H_5)_3$ (1.83 Å). The carbon-carbon lengths in the phosphabenzene ring have an average value of 1.396 Å with no significant deviations. The bond joining the two rings is 1.48 Å, in agreement with the value given [12] (1.47–1.48 Å) for a $C(sp^2)$–$C(sp^2)$ single bond.

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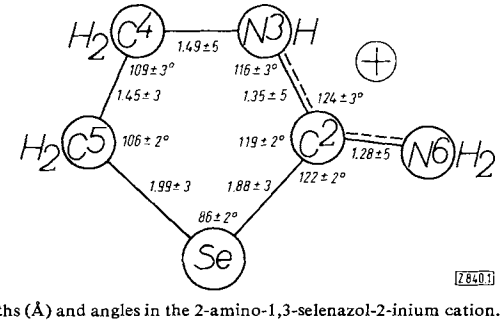
The Crystal Structure of 2-Amino-1,3-selenazol-2-inium Bromide

By *Louise Karle* [*]

The crystal structure of the anti-radiation drug 2-amino-1,3-selenazol-2-inium bromide [1] has been determined by means of X-ray diffraction with the help of a Patterson synthesis. The molecule is planar except for atom C^5 (see Fig.), which is displaced 0.43 Å from the plane. (The best plane through all the atoms except C^5 and Br is $7.01x-0.39y-7.11z-0.07 = 0$.) Both C···N distances are short. The shorter carbon-amine nitrogen bond, C^2···N^6, is only 1.28 Å while the C^2···N^3 bond in the ring is 1.35 Å. These distances indicate that the



Bond lengths (Å) and angles in the 2-amino-1,3-selenazol-2-inium cation.

positive charge is not localized on one of the nitrogen atoms, but shared between the two, with the greater charge concentration on the amine nitrogen atom. Furthermore, the ring nitrogen atom has only one Br^- neighbor (N···Br^- = 3.31 Å), whereas the amine nitrogen atom has three (N···Br^- = 3.27 Å, 3.46 Å, and 3.53 Å resp.). Each bromide ion in turn neighbors four co-planar nitrogens. The molecules pack in a close packing of the $(10\bar{1})$ planes, the distance between successive $(10\bar{1})$ planes being 3.52 Å. Interactions between a bromide ion and nitrogen atoms in adjacent planes are minimal because the interatomic distances involved are greater than 3.6 Å. Noteworthy are the unequal C^2–Se and C^5–Se distances (1.99 Å and 1.88 Å resp.) and the C–Se–C bond angle of 86 °. These values fall within the range of reported values for other organoselenium heterocycles [2]. Of particular similarity is the compound 3,3'-dioxo-2,2'-bibenzoselenolenylidene (C–Se–C = 80 °, Se–C = 1.97 or 1.75 Å) [3].

The substance crystallizes in space group $P\,2_1/c$ with four molecules per unit cell. The lattice constants are $a_0 = 7.606$ Å, $b_0 = 6.516$ Å, $c_0 = 13.574$ Å, $\beta = 99$ °; $D_m = D_x = 2.28$ g/cm³.

1056 intensities of independent reflections (245 unobserved) were estimated from Weissenberg photographs. Only the observed intensities were used for the computation of a Patterson map, on which just the Br–Br, Br–Se, and Se–Se peaks occurred with any intensity. Thus the co-ordinates of the Br and Se atoms were immediately determined. The resulting Fourier electron density map determined all but the hydrogen atom co-ordinates. An *R*-factor of 13.9% between observed and calculated structure factors was obtained by a least squares refinement using individual isotropic temperature factors.

The atom co-ordinates, the absolute standard deviation of the atom co-ordinates, and the temperature factors are given in the Table.

atom	*x*	*y*	*z*	Δ(10^{-3} Å)	B(Å^{-2})
Br	0.3381	0.7302	0.4213	2.9	4.27
Se	0.2010	0.0230	0.1841	3.4	4.76
C[2]	0.2995	0.2388	0.2666	23	2.92
N[3]	0.2724	0.4251	0.2240	20	3.19
C[4]	0.1540	0.4290	0.1260	31	4.19
C[5]	0.1634	0.2323	0.0766	26	3.73
N[6]	0.3771	0.2089	0.3560	26	4.92

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Crystal Structure of "$Ir(CO)_3Cl$" = $Ir(CO)_{2.93}Cl_{1.07}$[1]

By *K. Krogmann*, *W. Binder*, and *H. D. Hausen*[*]

Compounds with linear chains of metal atoms, in which the central atom has a somewhat higher oxidation number than the corresponding planar d^8-complexes (*e.g.* $Mg_{0.82}[Pt(C_2O_4)_2]\cdot 5.3\ H_2O$[2]), have been known hitherto, but only with Pt as chain atoms. In the search for Ir(d^8) compounds suitable for the synthesis of analogous chains, we came upon "$Ir(CO)_3Cl$", which was first described with this formula by *Hieber et al.*[3], as a representative of this class of compounds with Ir as central atom.

According to *Fischer et al.*[4] the substance results from reaction of $IrCl_3\cdot xH_2O$ (adsorbed on silica gel) with CO at 180 °C; the product is in the form of brown-violet needles having a metallic luster. An X-ray determination of the crystal structure reveals chains with Ir–Ir distances of 2.85 Å. This distance is the same as that in the above mentioned Pt compound and corresponds to a partially oxidized chain, whereas non-oxidized Ir(*I*) complexes such as $Ir(CO)_2acac$ have distances of 3.20 Å[5]. We therefore examined the composition of the compound and obtained reproducible analyses consistent with the formula $Ir(CO)_{2.93}Cl_{1.07}$ *(1)*, thus confirming the partially oxidized character of the iridium.

The crystal structure contains orthorhombic unit cells with $a = 5.69$ Å, $b = 15.20$ Å, $c = 12.93$ Å. The cell volume (1118.3 Å^3), the formula weight (312.2), and the measured density (3.63 g/cm^{-3}) indicate the number of formula units per cell as being $Z = 7.83 \approx 8$. The space group is Cmcm or $Cmc2_1$. Strong intensities appear in layers of the reciprocal lattice with $h = 2n$ only, proving a subcell for Ir with $a' = a/2 = 2.845$ Å, which is also the period of the Ir chain. 316 reflections were strong enough to be measured on Weissenberg photographs with CuK_α radiation. The positions of the light atoms were found by Patterson and Fourier syntheses and refined to $R = 11\%$.

In the structure there are staggered planar complexes, stacked in columns parallel to the *a*-axis (A). Most complexes are $Ir(CO)_3Cl$, one Cl coordination site interchanging ligands with one CO-site (A, B). The analytically proven "surplus" Cl might be found random in this position, leading to *cis*-$Ir(CO)_2Cl_2$ complexes in the chain (C).

(A)	(B)	(C)
$(OC)_2Ir(CO)Cl$	$(OC)_2IrCl(CO)$	$(OC)_2IrCl_2$
$Cl(OC)Ir(CO)_2$	$Cl(OC)Ir(CO)_2$	$Cl(OC)Ir(CO)_2$

One would expect a normal $Ir(CO)_3Cl$ complex to be volatile, soluble in many organic solvents, chemically reactive, and to show only weak absorption in the visible region of the spectrum. Compound *(1)* sublimes in streaming CO, but not *in vacuo*. It is only soluble in solvents which attack the coordination sphere, *e.g.* aqueous KCN or pyridine (CO evolution); it is stable in air and inert. Absorption of visible light is strong for all wavelengths if the light is polarized parallel to the needle (*a*-)axis, but weak if polarized perpendicular to it. The compound exhibits a small temperature independent paramagnetic component $\chi_p = +71.0\cdot 10^{-6}$, if the molar susceptibility of $\chi_{mol} = -31.0\cdot 10^{-6}$ is corrected for diamagnetic increments of the atoms concerned.

According to the structure, relatively strong bonds between Ir atoms exist in the chains. From the similarity of the properties of *(1)* and those of the partially oxidized Pt compounds[2,6] it may be assumed that delocalized charges occur in the chains; however, in contrast to the Pt compounds the charge balance in these compounds is maintained in the coordination sphere itself by $Ir(CO)_2Cl_2$ groups. The degree of partial oxidation in Ir^I (+0.07) is remarkably small compared to that in Pt^{II} (0.3).

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[1] Structures with Metal Chains, Part 7. This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and by Fa. W. C. Heraeus GmbH, Hanau. – Part 6: *K. Krogmann* and *G. Ringwald*, Z. Naturforsch. *23b*, 1112 (1968).

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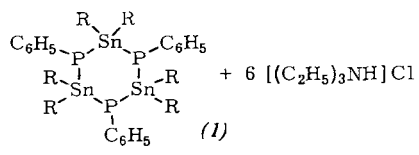
Cyclic Organostannylphosphines[**]

By *H. Schumann* and *H. Benda*[*]

Continuing previous work[1,2] we have found that cyclic organostannylphosphines of the type $(R_2Sn{-}PR)_3$ are formed on interaction of tetraphenyltin with phosphorus (P_4). The same type of compound arises also in reactions between triphenylstannyllithium and phenylphosphorus halides or phosphorus trichloride. Some of these reactions are not readily reproducible and their precise course has not yet been clarified.

Attempts to obtain such cyclic organostannylphosphines in an unambiguous manner from diorganotin dichlorides and phenylphosphine with thermal removal of HCl were unsuccesful until the following procedure was used: dimethyl-, dibutyl-, or diphenyl-tin dichloride and phenylphosphine are added (simultaneously at room temperature under nitrogen, during 2 h) to a benzene solution of triethylamine present in stoichiometric amount to act as complex-former and HCl-acceptor; this method, which accords with the dilution principle, leads to polymeric and trimeric *(1)* diorganostannylphenylphosphines.

$$3\ R_2SnCl_2 + 3\ C_6H_5PH_2 + 6\ (C_2H_5)_3N$$



$$\rightarrow \quad (1) \quad + 6\ [(C_2H_5)_3NH]Cl$$

	R	Yield (%)	M.p. (°C)	νSnP (nujol suspension)
(1a)	CH_3	73	134	388, 365, 318, 310, 284
(1b)	C_4H_9	61	Oil	388, 347, 307, 298, 289
(1c)	C_6H_5	53	155–160	372, 361, 335, 308, 297

Triethylammonium chloride and insoluble polymers are filtered off and the filtrate is concentrated in a vacuum, the products *(1)* being then precipitated on addition of pentane, and recrystallized from hot methylcyclohexane. They were shown to be homogeneous by thin-layer chromatography under argon[3]. Structures were proved by complete elemental analysis, cryoscopic determination of molecular weight, and IR and ^1H–NMR spectroscopy. In the IR spectra the vibrations due to alkyl and phenyl groups attached to tin and phosphorus were accompanied in all cases by five bands that are assigned to the Sn–P stretching vibrations. In accord with observations for dialkylsilicon sulfide[4] this indicates a chair form of the ring skeleton, having symmetry C_s and analogous to that for cyclohexane. The ^1H–NMR spectrum[5] of *(1a)* contains, as well as the multiplet of phenyl protons, the expected triplet for the protons of the two methyl groups bound to tin, namely at $\delta = 398.5$ Hz ($J_{^1H-C-Sn-^{31}P} = 4.4$ Hz, $J_{^1H-C-^{117}Sn} = 46.5$ Hz, $J_{^1H-C-^{119}Sn} = 51.5$ Hz).

(1a) is not very stable thermally: it decomposes above 175 °C into stoichiometric amounts of pentaphenylcyclopentaphosphane, bis(trimethylstannyl)phenylphosphine, and tin:

$$5\ [(CH_3)_2Sn\text{-}PC_6H_5]_3 \xrightarrow{\Delta}$$
$$(1a) \qquad 2\ [C_6H_5P]_5 + 5\ [(CH_3)_3Sn]_2PC_6H_5 + 5\,Sn$$

Ethereal hydrogen chloride cleaves *(1a)*, *(1b)*, and *(1c)* with liberation of phenylphosphine and formation of dimethyl-, dibutyl-, and diphenyl-tin dichloride, respectively, which also proves the constitutions.

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[2] *H. Schumann, H. Köpf,* and *Max Schmidt,* Chem. Ber. *97*, 2395 (1964).

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[5] 5% solution in benzene with benzene as internal standard.

closo-Tetrakis(phenylstannylphosphine), an Organostannylphosphine with a Cubane Structure[**]

By *H. Schumann* and *H. Benda*[*]

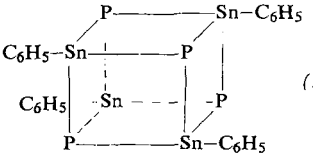
Among the oxidation products of the organostannyl phosphines formed on reaction of tetraphenyltin with phosphorus (P_4) in a sealed tube at 300 °C we have found a polymeric organotin phosphate that was apparently formed from a polymeric phenylstannylphosphine $(C_6H_5SnP)_n$[1]. The last-mentioned compound was not isolated under the conditions used at the time; it is also formed from anhydrous tin(II) chloride and diphenylphosphinolithium but this reaction is also not readily reproducible and its course is not clarified[2]:

$$n\ SnCl_2 + 2n\ LiP(C_6H_5)_2 \rightarrow (C_6H_5SnP)_n + nP(C_6H_5)_3 + 2nLiCl$$

We have now determined the structure of this organostannylphosphine by a clear synthesis.

If benzene solutions of phenyltin trichloride and triethylamine are added simultaneously under argon to benzene into which phosphine is being passed, the red solution obtained contains a resinous brown precipitate of triethylammonium chloride and polymeric products. These materials are removed, the filtrate is concentrated and freed from newly precipitated polymers, then methylcyclohexane is added; this leads to a yellow precipitate from which fractional precipitation by pentane affords tetrameric phenylstannylphosphine *(1)* in *ca.* 10% yield.

$$4\ C_6H_5SnCl_3 + 4\ PH_3 + 12\ (C_2H_5)_3N \longrightarrow$$



$$(1) \quad + 12\ [(C_2H_5)_3NH]Cl$$

Compound *(1)* decomposes above 160 °C (blackening) without melting; it cannot be kept for long, even in an inert atmosphere; it is largely polymerized to insoluble products even after two days. The homogeneous condition of the freshly prepared material is proved by thin-layer chromatography[3]. Complete elemental analyses, cryoscopic determinations of molecular weight, and the IR spectrum containing few lines indicate unambiguously that it has a cubane structure. In the infrared spectrum (Nujol) the vibrations of the phenyl groups bound to tin are accompanied by essentially only the Sn–P stretching vibration required for T_d symmetry at 328 cm^{-1}. The two infrared-active deformation bands lie in the longer-wavelength and no longer measurable region.

The reaction of methyl- or butyl-tin trichloride with phosphine leads, however, like that of methyl-, butyl-, or phenyltin trichloride with sodium phosphide in benzene, only to insoluble polymeric compounds.

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[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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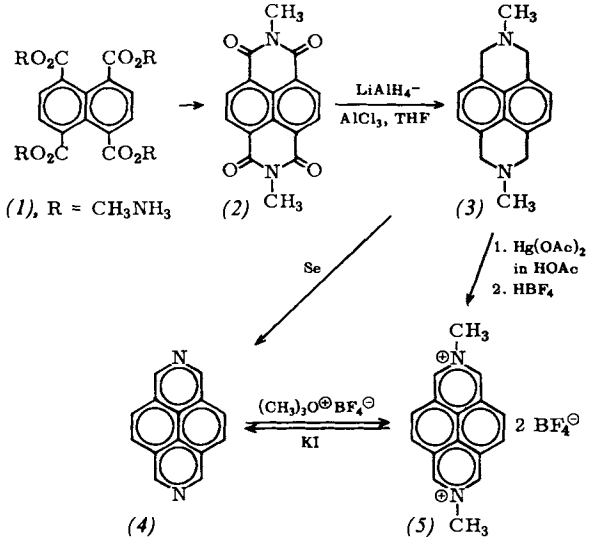
2,7-Diazapyrene and its Bis(*N*-methyl) Quaternary Salt

By *E. F. Lier*, S. *Hünig*, and *H. Quast* [*]

2,7-Diazapyrene *(4)*, which was recently synthesized [2] for the first time and by a theoretically interesting route, together with its bis(*N*-methyl)quaternary salt *(5)* were required for a study of the redox behavior of quaternary polynuclear heteroaromatic compounds [1]. We now report a synthesis giving good yields of both compounds.

1,4,5,8-Naphthalenetetracarboxylic acid, which is readily accessible commercially, was converted into the tetrakis(*N*-methylammonium) salt *(1)* by evaporating its solution in aqueous methylamine. When heated for 1 h at 150–203 °C in 1-methylpyrrolidone (500 ml), this salt *(1)* (0.1 mole) changes to the bis(*N*-methylimide) *(2)* [3], which can be isolated from the solution at 80 °C in 89% yield. Adding this imide (0.1 mole) with ice-cooling to a suspension of $LiAlH_4$ (0.7 mole) + $AlCl_3$ (0.235 mole) in tetrahydrofuran (600 ml) and then heating the mixture under reflux for 3.5 h yields 70% of the diamine *(3)*. This has the required equivalent weight, and its UV spectrum resembles that of 1,4,5,8-tetramethylnaphthalene [4].



Heating *(3)* (20 mmoles) with selenium (0.13 mole) at 260 to 265 °C for 3 h and then at 300–310 °C for 1 h, with subsequent chromatography on basic Al_2O_3 in benzene/chloroform (20:1), affords an 80% yield of nearly pure *(4)* as pale-yellow crystals. This product is obtained analytically pure by recrystallization from benzene and gives the NMR and UV values reported in the literature [2].

Trimethyloxonium fluoroborate in dichloromethane converts *(4)* smoothly into *(5)* (yield, 84%). *(5)* (1 mmole) is reconverted into *(4)* when heated with potassium iodide (16 mmoles) in triethylene glycol (100 ml) under nitrogen (yield, 50% after chromatography).

Boiling *(3)* (10 mmoles) for 30 min with mercury(II) acetate [5] (41 mmoles) in glacial acetic acid (200 ml) affords *(5)* directly. The cooled and filtered solution is treated with water (100 ml) and tetrafluoroboric acid ($d = 1.22$; 25 ml). On fractional concentration under reduced pressure an orange substance of unknown constitution (m.p. 274–276 °C) is first precipitated, and thereafter *(5)* in 20% yield. The electronic spectrum of *(5)* shows three bands with fine structure, the band of longest wavelength being shifted by 32 nm in comparison with that of *(4)*. The blue fluorescence of *(4)* is appreciably increased on conversion into *(5)*. As expected, three singlets appear in the NMR spectrum. In acetonitrile or dimethylformamide, compound *(5)* accepts one electron reversibly at −0.43 volt [6]. The green radical cation exhibits an ESR spectrum with hyperfine structure [7].

Data for new compounds (NMR spectral data in ppm, tetramethylsilane = 0): *(1)* (decomp. from 130 °C), NMR (D_2O) 2.55 (12H, S), 7.70 (4H, S); *(2)* (m.p. > 350 °C), NMR (trifluoroacetic acid) 3.28 (6H, S), 8.52 (4H, S), IR (Nujol) 1670, 1660, 1583 cm^{-1}; *(3)* (m.p. 237–239 °C, closed tube), NMR (trifluoroacetic acid) 4.52 (8H, M), 7.22 (4H, S), 8.18 (broad, 2H); *(4)* m.p. 283–284 °C (closed tube) [2], 304–306 °C; *(5)*, (m.p. > 330 °C), NMR (D_6-dimethyl sulfoxide) 4.95 (6H, S), 8.97 (4H, S), 10.37 (4H, S).

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[5] For the method cf. *N. J. Leonhard*, *A. S. Hay*, *R. W. Fulmer*, and *V. W. Gash*, J. Amer. chem. Soc. *77*, 439 (1955); *J. Knabe*, Arch. Pharmaz. *292*, 652 (1959).

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[7] Measurements by Dr. *D. Scheutzow*.

Use of the INDOR Technique in the Solution of Structural Problems in Organophosphorus Chemistry

By *R. Kosfeld*, *G. Hägele*, and *W. Kuchen* [*]

The reaction of thiophosphoryl halides of the types $PSCl_3$ and $RPSX_2$ (R = alkyl; X = Cl, Br) with Grignard reagents R'MgX' (R' = alkyl; X = Cl, Br, I) leads mainly to tetraalkyldiphosphine disulfides or trialkylphosphine sulfides, depending on the substituents R, X, R', and X' and the reaction conditions [1, 2].

By reaction of 1.76 mole of *tert*-C_4H_9MgCl with 0.43 mole of CH_3PSBr_2 in ether at 0 to 5 °C, followed by hydrolysis, we obtained a complex mixture which contained neither bis(methyl-*tert*-butyl)diphosphine disulfide $[CH_3(tert\text{-}C_4H_9)P(S)]_2$ nor methyldi-*tert*-butylphosphine sulfide $CH_3(tert\text{-}C_4H_9)_2PS$ in detectable quantities.

By means of the INDOR (internuclear double resonance) technique, heterospin decoupling, and ^{31}P- and ^1H–NMR spectroscopy, we were able to identify the individual components without prior physical or chemical separation.

As far as we know the INDOR technique [3] has not previously been applied to mixtures of structurally similar compounds. It offers two advantages over normal NMR spectroscopy:

1. For compounds having almost identical NMR spectra, all the nuclei in each molecule that couple with each other can be selectively identified.

2. The sensitivity is considerably increased, so that spectroscopic measurements on hetero nuclei coupled with protons can be carried out with specimens 5 mm in diameter.

In the analysis of highly resolved NMR spectra, the observed transition frequencies are used to find a set of constants which describe the system with sufficient accuracy; these constants are the chemical shift δ_{ij} and the coupling constant J_{ik}, the sign of which must be determined for coupling of several nuclei.

Further information can be obtained by double or multiple resonance measurements. In the case of double resonance there are five parameters: H_0, ω_1, H_1, ω_2, and H_2. H_0 is the homogeneous constant magnetic field, H_1 is the observation field, and H_2 is the irradiation field, while ω_1 and ω_2 are the frequencies [in our measurements: $\omega_1/2\pi = 90$ MHz (^1H); $\omega_2/2\pi = 36.431$ MHz (^{31}P)]

Table: Components identified with the aid of the INDOR technique in the reaction mixture from the reaction of *tert*-C_4H_9MgCl with $CH_3P(S)Br_2$. The values in parentheses are the corresponding data [4] for the pure substances [5].

	δ_{PCH_3} (ppm)[3]	$^2J_{PH}$ (Hz)	δ_{PCCH_3} (ppm)[3]	$^3J_{PH}$ (Hz)	δ_P [a] (ppm)	δ_P [b] (ppm)	δ_P [c] (ppm)	
CH_3(*tert*-C_4H_9)P(S)Br	2.36 (2.37)	11.4 (11.5)	1.38 (1.38)	21.6 (20.8)	−102.9 (−103.1)	−101.8 (−)	−103.2 (−)	
CH_3(*tert*-C_4H_9)P(S)SH	2.04 (2.03)	12.0 (12.0)	1.31 (1.32)	18.9 (19.5)	− 79.0 (−)	− (−)	− 78.8 (−)	δ_{SH} = 3.67 (2.58) ppm
CH_3(*tert*-C_4H_9)P(S)H	1.70 (1.68)	13.4 (13.4)	1.21 (1.26)	18.9 (18.5)	− 36.2 (−)	− 35.7 (−)	− (−)	δ_{PH} = 6.35 (6.1) ppm; $^1J_{PH}$ = 434.5 (427) Hz; $^3J_{HH}$ = 4.5–4.8 (4.6) Hz
CH_3(*tert*-C_4H_9)P(S)OH	1.93 (1.83)	11.8 (12.3)	1.25 (1.25)	17.8 (17.3)	− (−)	− (−)	− (−)	δ_{OH} = 7.4 (7.2) ppm

[a] ^{31}P-Resonance; [b] P—H-decoupling; [c] ^{31}P-INDOR.

In the INDOR technique, the ratio $\omega_1/\gamma H_0$ is kept constant and ω_2 is varied. If the condition for the Overhauser effect $(\gamma H_1)^2 T_1 T_2 = 1$ is satisfield [this condition is more rigorous than that for the tickling experiment $\gamma H_2/2\pi \approx \Delta\nu$ ($\Delta\nu$ = line width)], the radiation of H_2 leads to a change in the difference in occupancy of the energy levels, and hence to a change in the multiplet lines.

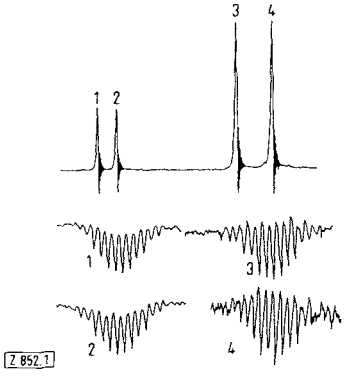

Fig. 1. ^{1}H—NMR (90 MHz) of CH_3(*tert*-C_4H_9)P(S)Br (top) and four INDOR spectra (bottom) of the proton resonance signals.

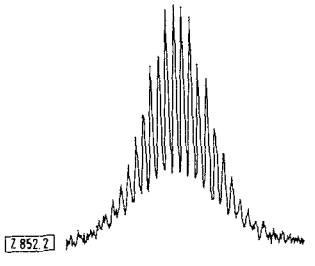

Fig. 2. ^{31}P—NMR spectrum (36.431 MHz) of CH_3(*tert*-C_4H_9)P(S)Br.

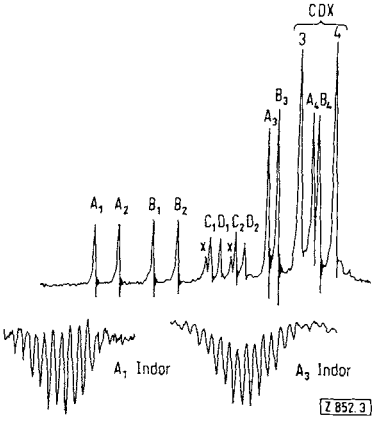

Fig. 3. ^{1}H—NMR spectrum (90 MHz) of the reaction mixture (top) and two INDOR spectra (bottom) recorded with the proton resonance signals A_1 and A_3 of the component CH_3(*tert*-C_4H_9)P(S)Br. The signals of the individual components are indicated by capitals.

The principle of this procedure is shown in Fig. 1 for the case of pure methyl-*tert*-butylthiophosphoryl bromide CH_3(*tert*-C_4H_9)P(S)Br. Figure 2 shows the ^{31}P NMR spectrum of this substance. By this method, which is demonstrated in Figure 3 for the component CH_3(*tert*-C_4H_9)P(S)Br, the compounds listed in Table 3 were identified in the reaction mixture mentioned earlier.

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[5] *W. Kuchen* and *G. Hägele*, unpublished.

Volatile Transition Metal Alkanefluorodithiophosphonates [1]

By *H. W. Roesky* [*]

We recently reported the preparation of alkanefluorodithiophosphonic acids R(F)P(S)SH (R = CH_3, C_2H_5) [2]. These compounds react with transition metals with liberation of hydrogen, *e.g.*

$$2\,Cr + 6\,HS{-}\underset{F}{\overset{S}{P}}{-}C_2H_5 \rightarrow 2\,Cr(S{-}\underset{F}{\overset{S}{P}}{-}C_2H_5)_3 + 3\,H_2$$

The resulting alkanefluorodithiophosphonates (cf. Table) are characterized by considerable volatility under vacuum, and dissolve in acetone without decomposing.

The IR spectra of the metal compounds (in Nujol or capillary film) show mainly the absorption bands of the alkanefluorodithiophosphonic acids, apart from the ν(SH) vibrations, in the NaCl and KBr ranges. The absorptions around 300 cm^{-1} have been tentatively assigned to metal-sulfur stretching vibrations.

The ^{19}F—NMR spectrum of the zinc compound (melt) shows a double triplet with δ_F = 49.7 ppm (against CCl_3F; external), $J_{F\text{-}P}$ = 1111.7 Hz, $J_{CH_2\text{-}F}$ = 6.5 Hz. The ^{1}H—NMR spectrum contains a double triplet for the methyl group: δ_{CH_3} = −2.00 ppm (against TMS; external), $J_{CH_3\text{-}P}$ = 25.5 Hz, $J_{H\text{-}H}$ = 7 Hz, and a multiplet for the methylene group: δ_{CH_2} = −3.11 ppm.

Procedure

Acid is added dropwise to excess metal powder under purified and dried nitrogen. Some reactions (Mn, Ni, Zn) are exo-

	Color	Yield (%)	M.p. [B.p.] (°C/Torr)	Subl.-Temp. (°C) [b]	ν (M—S) (cm^{-1})	UV [e] ε (cm^{-1})
$Ni(CH_3PS_2F)_2$	brown-black	40	133 decomp.	90—100	320 [d]	980 28020 874 26000 71 18870 63 14280
$Ni(C_2H_5PS_2F)_2$	brown-black	65	78	100—110	280 298	1453 28300 1016 25900 76 18870 70 14280
$Co(C_2H_5PS_2F)_2$	green [a]	7	[105/0.05] decomp.	—	318	2640 28950 119 23420 Sh 48 17850 Sh 53 16670
$Mn(C_2H_5PS_2F)_2$	pale pink	3	91	110—120	312	— —
$Cr(C_2H_5PS_2F)_3$	violet	28	[195/0.2]	—	276	3922 28700 195 18860 286 14500 1444 28250 Sh 145 19040 [f] 174 14500
$Zn(C_2H_5PS_2F)_2$	white	23	78—80.5	90—100	290 [c]	— —
$Cd(C_2H_5PS_2F)_2$	white	15	148—148.5	150—160	320	— —

[a] The compound turns brown soon after distillation, even when kept in a closed vessel.
[b] In an oil-pump vacuum at 0.05—0.1 torr. [c] Shoulder at 306 cm^{-1}. [d] Shoulder at 292 cm^{-1}.
[e] In acetone. [f] In methanol.

thermic at room temperature; in the other cases the reaction mixture is heated on a water bath for a few hours after the addition of the acid. The reactions with Mn, Ni, Zn, and Cd are preferably carried out directly in a sublimation apparatus and the products purified by double vacuum sublimation.

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[1] Part 23 of: Phosphorus Compounds. — Part 22: *F. N. Tebbe, H. W. Roesky, H. Rode,* and *E. L. Muetterties,* J. Amer. chem. Soc., in press; Part 21: *H. W. Roesky* and *H. H. Giere,* Inorg. nuclear Chem. Letters, in press.

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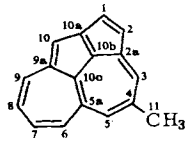
Crystal and Molecular Structure of 4-Methylpentaleno[6,6a,1,2-*def*]heptalene

By *H. J. Lindner* [*]

To obtain further information about 4-methyl-pentaleno-[6,6a,1,2-*def*]heptalene [1] $C_{17}H_{12}$ *(1)*, a polycyclic conjugated non-benzenoid system containing $4n$ π electrons ($n = 4$), by determination of its molecular geometry, an X-ray structural analysis was carried out.



(1)

(1) crystallizes in black monoclinic needles: the space group is P 2_1, with the lattice constants $a = 8.04 \pm 0.02$, $b = 6.67 \pm 0.02$, $c = 10.94 \pm 0.02$ Å; $\beta = 106.9 \pm 0.1°$. The unit cell contains two molecules. The intensities of 986 symmetry-independent reflections of the $h\,0\,l$ and $h\,4\,l$ layers were measured by means of an automatic, punched-tape-controlled Weissenberg diffractometer (Stoe-Güttinger system) with $Cu_{K\alpha}$ radiation and corrected in the usual manner.

The phases of 165 reflections with E values > 1.2 were determined by the *Karle* and *Karle* [2] symbolic addition method for non-centrosymmetric crystals. The Fourier synthesis with the E values of these reflections led to a structural model that was refined to within an R factor of 0.096 by further Fourier syntheses and by the method of least squares with isotropic temperature factors.

The molecule is planar. The bond lengths and angles are shown in Figures 1 and 2.

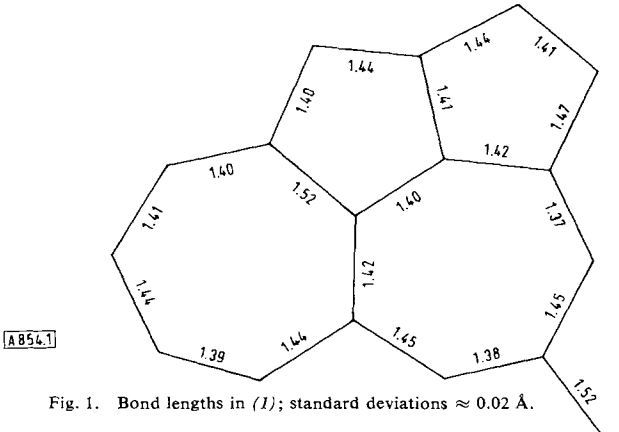


Fig. 1. Bond lengths in *(1)*; standard deviations ≈ 0.02 Å.

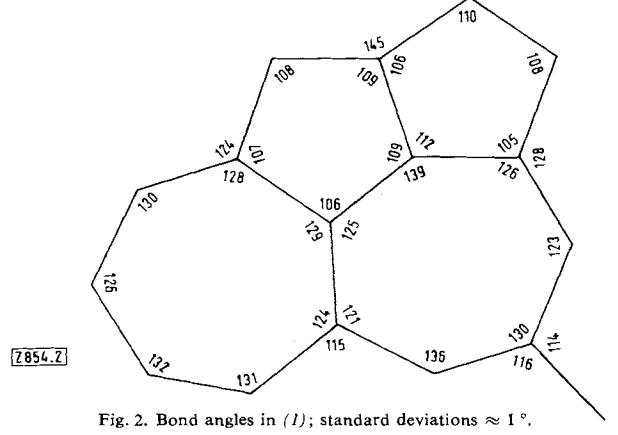


Fig. 2. Bond angles in *(1)*; standard deviations ≈ 1 °.

The alternance of the bond lengths agrees well with the results of quantum-chemical calculations [3].

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[3] *U. Müller-Westerhoff,* unpublished.

Trithiomolybdates

By *A. Müller, E. Diemann, B. Krebs,* and *M. J. F. Leroy* [*]

Whereas the preparation of dithiomolybdates and tetrathiomolybdates by the introduction of H_2S into molybdate solution presents no difficulties, crystalline trithiomolybdates have not so far been obtained in this way [1]. We have now found a simple method for the preparation of crystalline Cs_2MoOS_3 and Tl_2MoOS_3.

H_2S is passed into a mixture of 15 ml of water and 15 ml of NH_3 solution ($d = 0.94$) containing 5 g of ammonium molybdate after addition of an excess of aqueous CsCl solution and acetic acid (up to pH 10). Orange to red crystals of Cs_2MoOS_3 *(1)* separate out. The less soluble Tl_2MoOS_3 *(2)* can be prepared from a solution of *(1)* by addition of $TlNO_3$.

(1) and *(2)* have been characterized by analysis, by their electronic and vibration spectra, and by X-ray investigation. *(1)* crystallizes in columns or plates with (100), (010), and (001) as the surface planes. Space group: D_{2h}^{16}, (Pnma); lattice constants: $a = 9.72 \pm 0.02$, $b = 7.21 \pm 0.02$, $c = 12.20 \pm 0.03$ Å, $V = 855.0$ Å^3. It is found from the measured density $d_{py} = 3.66$ g/cm^3 that $Z = 4$ formula units ($d_{X-ray} = 3.681$ g/cm^3). It seems certain from the similarity of the cell dimensions and the distribution of the reflection intensities in comparison with Cs_2MoS_4 [2] and other substances that crystallize in the β-K_2SO_4 type that *(1)* also belongs to this type.

The IR spectrum of solid *(1)* in Nujol contains the following bands, which conclusively demonstrate the presence of $MoOS_3^{2-}$ with approximately C_{3v} symmetry: 859 (ν_1 (A_1) $\triangleq$ νs (MoO)), 465 (ν_2 (A_1) $\triangleq$ νs (MoS)), 200 (ν_3 (A_1) $\triangleq$ δ_s (MoS_3)) and ν_6 (E) $\triangleq$ δ_{as} (MoS_3)), 475 (ν_4 (E) $\triangleq$ ν_{as} (MoS)), and 265 cm^{-1} (ν_5 (E) $\triangleq$ ρ_r (MoS_3)). The stretching vibrations of *(2)* are strongly displaced toward longer wavelengths (838), 460, and 440 cm^{-1}). Assuming a diagonal MVFF [3] F-matrix, one obtains the following force constants: $f_{MoO} = 5.89$ (5.85), $f_{MoS} = 3.11$ (3.18), $f_{MoS/MoS} = 0.30$ (0.27), $f_{SMoS} = 0.24$ (0.23), $f_{OMoS} = 0.21$, and $f_{SMoS/SMoS} = 0.00$ (0.00) mdyne/Å (corresponding values for MoO_4^{2-} and MoS_4^{2-} in parentheses [4]). The similarity of the force constants shows that the metal chalcogen bond orders are the same and the bond lengths similar in all three ions.

The electronic absorption spectrum of $MoOS_3^{2-}$ contains characteristic maxima at 21500 ($\varepsilon = 2.3 \times 10^3$), 25500 ($\varepsilon = 8.7 \times 10^3$, $f = 0.10$), 32000 ($\varepsilon = 6.6 \times 10^3$, $f = 0.09$), 38500 (shoulder), and 44100 cm^{-1} ($\varepsilon = 1.5 \times 10^4$ l·mole^{-1}·cm^{-1}, $f = 0.3$). The first bands are due to electronic reduction transitions S $\rightarrow$ Mo [5]. The high values of the oscillator strength f point to strong covalent Mo–S and Mo–O bonds. The reflection spectrum of *(1)* in the visible region is identical with the solution spectrum. This shows that isolated $MoOS_3^{2-}$ ions are present both in solution and in the solid state.

(1) gives a neutral reaction in aqueous solution. The parent acid is thus strongly dissociated. The equivalent conductivity of the $MoOS_3^{2-}$ ion is $\Lambda_{25}^{\infty} = 77\ \Omega^{-1}$ cm^2 eqt^{-1} (MoO_4^{2-}: 74.5 Ω^{-1} cm^2 eqt^{-1}).

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Kinetics of the Aminolysis of Methoxyphenylcarbenepentacarbonylchromium(0) [1,2]

By *B. Heckl, H. Werner,* and *E. O. Fischer* [*]

Methoxyorganylcarbenepentacarbonylchromium complexes $Cr(CO_5)C(OCH_3)R'$ (*(1a)*: $R' = CH_3$, *(1b)*: $R' = C_6H_5$ [3]) react as analogs of esters with amines. For example, in the reaction of *(1a)* with NH_3 [4] and NH_2R [5], the methoxy group is substituted and aminocarbene complexes are formed.

We have now found that aminolysis also occurs when primary amines are allowed to act on *(1b)* in solvents such as *n*-hexane, ether, or dioxane at ~30 °C:

$$(1b) + NH_2R \rightarrow Cr(CO)_5C(NHR)C_6H_5 + CH_3OH$$

(2a): $R = C_6H_{11}$
(2b): $R = n\text{-}C_4H_9$
(2c): $R = CH_2C_6H_5$

The compounds *(2)* form yellow diamagnetic crystals, which are very readily soluble in organic solvents and are only slightly affected by oxidizing agents.

The rate of aminolysis can be determined by spectrophotometric methods (*(1b)*: $\lambda_{max} = 406$ nm, *(2a)–(2c)*: $\lambda_{max} = 362$–366 nm; in hexane [6]). The pseudo-first order rate constants for $R = C_6H_{11}$ are shown in Table 1.

Table 1. Pseudo-first order rate constants of the reaction of $Cr(CO)_5C(OCH_3)C_6H_5$ *(1b)* with $NH_2C_6H_{11}$ at 32.5 ± 0.1 °C.

[*(1b)*] (mmol/l)	[$NH_2C_6H_{11}$] (mmol/l)	Solvent	$k_{ps} \cdot 10^3$ (sec^{-1})
0.33	60	*n*-Decane	0.46
0.33	80	*n*-Decane	1.10
0.33	90	*n*-Decane	1.86
0.33	100	*n*-Decane	2.79
0.33	110	*n*-Decane	4.29
0.33	120	*n*-Decane	5.13
0.33	16.6	Dioxane	0.58
0.33	20.0	Dioxane	0.80
0.33	23.3	Dioxane	1.28
0.33	26.6	Dioxane	1.65
0.33	30.0	Dioxane	2.11
0.33	36.6	Dioxane	3.34
0.33	43.3	Dioxane	4.79

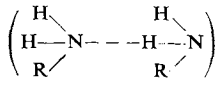
Plots of k_{ps} against [NH_2R] always lead to exponential curves, so that second order kinetics (*i.e.* first order with respect to the concentrations of complex and of amine) can be definitely ruled out. On the other hand, a very good linear relationship is found for k_{ps} and $[NH_2R]^3$ in *n*-decane and for k_{ps} and $[NH_2R]^2$ in dioxane.

$$n\text{-Decane: } \frac{d[(2)]}{dt} = k\,[(1b)][NH_2R]^3$$

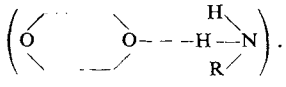
$$\text{Dioxane: } \frac{d[(2)]}{dt} = k'\,[(1b)][NH_2R]^2$$

In view of these unexpected and at first sight very surprising results, the following mechanism is suggested: The first step is the formation of an adduct (*A*) from one molecule of carbene complex and one of amine. The existence of hydrogen bonds between the NH protons and the oxygen atom of the OCH_3 group is shown by ^1H–NMR measurements[7]. The hydrogen bonding weakens the double-bond component between O and $C_{carbene}$ and so facilitates nucleophilic substitution on the carbene carbon atom.

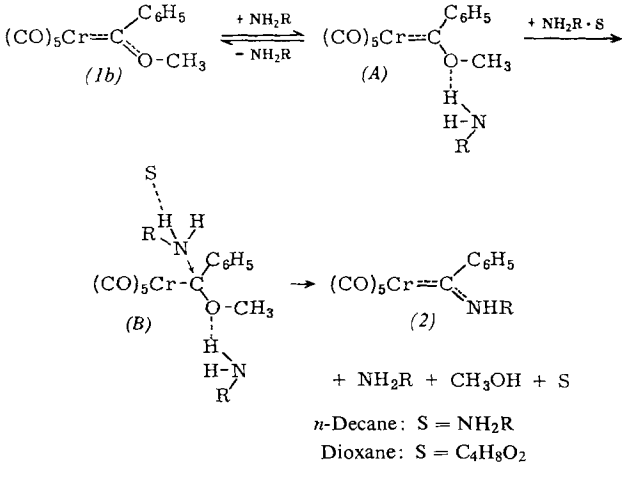
The attacking agent in *n*-decane could be an amine polarized by a second NH_2R molecule



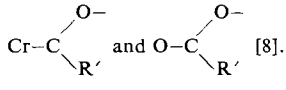
or an ion pair ($NH_3R^+ \cdot NHR^-$), and that in dioxane an amine molecule polarized by the solvent



In our view, this assumption provides a plausible explanation for the difference in the reaction order in these solvents and the higher reaction rate in dioxane (cf. Table 1).



The indicated mechanism for the aminolysis of *(1b)* again indicates the analogy between the groupings



[8].

The much greater reactivity of the former suggests less resonance stabilization and supports the view expressed earlier[3] that the $Cr-C_{carbene}$ back-bonding is only weak.

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Elementary Steps in Acid-Base Catalysis. Proton Transfer Reactions in Aqueous Solutions.

By *M.-L. Ahrens* and *G. Maass*[*]

Proton transfer reactions characterized by the simple mech-

$$X + YH \underset{\overleftarrow{k}}{\overset{\overrightarrow{k}}{\rightleftharpoons}} XH + Y \qquad (1)$$

anism are described by a generalized Brønsted equation[1]:

$$\frac{d \log \overrightarrow{k}}{d \Delta pK} = \alpha \text{ (2a) and } \frac{d \log \overleftarrow{k}}{d \Delta pK} = -\beta = -(1-\alpha) \qquad (2b)$$

$\overrightarrow{k}$ and $\overleftarrow{k}$ are the rate constants for the proton transfer from the donor YH to the acceptor X and for the reverse reaction respectively. ΔpK is defined by $\Delta pK = pK_X - pK_Y$. The proton transfer is represented in a simplified form in Scheme (1). In the general case it is necessary to consider the protolysis and hydrolysis of XH and YH and the possibility that the proton transfer takes place *via* one or more water molecules. The latter point may be neglected, whereas a correction for hydrolysis is necessary in some cases in the calculation of the rate constants.

The coefficient α defined in equation (2a) is restricted to values $0 \leqslant \alpha \leqslant 1$. For $\Delta pK \gg 0$, *i.e.* $pK_X \gg pK_Y$, the proton transfer is diffusion-controlled, *i.e.* the rate cannot be increased further by increasing the pK difference. This gives the limiting value of $\alpha = 0$, and β is accordingly equal to 1. The situation is reversed for $\Delta pK \ll 0$. In this case the reverse reaction proceeds at its maximum rate (diffusion controlled), so that $\beta = 0$ and $\alpha = 1$. When the acidities of X and Y are nearly equal, so that $\Delta pK \approx 0$, the probabilities of recombination of the proton with each of them will be approximately the same, so that α will be different from 0 or 1. In the ideal case, this transition is restricted to a relatively narrow range around $\Delta pK = 0$. Actually this range extends over several orders of magnitude in most systems. This is understandable in view of the fact that the proton transfer takes place in a hydrogen bridge between the acceptor and the donor. It is therefore to be expected that the rate of the proton transfer will vary in the same way as the tendency of the reactants to form hydrogen bonds. The rate constants should accordingly decrease in the order

$$OH\ldots O > OH\ldots N > NH\ldots N > SH\ldots X > PH\ldots X > CH\ldots X$$

and the transition range $0 < \alpha < 1$ should become wider. In addition to these effects, steric hindrance or charge delocalization as a result of resonance stabilization in the reactants can lead to a further decrease in the rate of proton transfer and cause deviations from ideal behaviour. In general, a value $\alpha \neq 0$ or 1 is expected whenever the proton transfer between the donor and the acceptor in both directions is associated with the crossing of a fairly high activation barrier. The validity of the generalized Brønsted equation (2a, b) was confirmed by earlier investigations[2]. The present measure-

ments are an extension to proton transfer reactions in systems having a low tendency toward H-bond formation, as in transitions between mercapto groups. Each acceptor X was tested with a series of chemically similar donors YH having different acidities.

The very fast reactions were followed by ultrasonic relaxation methods in the frequency range of 0.3 to 100 MHz[2,3]. The rate constants $\vec{k}$ and $\overleftarrow{k}$ are listed in Tables 1 to 5. The ionic strength μ and the temperature t were constant for all the experiments.

Tables 1 to 5. Rate constants for the proton transfer between acceptor X and donor YH. μ = 1M, t = 20 °C.

Table 1. X = acetate, pK_X = 4.75.

YH	ΔpK	$\vec{k}$ ($l mol^{-1} sec^{-1}$)	$\overleftarrow{k}$ ($l mol^{-1} sec^{-1}$)
Dichloroacetic acid	3.27	$1.1 \cdot 10^{10}$	$5.8 \cdot 10^{6}$
Monochloroacetic acid	1.9	$2.1 \cdot 10^{9}$	$2.4 \cdot 10^{7}$
Formic acid	1.0	$1.0 \cdot 10^{9}$	$4.9 \cdot 10^{8}$
Propionic acid	−0.12	$2.9 \cdot 10^{8}$	$3.9 \cdot 10^{8}$
Malonic acid	−0.95	$6.2 \cdot 10^{7}$	$5.6 \cdot 10^{8}$
Cacodylic acid	−1.44	$6.2 \cdot 10^{7}$	$1.7 \cdot 10^{9}$
KH_2PO_4	−2.45	$1.7 \cdot 10^{7}$	$4.8 \cdot 10^{9}$

Table 2. X = Imidazole, pK_X = 7.0.

YH	ΔpK	$\vec{k}$ ($l mol^{-1} sec^{-1}$)	$\overleftarrow{k}$ ($l mol^{-1} sec^{-1}$)
Pyridinium	1.82	$1.8 \cdot 10^{9}$	$2.7 \cdot 10^{7}$
α-Picolinium	1.03	$6.7 \cdot 10^{8}$	$6.4 \cdot 10^{7}$
α,γ-Lutidinium	−0.14	$3.7 \cdot 10^{8}$	$3.7 \cdot 10^{8}$
s-Collidinium	−0.31	$3.3 \cdot 10^{8}$	$6.7 \cdot 10^{8}$
Ammonium	−2.25	$1.5 \cdot 10^{7}$	$2.7 \cdot 10^{9}$
Propylammonium	−3.75	$1.4 \cdot 10^{6}$	$8.0 \cdot 10^{9}$

Table 3. X = Methoxycarbonylmethylthiolate, pK_X = 7.8.

YH	ΔpK	$\vec{k}$ ($l mol^{-1} sec^{-1}$)	$\overleftarrow{k}$ ($l mol^{-1} sec^{-1}$)
Pyridinium	2.62	$6.2 \cdot 10^{8}$	$1.5 \cdot 10^{6}$
α-Picolinium	1.83	$5.7 \cdot 10^{8}$	$8.4 \cdot 10^{6}$
Imidazolium	0.8	$6.5 \cdot 10^{7}$	$1.0 \cdot 10^{7}$
s-Collidinium	0.49	$3.7 \cdot 10^{7}$	$1.2 \cdot 10^{7}$
Morpholinium	−0.9	$5.5 \cdot 10^{6}$	$4.3 \cdot 10^{7}$

Table 4. X = 2-Hydroxethylthiolate, pK_H = 10.3.

YH	ΔpK	$\vec{k}$ ($l mol^{-1} sec^{-1}$)	$\overleftarrow{k}$ ($l mol^{-1} sec^{-1}$)
Methylmercapto-acetate	2.50	$2.4 \cdot 10^{8}$	$7.5 \cdot 10^{5}$
Ethylmercapto-acetate	2.35	$2.0 \cdot 10^{8}$	$8.8 \cdot 10^{5}$
Thioglycol	0.8	$1.5 \cdot 10^{7}$	$2.5 \cdot 10^{6}$
Thiomalic acid	0.6	$1.8 \cdot 10^{7}$	$4.5 \cdot 10^{6}$
3-Mercapto-propionic acid	−0.2	$3.6 \cdot 10^{6}$	$1.2 \cdot 10^{7}$

Table 5. X = Methoxycarbonylmethylthiolate, pK_X = 7.8.

YH	ΔpK	$\vec{k}$ ($l mol^{-1} sec^{-1}$)	$\overleftarrow{k}$ ($l mol^{-1} sec^{-1}$)
Thiomalic acid	−1.9	$1.8 \cdot 10^{6}$	$1.4 \cdot 10^{8}$
Mercaptoacetic acid	−2.5	$7.5 \cdot 10^{5}$	$2.4 \cdot 10^{8}$
3-Mercapto-propionic acid	−2.7	$6.6 \cdot 10^{5}$	$3.3 \cdot 10^{8}$

The results show that the transfer range with α values between 0 and 1 increases from the system O···H···O through N···H···N to S···H···N and S···H···S. This is in agreement with the above-mentioned relation between the reaction rate and the tendency toward hydrogen bond formation.

Deviations due to individual molecular structure effects are particularly noticeable in a comparison of Tables 4 and 5. Though both tables refer to S···H···S transfers, the log $\vec{k}$ (or log $\overleftarrow{k}$) values cannot be represented by a single curve in a log $k-\Delta pK$ diagram. The values for the methyl mercaptoacetate systems are displaced by a constant factor in relation to those for the 2-hydroxyethylthiolate systems, though the general form of the curve remains unchanged. The difference exceeds the experimental error, and suggests that the introduction of the hydrophobic methyl group in the ester leads to increased structure in the water and hence to an increase in the reaction distance, which may result in an acceleration of the reaction.

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Diphthalocyaninato-thorium(IV) and -uranium(IV) [1]

By *F. Lux*, *D. Dempf*, and *D. Graw* [*]

During investigations on the separation of fission products from nuclear fuels in nonaqueous solutions [2–5], a sublimable phthalocyanin complex of neptunium was detected by radiochemical means [2]; this was the first volatile neptunium complex known. Neptunium and uranium were found in this work to differ in behavior, so that a thorough preparative study of phthalocyanin complexes of actinoids became desirable; this would be the more interesting in that a large majority of the actinoid complexes previously known contain ligands that are bonded to the central atom by oxygen.

Results reported previously [6–11] are in part contradictory [7,8]; in no case has the isolation of a phthalocyaninatoactinoid been proved unambiguously.

Thorium tetrachloride and phthalodinitrile (molar ratio 1:1 or 1:2) at 230–250 °C interact with evolution of HCl [6,10]. After extraction of the blue-black solidified melt with acetone, a solution of the residue in quinoline gives an electronic spectrum characteristic of phthalocyanin-metal complexes [11]; this contains only one absorption band between 700 and 600 nm, in this case at 685 nm. The thorium:chlorine ratio and the evolution of HCl indicate that some of the benzene rings of the phthalocyanin complex are chlorinated. The chlorinated product does not sublime: it decomposes with formation of metal-free phthalocyanin derivatives.

To prevent halogenation of the ligand, we treated thorium tetraiodide with phthalodinitrile at 240 °C. After extraction of the excess of nitrile, sublimation at 550 °C/10^{-5} torr, which involved evolution of iodine, yielded dark violet crystals of diphthalocyaninatothorium(IV) *(1)*. Dark violet diphthalocyaninatouranium(IV) *(2)* is formed analogously from uranium tetraiodide and phthalodinitrile.

These products are very stable thermally and resistant to air. *(1)* can be sublimed at 600 °C in a N_2 stream at atmospheric pressure with formation of needle-shaped crystals. *(1)* and *(2)* are sparingly soluble in benzene or tetrahydrofuran but more soluble in pyridine, quinoline, 1,2,4-trichlorobenzene, 1-chloronaphthalene, or the hexamethyltriamide of phosphoric acid; neither compound can be recrystallized from concentrated sulfuric acid.

The IR spectra (KBr disks; 2000 to 400 cm^{-1}) of *(1)* and *(2)* are almost identical with each other and very similar to the IR spectrum[12] of the analogous tin complex[13]; *(1)* and *(2)* show three bands between 1380 and 1280 cm^{-1} at 1329, 1307 or 1304, and at 1281 cm^{-1}, whereas the tin complex has only two bands in this region at 1335 and 1287 cm^{-1}. The IR spectra of *(1)* and *(2)* are characteristic of phthalocyanin-metal complexes[11].

(1) (cm^{-1}): 1608 (w), 1497 (sh), 1471 (m), 1450 (vw), 1402 (w), 1381 (w), 1329 (s), 1307 (m), 1281 (m), 1180 (vw), 1160 (w), 1112 (s), 1069 (s), 999 (w), 941 (vw), 880 (m), 866 (vw), 811 (w–m), 790 (w), 771 (m), 740 (m), 725 (vs), 625 (w), 560 (vw), 492 (w).

(2) (cm^{-1}): 1606 (w), 1481 (m), 1471 (m), 1405 (w), 1370 (w, broad), 1329 (s), 1304 (m), 1281 (w), 1160 (w), 1112 (s), 1066 (s), 999 (w), 940 (vw), 881 (m), 865 (w, sh), 810 (w–m), 790 (vw), 771 (m), 740 (m), 724 (vs), 625 (vw), 495 (w).

The electronic spectra (in pyridine: 700 to 300 nm) also accord with expectation[11]. *(1)*: λ_{max} = 650, 339 (Soret band) (log ε = 5.16, 5.03). *(2)*: λ_{max} = 647, 339 nm (Soret band) (log ε = 5.28, 5.20).

As expected, *(1)* is diamagnetic (at room temperature) and *(2)* is paramagnetic (*ca.* 3.1 B.M. between 100 and 239 °K)[14].

Mass-spectrometric molecular weights[15]: *(1)*, 1256 (±1); *(2)*, 1262 (±1). The molecules are barely fragmented at an electron energy of 50 eV, which confirms the very great stability of the compounds disclosed already by the behavior on sublimation.

Only one diphthalocyanin complex was previously known, namely, diphthalocyaninatotin(IV)[13].

Compounds *(1)* and *(2)* should have antiprismatic or bipyramidal structures, as previously proposed[16] for the tin compound. The mutual steric hindrance between the two ligands would be less in the archimedian antiprismatic arrangement. Magnetochemical results[14] also favor such structures. X-ray structure analysis is in progress.

Experimental:

A mixture of thorium iodide (1.83 g) and phthalodinitrile (6.3 g) (molar ratio 1:20) was stirred in an atmosphere of inert gas at 240 °C for 30 min, iodine being evolved and the melt becoming dark green. After cooling to room temperature, the solidified melt was powdered and extracted with benzene. The residue was dried in a high vacuum, enclosed in a platinum net, and heated in a quartz sublimation apparatus at 10^{-5} torr; at *ca.* 200 °C a rise in pressure and evolution of iodine were observed; the temperature was then raised to 550 °C. The material separating in the lower zone of the sublimate formed was similarly sublimed twice more for purification. Yield: 43%.

There is no need to use pure UI_4[17,19] in the analogous preparation of the uranium compound. Uranium turnings (1.3 g) were converted into uranium hydride. After decomposition of the hydride at 350 °C, iodine (4.2 g) was added to the uranium powder produced and the whole was heated in a closed vessel at 530 °C for 1 h. After cooling, the sublimed iodine was scratched off the walls of the vessel, and the mixture was heated for a further 12 h at 530 °C. The product was then treated with phthalodinitrile. Yield: 38%.

Enclosure of the substance in platinum gauze is particularly necessary for good yields in the first sublimation, and sublimation from a platinum crucible is necessary to afford a pure product. The layer of material in the sublimate attached directly to the wall of the vessel is discarded, to avoid products with too high a metal content; presumably at high temperatures the compounds react to some extent with the oxygen of the quartz, as was observed in the preparation of protactinium tetraiodide[18].

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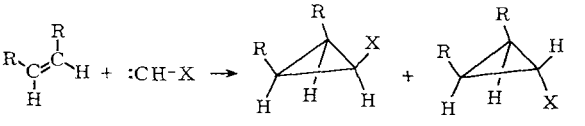
Monofluorocarbene and its *syn/anti* Selectivity[**]

By *M. Schlosser* and *G. Heinz*[*]

It has hitherto remained unexplained why addition of a carbene[1] to an olefin generally affords the thermodynamically less stable *syn*-substituted cyclopropane *(1)*[2].



R = H, Alkyl *syn-(1)* *anti-(1)*
X = Alkyl, Aryl, OR, Cl, Br

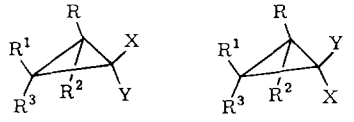
Attempts have been made to explain this stereoselectivity by assuming that in the transition state the London dispersion forces bring the alkyl groups of the olefin and the carbene ligands as close together as possible[3]. If this hypothesis were correct, then monofluorocarbene should add quite unselectively to olefins because of the small polarizability of the fluorine atom[4], and the *syn/anti* selectivity of a doubly substituted carbene :CXY should be the sum of the individual selectivities of X and Y[5].

We found that these expectations are not fulfilled. We were able to produce fluorocarbene[1,6] from dibromofluoromethane and *n*-butyllithium and to add it stereospecifically to several olefins, yielding fluorocyclopropanes (see Table 1). The *syn/anti* selectivity was then seen to be similar to that for chlorocarbene. The directive powers of carbene substituents are not additive, *i.e.*:

Table 1. Fluorocyclopropanes obtained by addition of fluorocarbene to olefins, and comparison of the observed *syn/anti* proportions thereof with those in the corresponding chloro- and chlorofluoro-cyclopropanes.

Reaction conditions: To 0.6 mole of olefin and 0.2 mole of halomethane ($CHBr_2F$, CH_2Cl_2, or $CHCl_2F$ [9]) at +15 °C was added, dropwise with stirring, 0.1 mole of *n*-butyllithium in 65 ml of hexane.

Structure determined by C, H analyses, mass spectra, and proton resonance.

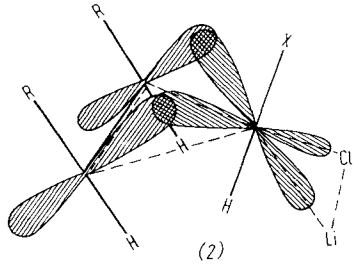


syn *anti*

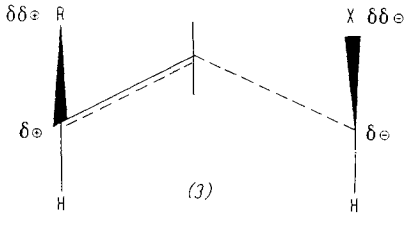
R	R^1	R^2	R^3	X = F, Y = H Yield (%)	*syn:anti*	X = Cl, Y = H Yield (%)	*syn:anti*	X = Cl, Y = F Yield (%)	*syn:anti*
CH_3	CH_3	CH_3	CH_3	10	—	—	—	45	—
n-C_5H_{11}	H	H	H	3	2.0:1	12	2.1:1	11	2.0:1
n-C_3H_7	H	H	n-C_3H_7	3	—	—	—	12	—
n-C_3H_7	n-C_3H_7	H	H	2	1.9:1	10	1.7:1	11	2.0:1
—$(CH_2)_4$—		H	H	6	2.3:1	28	2.4:1	21	2.2:1

$$\Delta\Delta G^{\ddagger}_{syn/anti}(:CClF) \neq \Delta\Delta G^{\ddagger}_{syn/anti}(:CHCl - \Delta\Delta G^{\ddagger}_{syn/anti}(:CHF) \quad [7]$$

Contrathermodynamic stereoselectivity – an apparently widespread phenomenon [8] – is in our opinion not yet fully understood. We are now trying to obtain an insight by MO calculations into whether perhaps an unusual geometry, *e.g.*,



(2)



(3)

the "bent" arrangement of overlapping *p*-orbitals as in *(2)*, or electronic effects, *e.g.*, opposing polarization of the C–C bond of the olefin (R = H) and of the C–X bond of the carbene as in *(3)* favour the *syn*-oriented transition state.

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[**] The authors thank the Fonds der Chemischen Industrie for support of these investigations.

[1] We do not differentiate here between a "free" carbene and its lithium salt adduct (carbenoid).

[2] Review: *W. Kirmse*: Carbene Chemistry, Academic Press, New York 1964.

[3] *G. L. Closs* and *R. A. Moss*, J. Amer. chem. Soc. *86*, 4042 (1964); *R. A. Moss* and *R. Gerstl*, Tetrahedron *22*, 2637 (1966).

[4] Summary: *J. A. Ketelaar*: Chemische Konstitution. Vieweg, Brunswick 1946, p. 82.

[5] *G. L. Closs* and *J. J. Coyle*, J. org. Chemistry *31*, 2759 (1966).

[6] Fluorocarbene is also formed transitorily in the decomposition of some photochemically or radiochemically excited fluorohalogenomethanes and then adds unselectively to olefins (*Y. N. Tang* and *F. S. Rowland*, J. Amer. chem. Soc. *89*, 6420 (1967); *T. Marolewski* and *N. C. Yang*, Chem. Commun. *1967*, 1225).

[7] "*syn*" with respect to the position of the chlorine atom in chloro- and chlorofluoro-cyclopropanes and of the fluorine atom in fluorocyclopropanes.

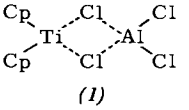
[8] Cf. *M. Schlosser* and *K. F. Christmann*, Liebigs Ann. Chem. *708*, 12 (1967).

[9] Similar results were obtained on using Br_2CHCl in place of CH_2Cl_2, or Br_2CClF in place of $CHCl_2F$.

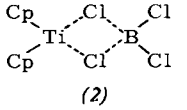
ESR-Investigation of a New Titanium-Boron Complex [1]

By *G. Henrici-Olivé* and *S. Olivé* [*]

The Ti(III)-Al complex *(1)* [2–4] has been investigated in some detail in connection with Ziegler-Natta catalysis; its ESR signal is shown in Fig. 1 (left) [2]. The six equivalent lines of the signal are due to interaction of the unpaired electron of the Ti^{III} with the Al nucleus (nuclear spin $I = 5/2$). It appears that, in this complex, the Ti^{III} species acts as an intramolecular electron donor towards the acceptor $AlCl_3$. Even better acceptor properties are exhibited by boron trihalides [5]; we therefore decided to prepare the boron analog of the complex *(1)*.



(1)



(2)

Dicyclopentadienyl-propyl-titanium chloride was reduced with alkali metal (Na, K) in toluene and in presence of an excess of BCl_3. The reaction solution showed, after having been stirred for *ca.* $^1/_2$ h, a strong ESR signal (Fig. 1, right). The four equivalent lines are clearly due to a nucleus of $I = 3/2$. Since identical signals are obtained with Na or K, an interaction of the unpaired electron of the Ti^{III} with the alkali metal [1] can be excluded in the present case; the quartet is thus obviously due to ^{11}B (natural abundance 81%). A further seven lines should be expected for ^{10}B (natural abundance 19%, $I = 3$). However, the hyperfine splitting is reduced by a factor $g(^{10}B)/g(^{11}B) \approx 0.3$; hence these weaker lines are lost under the four major lines.

On increasing the signal level, the ^{47}Ti and ^{49}Ti satellite lines can be observed which also split into quartets (Fig. 2). The bulk diagram has been constructed for both magnetic iso-

topes using $a(^{47,49}Ti) = 10.8$ and $a(^{11}B) = 5.9$ gauss. The upfield satellite lines are less resolved in the measured spectrum; the inner lines are masked by the lines of the main signal.

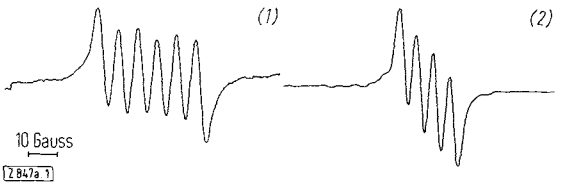


Fig. 1. ESR signal of $Cp_2TiCl_2AlCl_2$ *(1)* and $Cp_2TiCl_2BCl_2$ *(2)*.

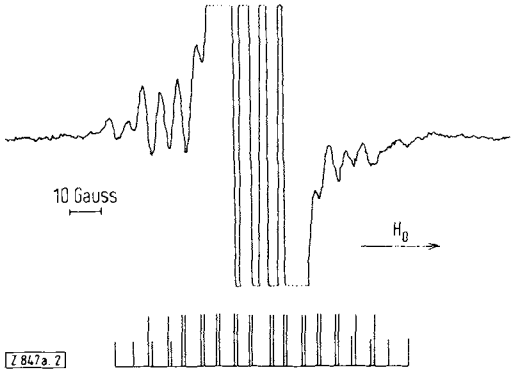


Fig. 2. ^{47}Ti and ^{49}Ti satellites in the ESR signal of $Cp_2TiCl_2BCl_2$ *(2)*. Above: recorded lines. Below: calculated bulk diagram.

As far as the accuracy of the ESR quantitative determination can be relied upon, it would seem that all, or the greater part, of Ti was present in the signal-producing form.

The spectroscopic parameters of complex *(2)* are similar to those of complex *(1)* (see Table 1), thus suggesting that both complexes have the same structure. It is possible, with the aid of the isotropic coupling constants of the free atoms B and Al [6], to estimate the density of the unpaired spin at the B and Al nucleus, ρ_M. The greater spin density at the B in *(2)* than at the Al in *(1)* confirms the greater acceptor ability of BCl_3, also toward the donor Cp_2TiCl. In perfect agreement with this statement the spin density at the Ti nucleus is smaller in the case of complex *(2)* (see column 3 of the Table).

Table 1. Comparison of ESR spectroscopic data of $Cp_2TiCl_2AlCl_2$ *(1)* and $Cp_2TiCl_2BCl_2$ *(2)*.

Cpd.	g-Value	$a(^{47,49}Ti)$ (gauss)	a(M) [a] (gauss)	Isotropic coupling (MHz) [b]	ρ_M (%)
(1)	1.975	11.5	6.9	2746	0.70
(2)	1.975	10.8	5.9	2020	0.81

[a] a = hyperfine splitting parameter; M = metal: ^{27}Al in complex *(1)*, ^{11}B in *(2)*.
[b] Isotropic coupling constant for the free atom [6].

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[1] Part 3 of "ESR Investigations of Transition Metal Complexes"; Part 2; Angew. Chem. *80*, 398 (1968); Angew. Chem. internat. Edit. *7*, 386 (1968).

[2] *G. Henrici-Olivé* and *S. Olivé*, Angew. Chem. *79*, 764 (1967); Angew. Chem. internat. Edit. *6*, 790 (1967).

[3] *H. J. M. Bartelink, H. Bos, J. Smidt, C. H. Vrinssen*, and *E. H. Adema*, Recueil Trav. chim. Pays-Bas *81*, 225 (1962), and references therein.

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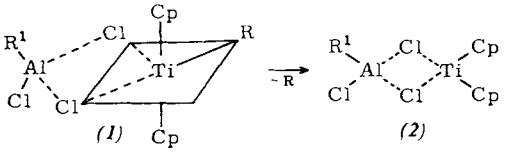
ESR-Investigation on the Stability of the Titanium-Carbon Bond in Soluble Ziegler-Natta Catalysts [1]

By *G. Henrici-Olivé* and *S. Olivé* [*]

The stability of the transition metal-carbon bonds is often decisive for homogeneous catalysis on these metals [2]. Soluble Ziegler-Natta catalysts of type *(1)* [3–5] represent a



(1a), R = C_2H_5, R^1 = C_2H_5
(1b), R = CH_3, R^1 = C_2H_5
(1c), R = C_2H_5, R^1 = CH_3
(1d), R = CH_3 R^1 = CH_3
(2a), R^1 = C_2H_5
(2b), R^1 = CH_3

Cp = cyclopentadienyl

very convenient model for the study of the Ti–C stability and the possibilities of influencing it. The reaction rate of the reduction $Ti^{IV} \rightarrow Ti^{III}$, as a consequence of the loss of R [3,4], can be measured magnetically and is a direct function of the stability of the relevant bond.

Figure 1 shows the ESR spectra observed during reduction of *(1a)–(1d)*. The hyperfine structure (six equivalent lines, not quite resolved; cf. [3]) is due to the interaction of the unpaired electron of the Ti^{III} with the Al nucleus. The last two spectra clearly differ from the first two; they show greater distance between lines and therefore appear better resolved. The splitting constant a_{Al} is determined by the ligands on

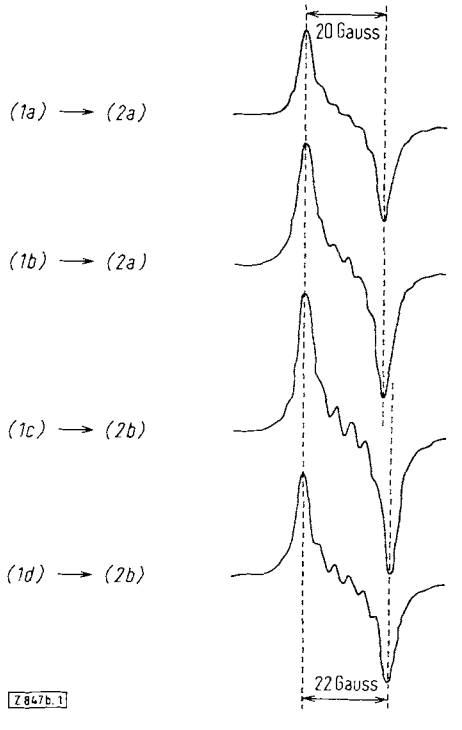


Fig. 1. The spectra observed on reduction *(1)*→*(2)*. $[Ti^{IV}]_0$ = 20×10^{-3} mol·l^{-1}; Al/Ti = 2; T = 20 °C. Solvent: toluene. The spectra were recorded after about 20% reduction.

the Al, as has been shown for similar complexes [4]. No noticeable exchange between R′ on the Al and R on the Ti occurs before relatively slow reduction reactions take place.

The methyl group is a weaker donor than the ethyl. This difference may cause great changes in transition metal complexes [6,7]. In *(2a)* $R' = C_2H_5$ is more effective than $R' = CH_3$ in *(2b)* against the delocalization of the unpaired electron of the Ti^{III}: consequently there is a lower spin density at the Al nucleus with $R' = C_2H_5$ (lines in the spectra are closer together). The donor ligands on the Al thus influence the electronic distribution in the whole complex; this influence is also to be expected for the Ti^{IV} species, and has in fact been detected. The higher the donor ability of R′ the higher the electron density on the Ti, and the higher the instability of the Ti–R bond. Such behavior is well illustrated by the reduction rate curves shown in Fig. 2, for the systems *(1a)* → *(2a)* (uppermost curve) and *(1c)* → *(2b)* (middle curve). This result confirms the hypothesis [5] that the stability of a carbon-metal bond can be varied at will by varying the ligands. The

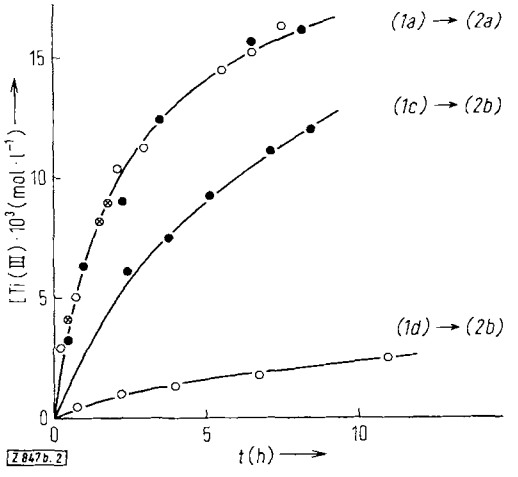


Fig. 2. Concentration of Ti(III) as a function of time.
• : from the magnetic susceptibility.
○ ⊗: from the ESR spectra (two series of experiments).

observed higher stability of the $Ti-CH_3$ bond in the system *(1a)* → *(2b)* (Fig. 2, lowest curve) can be interpreted according to the Mulliken model of the CH_3 group [8]. This model considers the methyl as a triply bonded $-C\equiv H_3$ species, and "H_3" as a heteroatom. The two bonding π-MO's perpendicular to the axis of $-C\equiv H_3$ (and the corresponding antibonding MO's) have the right symmetry to match with the d–π-Ti orbitals (d_{xz}, d_{yz}). This convenient configuration is obviously not available in the case of other alkyls.

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[1] Part 4 of: ESR Investigations of Transition Metal Complexes. – Part 3 *G. Henrici-Olivé* and *S. Olivé*, Angew. Chem. *80*, 796 (1968); Angew. Chem. internat. Edit. *7*, 821 (1968).

[2] See, *e.g.*, *J. Halpern*, Chem. Engng. News *44*, p. 68 (1966).

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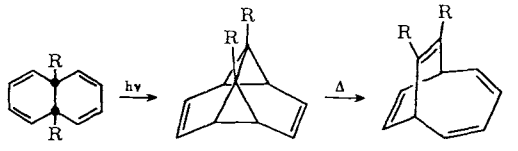
Degenerate Thermal Valence Isomerization of the Bicyclo[4.2.2]deca-2,4,7,9-tetraene Skeleton

By *W. Grimme, H. J. Riebel*, and *E. Vogel* [*]

The photochemical isomerization of *cis*-9,10-dihydro-9,10-naphthalenedicarboxylic anhydride *(1a)* to an anhydride with the bicyclo[4.2.2]deca-2,4,7,9-tetraene structure [1] disclosed a rearrangement that has since been demonstrated also for the parent hydrocarbon *(1b)* [2], the ester *(1c)* [3], and the compounds *(1d)* and *(1e)* [4]. The isolation and/or detection of the tetracyclo[4.4.0.0^{2,10}.0^{5,7}]deca-3,8-diene intermediates *(2d)* [4], *(2e)* [4], and *(2b)* [5] suggested that the rearrangement took the course shown in Scheme 1.



(1) *(2)* *(3)*

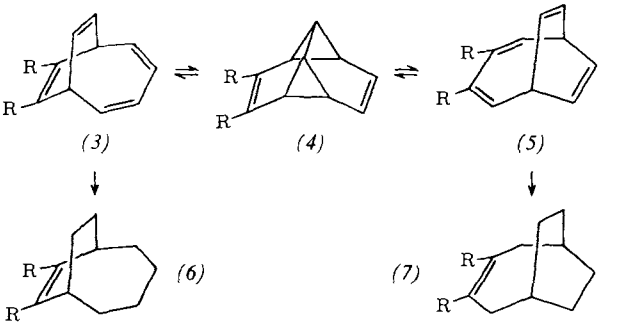
(a), R-R = -C(=O)-O-C(=O)- *(d)*, R-R = $-CH_2-O-CH_2-$

(b), R = H *(e)*, R-R = -C(=O)-N(CH_3)-C(=O)-

(c), R = CO_2CH_3 *(f)*, R = CO_2H

Scheme 1.

The bicyclo[4.2.2]deca-2,4,7,9-tetraene photoisomer obtained from *(1a)* should then have structure *(3a)*, in which the anhydride group is attached to one of the isolated double bonds. However, chemical degradation of the photoisomer showed that it has structure *(5a)* with the anhydride group attached to the diene system.



(3) *(4)* *(5)*

(a), R-R = -C(=O)-O-C(=O)- *(c)*, R = CO_2CH_3 *(f)*, R = CO_2H

Scheme 2.

On catalytic hydrogenation over platinum in glacial acetic acid the photoanhydride gives a hexahydro compound [m.p. 143 °C; UV spectrum, λ_{max} = 257 nm (ε = 5000) in dioxane], from which *cis*-1,4-cyclohexanediacetic acid [6] (identified by means of the dimethyl ester prepared with diazomethane) is formed on ozonolysis and subsequent oxidation by peracetic acid. Thus the hydrogenation product is *(7a)* and accordingly the photoanhydride itself must be *(5a)* [7].

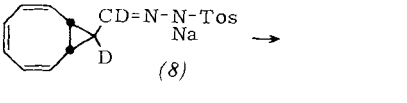
The mode of formation of the photoanhydride is clarified by the structure and properties of the acid obtained on its hydrolysis. The spectra of the acid and of its dimethyl ester [m.p. 49 °C; UV spectrum, λ_{max} = 214 nm (ε = 10300) with shoulders at 259 (2900), 267 (2900), and 277 nm (2200) in methanol; NMR spectrum, three separate groups of signals at τ = 3.82, 4.14, and 4.33 (each 2 H) and a multiplet at τ = 6.30 (8 H) superimposed by the signal of the methyl groups, in $CDCl_3$ at 100 MHz] can be interpreted only if the substituents in these compounds are attached to one of the isolated double bonds, according to *(3f)* and *(3c)*. This assignment was substantiated chemically as follows. Hydrogenation

of the acid *(3f)* affords a hexahydro acid to be considered as *(6f)*, from which an anhydride *(6a)* [m.p. 114 °C; UV spectrum, λ_{max} = 262 nm (ε = 4100) in dioxane], isomeric with *(7a)*, is formed by acetyl chloride. If *(6f)* is oxidatively degraded in the way used for *(7a)* (see above), then on treatment of the oxidation product with diazomethane an ester can be isolated that is shown to be dimethyl 1,4-cyclooctanedicarboxylate[8].

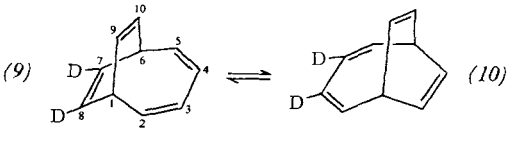
It is interesting that two different anhydrides can be obtained from *(3f)*, depending on the conditions of the dehydration. Heating at 180 °C or the action of acetyl chloride at room temperature regenerates *(5a)*, whereas treatment with ethoxyacetylene[10] at −30 °C yields an isomeric anhydride that is readily rearranged thermally to *(5a)*. The unstable anhydride must be *(3a)*, since its catalytic hydrogenation over platinum in methanol at −10 °C yields *(6a)*. Irradiation of *(1a)* at 0 °C leads, as expected, also to *(3a)*. The kinetics of the thermal isomerization of *(3a)* to *(5a)* in $CDCl_3$ was followed by NMR spectroscopy[11]; the reaction is of the first order, its rate constants being in accord with the Arrhenius equation: $k = 5.5 \cdot 10^{13} \cdot \exp.\ [(-24.5 \pm 2.7)\ \text{kcal}/RT]\ \text{sec}^{-1}$.

The reversible exchange of positions of functional groups observed on hydrolysis of *(5a)* or dehydration of *(3f)* is explained without difficulty by assuming a sequence of intramolecular diene and retro-diene reactions in which the tetracyclo[4.4.0.0^{2,10},0^{5,7}]deca-3,8-dienes *(4f)* or *(4a)* occurs as intermediate (Scheme 2).

The degenerate valence isomerization of the bicyclo[4.2.2]deca-2,4,7,9-tetraene skeleton established for the anhydride *(3a)* was detected by deuterium labeling for the parent compound *(3b)* also.



(8)



(10)

[9,10-D$_2$]-cis-Bicyclo[6.1.0]nona-2,4,6-triene-*anti*-9-carboxaldehyde tosylhydrazone *(8)* was obtained from ethyl [α-D]-diazoacetate and $LiAlD_4$ in analogy to the synthesis of the unlabeled compound[12]. It was converted into its sodium salt, which on thermolysis in diethylene glycol dimethyl ether (90 °C) gave dideuterated bicyclo[4.2.2]deca-2,4,7,9-tetraene (deuterium content determined by mass spectrometry = 97.5%). NMR spectroscopy was used to determine the position of the deuterium in the thermolysis product, which according to the mechanism assumed for decomposition of *(8)* should be *(9)*[13]. The product was purified by gas chromatography (column temperature 130 °C); its spectrum then consisted of four groups of signals, which can be assigned by spin decoupling as shown in Table 1.

Table 1. NMR signals of D$_2$-bicyclo[4.2.2]deca-2,4,7,9-tetraene (measured in CCl_4 against tetramethylsilane as internal standard at 100 MHz).

Proton	H^2, H^5	H^3, H^4	H^7—H^{10}	H^1, H^6
ν [τ]	3.94	4.33	4.53	6.88
Relative intensity:				
found	2.0	1.48	2.74	2.0
calculated [a]	2.0	1.36	2.72	2.0

[a] For a 2:1 mixture of *(9)* and *(10)* with 97.5% labeling.

The relative intensities of the signals show the presence of a 2:1 mixture of *(9)*[14] and *(10)*. The proportions of *(9)* and *(10)* correspond to the statistical weight of the two labeled isomers after equilibration as in Scheme 2. The formation of *(9)* on thermal decomposition of *(8)* and its degenerate valence isomerization under the conditions of the synthesis are thus proved.

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[7] *J. J. Bloomfield*, Monsanto Company, St. Louis, has meanwhile also recognized the photoanhydride as *(5a)* (personal communication).

[8] The assignment of structure is based on comparison of the IR spectrum with that of dimethyl 1,4-cyclooctanedicarboxylate (presumably a mixture of *cis-trans*-isomers) obtained by catalytic hydrogenation of dimethyl 1,3,5-cyclooctatriene-1,6-dicarboxylate [9].

[9] *E. Vogel, O. Roos*, and *K.-H. Disch*, Liebigs Ann. Chem. *653*, 55 (1962).

[10] *J. F. Arens* and *T. Doornbos*, Recueil Trav. chim. Pays-Bas *74*, 79 (1955).

[11] The intermediate *(4a)* was not observed during the isomerization; however, even at −10 °C *(3a)* seems to be in equilibrium with a small amount of *(2a)*.

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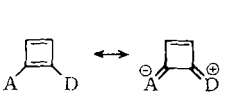
[13] *M. Jones, Jr.* and *S. D. Reich*, J. Amer. chem. Soc. *89*, 3935 (1967).

[14] The presence of a D$_2$-bicyclo[4.2.2]deca-2,4,7,9-tetraene in which one deuterium atom is attached at each of the isolated double bonds is excluded because the signal for H^7—H^{10} shows no H—D coupling.

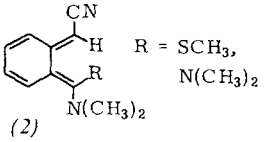
A Stable Cyclobutadiene

By *R. Gompper* and *G. Seybold*[*]

Cyclobutadiene[1] and its alkyl, aryl, and halogen derivatives have hitherto been detected only indirectly. *Roberts*[2] predicted a greater stability for 1-(*p*-dimethylanilino-2-(*p*-nitrophenyl)cyclobutadiene by reason of a "push-pull" effect of the substituents D (electron donor) and A (electron acceptor) in accord with *(1)*. An HMO calculation[3] for



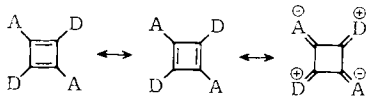
(1)



(2)

2-amino-1,3-cyclobutadiene-1-carbonitrile supports this view. How strong the stabilizing action of D and A actually is has been shown for the six-membered ring by the synthesis of *o*-quinodimethane *(2)*[4] which is stable at room temperature. All attempts to prepare cyclobutadienes *(1)* have, however, hitherto failed[5]. The stabilizing effect of D and A must be stronger in the cyclobutadienes *(3)* than in *(1)*.

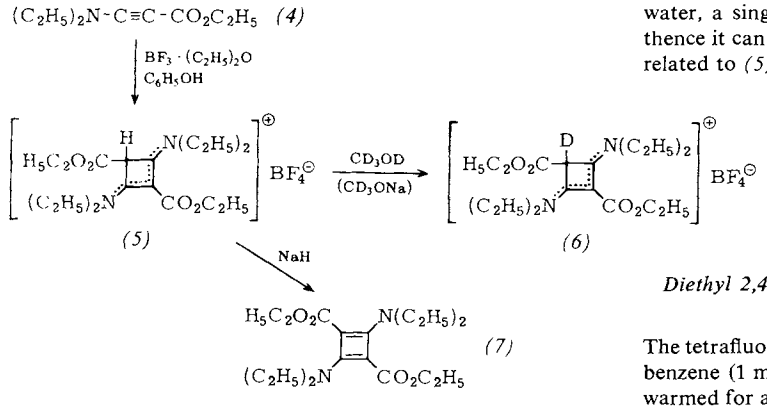
As *Viehe*[6] showed (see also ref. 7), ynamines can be "dimerized" to cyclobutenecyanines. – If ethyl (diethylamino)-propiolate *(4)* (prepared from ethyl 2-bromo-3-(diethylamino)acrylate by means of sodamide in liquid ammonia[8])



(3)

in dichloromethane is treated slowly, under nitrogen, with a solution of boron trifluoride-ether and phenol in dichloromethane (as described experimentally in ref. 7), subsequent evaporation of the solvent, chromatography of the residual yellow oil (silica gel/chloroform), and two recrystallizations of the resulting crystals from ethanol/ether yield colorless needles of m.p. 64–65 °C (yield, *ca.* 35%). In view of the data for "dimerization" of ynamines [6,7] this product must be the cyclobutenecyanine salt *(5)*.

Elemental analysis, the IR spectrum (1725, 1685, 1600, 1450, and 1080 cm^{-1}), the UV spectrum (λ_{max} = 286.5 nm, log ε = 4.51, in $CHCl_3$), the 60-MHz ^1H–NMR spectrum [in tetrahydrofuran: τ = 4.9 (1H, S); τ = 5.7 (4H; OCH_2; split quadruplet); τ = 5.93 (4H; NCH_2; Q); τ = 6.35 (4H; NCH_2; Q); τ = 8.69 (18H, split triplet)], the ^{19}F–NMR spectrum (in $CDCl_3$: singlet at −13.7 ppm relative to external C_6F_6; cf. the value for $NaBF_4$ [9]), and the ^{11}B–NMR spectrum (in $CHCl_3$: singlet at 0.09 ppm relative to external BF_3-ether) are in agreement with structure *(5)* and with the data for related compounds [6,7]. The mass spectrum contains, besides the peak at *m/e* = 339 (75%) for the cation of *(5)*, the peak



at 338 for the molecule ion of *(7)* as the most intense feature. If a catalytic amount of CD_3ONa is added to a solution of *(5)* in CD_3OD at room temperature the singlet for the tertiary proton at τ = 4.9 disappears within less than 2.5 min. Since the remaining signals of the NMR spectrum are not changed, there can be no change in the molecular structure of *(5)* except for an H–D exchange by which *(6)* is formed [*(6)* has not been isolated as yet]. The simplest explanation for the formation of *(6)* from *(5)* is intermediate occurrence of *(7)* which is rapidly deuterated to give *(6)*.

Solutions of *(5)* in tetrahydrofuran (THF) or D_8–THF or benzene assume a yellow color on addition of sodium hydride, and hydrogen is evolved. If the solutions are filtered from the excess of NaH the yellow color is retained for some time at room temperature, so that an NMR spectroscopic study can be made. The spectra are then only explicable on the basis that the symmetrically substituted cyclobutadiene *(7)* is present. In D_8–THF: τ = 6.0, Q; τ = 8.7, T (the high-resolution spectrum shows that the signals of the quadruplet are more strongly and those of the triplet less split); intensity ratio 2:3. In C_6D_6: τ = 5.84 (OCH_2); τ = 6.08 (NCH_2; M); τ = 8.93 (T); intensity ratio 2:3. The two quadruplets of the OCH_2 and NCH_2 protons of *(7)* overlap, so that a six-line spectrum arises (intensity ratios 1:3:5:7:6:2).

If trifluoroacetic acid is added to a solution of *(7)* in D_8–THF the yellow color disappears almost completely, and the NMR spectrum then shows in the CH_2 and CH_3 region once more the splitting picture of the spectrum of *(5)*. Only the singlet due to the tertiary proton is shifted, from = 4.9 to 5.2. This shift is ascribed to the difference in anion ($CF_3CO_2^-$) and the change of solvent due to the excess of trifluoroacetic acid; this shift (to τ = 5.05) occurs also in the NMR spectrum of *(5)* in D_8–THF/CF_3CO_2H.

If solutions of *(7)* in anhydrous benzene or THF are evaporated at 0 °C in a rotary evaporator, a yellow oil remains that crystallizes either spontaneously or when rubbed. It affords yellow leaflets, which rapidly liquefy in the air. The IR spectrum (strongest bands at 1610, 1560, and 1140 cm^{-1}) are distinctly different from those of the starting product *(5)*. UV spectrum: λ_{max} = 309 nm in benzene, 295 nm in THF. The most intense peak in the mass spectrum [10] is at *m/e* = 338 [≡ molecule-ion of *(7)*]; it is accompanied by an appreciably weaker peak at *m/e* 356, which is ascribed to the molecule ion of a "hydrate" of *(7)*. The high-resolution mass spectrum [10] gives for the peak at *m/e* = 338 an analytical composition $C_{18}H_{30}N_2O_4$, confirming the presence of *(7)*. For the peak at *m/e* = 356 the result is $C_{18}H_{32}N_2O_5$ [≡ *(7)*·H_2O].

Decomposition (thermal or under electron impact) of the "hydrate" to the cyclobutadiene *(7)*, which seems a possibility and could have falsely indicated the occurrence of *(7)*, is excluded by the mass spectrum of the pure "hydrate" (*m/e* = 356, 311, 284, 283, 256, 238, 210, 184, 100, 72); the fragmentation patterns of the two compounds differ fundamentally; in particular, the peak at *m/e* = 338 is missing from the mass spectrum of the "hydrate".

If the solution of *(7)* in D_6-acetone is treated with a little water, a singlet appears in the NMR spectrum at τ = 4.85; thence it can be concluded that the "hydrate" is a compound related to *(5)*.

Diethyl 2,4-bis(diethylamino)-1,3-cyclobutadiene-1,3-dicarboxylate (7):

The tetrafluoroborate *(5)* (100 mg) is suspended in anhydrous benzene (1 ml), NaH (100 mg) is added, and the mixture is warmed for a short time at *ca.* 40 °C, then cooled and filtered through a small fritted filter (G 3) into a Schlenk tube. The yellow filtrate is frozen and the benzene removed by means of an oil pump at 0 °C (duration *ca.* 2 hr). Pale yellow crystals from the residue, m.p. 50–52 °C. According to the mass spectrum [10] [*m/e* = 338 (100%), 309 (65%), 293 (30%), 249 (40%), 72 (40%), 29 (40%)] the "hydrate" content of this product is < 0.3%. The ^1H–NMR spectrum of this preparation in D_6-acetone [τ = 6.0 (NCH_2); τ = 5.7 (OCH_2)] is in accord with structure *(7)*. – All operations were carried out under very pure nitrogen.

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[10] We thank Dr. *A. Prox* for analysis of the mass spectrum of compound *(7)*.

Tris(*o*-arylenedioxo)- and Bis(*o*-arylenedioxo)-organosilicic Acids Containing Hexacoordinated and Pentacoordinated Silicon

By *H. Meyer, G. Nagorsen*, and *A. Weiss*[*]

The reaction of molten pyrocatechol with halogenosilanes under nitrogen leads to the formation of complex *o*-phenylenedioxosilicic acids containing hexacoordinated and pentacoordinated silicon:

$$3\ C_6H_4(OH)_2 + SiCl_4 \rightarrow \underset{(1)}{H_2[Si(O_2C_6H_4)_3]} + 4\ HCl$$

$$2\ C_6H_4(OH)_2 + RSiCl_3 \rightarrow H[SiR(O_2C_6H_4)_2] + 3\ HCl$$

(2a) $R = CH_3$
(2b) $R = C_6H_5$

Other *o*-dihydroxyarenes, such as 2,3-dihydroxynaphthalene, can react similarly.

The structure of tris(*o*-phenylenedioxo)silicic acid *(1)* is found from the molecular weight (370; cryoscopically in camphor) and the ^1H–NMR spectrum, which contains 2 singlets at $\tau = 3.08$ and 4.14 (in $DCCl_3$; TMS as external standard; the acid protons appear at $\tau = 4.14$), and so indicates that the three pyrocatechol residues are equivalent. *(1)* differs characteristically in its ^1H–NMR spectrum from the product first obtained by *Rosenheim et al.*[1] from $SiCl_4$ and pyrocatechol in ether; the latter product gives three signals at $\tau = 2.85$, 3.14, and 7.68 (in $DCCl_3$; TMS as external standard). *(1)* is dibasic, appears to be trimeric in benzene as a result of hydrogen bonding, and reacts with 2 moles of alkylamine to form a salt.

The ^1H–NMR spectra of bis(*o*-phenylenedioxo)methyl- and bis(*o*-phenylenedioxo)phenylsilicic acids, (2a) and (2b), show that the two pyrocatechol residues are again equivalent in these cases. These compounds also form salts with alkylamines[2]. Powder diagrams show that *(1)* and *(2)*, unlike the alkylammonium salts, are amorphous.

Procedure:

Preparation of *(1)*:

6.6 g (60 mmole) of pyrocatechol are melted under dry nitrogen. 3.4 g (20 mmole) of silicon tetrachloride are added dropwise to the melt with vigorous stirring at a bath temperature of 140 °C and over a period of 30 minutes. After a further 30 minutes, unreacted pyrocatechol and other volatile components are removed at ≈ 120 °C/10^{-2} torr. After cooling, the residue is dissolved in the minimum quantity of boiling absolute benzene and *(1)* is precipitated with absolute petroleum ether. Removal of the remaining solvent at 100 °C/10^{-2} torr leaves a red, vitreous mass that is sensitive to moisture. Yield ≈ 4 g (57%).

Preparation of *(2)*:

11 g (0.1 mole) of pyrocatechol are reacted as described above with 10.6 g (0.05 mole) of freshly distilled phenyltrichloro-silane or 7.74 g (0.05 mole) of freshly distilled methyltrichlorosilane. Yield without reprecipitation: 13 g (82%) of *(2a)* or 8.8 g (68%) of *(2b)*.

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Detection of Open-Chain Intermediates in the Formation of β-Lactams from Ketenes and Azomethines

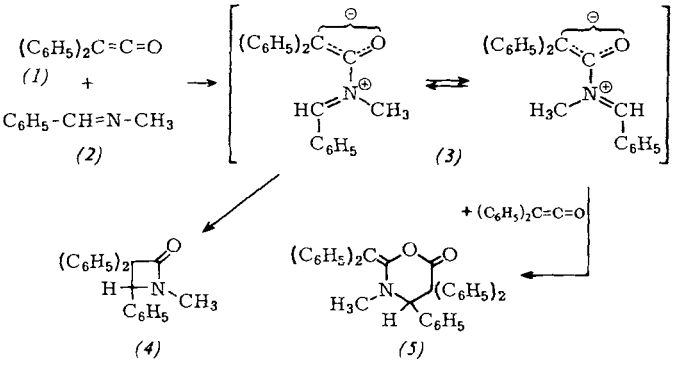
By *R. Huisgen, B. A. Davis*, and *M. Morikawa*[*]

β-Lactams were first obtained by *Staudinger* on cycloaddition of ketenes to *N*-aralkylidene-arylamines[1,2]. Other types of azomethines as well as heteroaromatic bases preferentially formed adducts with two equivalents of dimethylketene[3], which have recently been found to be hydrogenated 2-methylene-1,3-oxazin-6-ones[4,5].

We observed that in the system diphenylketene *(1)* + benzylidenemethylamine *(2)*, the 1:1 adduct *(4)* or the 2:1 adduct *(5)* is preferentially formed according to the reaction conditions. We therefore conclude that a common intermediate *(3)* is involved.

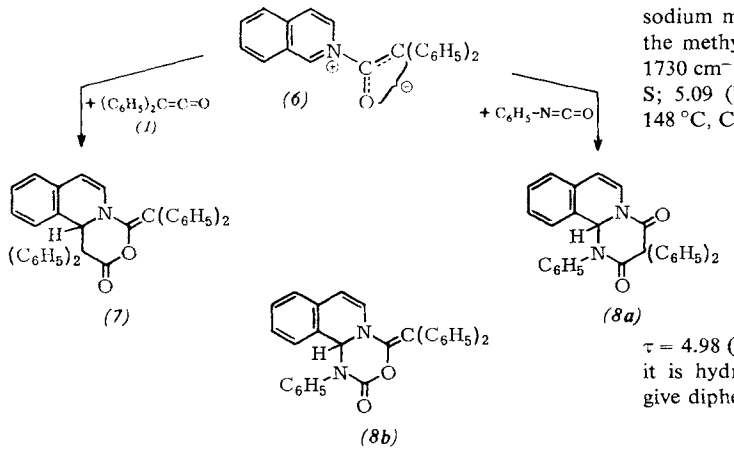
When 10.5 mmole of *(1)* in 15 ml of acetonitrile were added dropwise to a solution of 135 mmole of *(2)* in 85 ml of acetonitrile at room temperature, the rapid disappearance of the yellow ketene color showed that the ketene was quickly consumed. After removal of the excess of *(2)* by high-vacuum distillation, the NMR analysis indicated 82% of the β-lactam *(4)* together with 6% of the 2:1 adduct *(5)*.

On the other hand, when 6.8 mmole of *(2)* in 35 ml of acetonitrile were added dropwise to 55 mmole of *(1)* in 50 ml of acetonitrile, the yields were 81% of the 1,3-oxazinone derivative *(5)* and 19% of *(4)*[6]. When these two procedures were carried out in benzene with the same proportions, 71% of *(4)* + 17% of *(5)* were obtained in the first case and 95% of *(5)* in the second.



The β-lactam *(4)* did not form the 2:1 adduct *(5)* with excess diphenylketene *(1)* even after 6 hours at 140 °C. Thus the above reactions evidently involved an open-chain intermediate, presumably the 1,4-dipole *(3)*[7], which either closes the lactam ring or undergoes cycloaddition with a second molecule of diphenylketene to form *(5)*.

(1) and isoquinoline in ether at 20 °C gave 89% of a 2:1 adduct, which we assume to have the formula *(7)*, by analogy with the dimethylketene-quinoline adduct[5]. On the other hand, when isoquinoline and excess phenyl isocyanate were dissolved in benzene (the components do not react with each other in the cold) and diphenylketene slowly added, 30% of

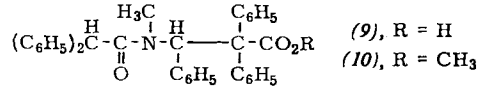


(7) (8a) (8b)

the 1:1:1 adduct *(8)* were isolated[8][**]. Thus the second ketene molecule can be replaced in its role as the dipola rophile and the intermediate 1,4-dipole *(6)* is intercepted by phenyl isocyanate.

Gomes and *Joullié*[9] recently reacted benzylideneaniline with ketene in SO_2 and obtained a thiazolidone 1,1-dioxide as a five-membered cycloadduct. *Kagan* and *Luche*[10] stopped the reaction of *(1)* with benzylideneaniline by the addition of methanol, and isolated 10% of an open-chain methanol adduct of the 1,4-dipole.

Properties and proof of structures of new compounds[11]: 1-Methyl-3,3,4-triphenyl-2-azetidinone *(4)*, m.p. = 118 °C, C=O 1752 cm^{-1}; NMR ($CDCl_3$, 60 MHz): τ = 7.17 (CH_3), S; 4.73 (*tert.*H), S. 3-Methyl-4,5,5-triphenyl-2-diphenylmethyleneperhydro-1,3-oxazin-6-one *(5)*: m.p. = 208–209 °C (dec.), C=O and C=C 1757 and 1630 cm^{-1}; NMR ($CDCl_3$): τ = 7.67 (CH_3), S; 5.08 (*tert.*H), S. When shortly boiled in 80% dioxane, *(5)* was converted into *(9)*: m.p. = 201–203 °C, amide-I 1616, acid C=O 1727 cm^{-1}. *(9)* is insoluble in aqueous sodium hydroxide solution, but can be titrated in dimethyl sulfoxide with NaOH.



(9), R = H
(10), R = CH_3

NMR (CD_3SOCD_3): τ = 7.31 (CH_3), S. The singlet at τ = 4.82 corresponds to the benzhydryl proton, since this signal is absent in the case of the product from *(5)* + D_2O; the signal of the second *tert.*H lies below the phenyl signals. *(5)* and sodium methoxide/methanol or *(9)* and diazomethane gave the methyl ester *(10)*: m.p. = 142–143 °C, C=O 1650 and 1730 cm^{-1}; NMR ($CDCl_3$) τ = 7.21 (NCH_3), S; 6.43 (OCH_3), S; 5.09 (benzhydryl H), S. *(7)*: 93% yield, m.p. = 146 to 148 °C, C=O and C=C 1635 and 1758 cm^{-1}; NMR ($CDCl_3$): τ = 4.98 (*tert.*H), S. *(7)* does not react with aqueous dioxane; it is hydrolyzed by dioxane/aqueous hydrochloric acid to give diphenylacetic acid and isoquinoline.

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[**] It is not yet certain whether this is *(8a)* or *(8b)*. No decision can be reached from the IR and NMR spectra.

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[11] Correct elementary analyses and molecular weight determinations have been carried out for all the new compounds.

CONFERENCE REPORTS

Preparation and Properties of the Diastereoisomeric 1,3,5-Triglycidyl-*s*-triazinetriones

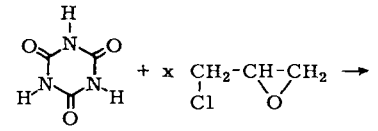
By *M. Budnowski*[*]

Interaction of epichlorohydrin *(2)* and cyanuric acid *(1)* above 60 °C leads to the *N*-alkyl compounds *(3)* in a thermodynamically controlled reaction. A relatively small excess of *(2)* favors formation of the addition product *(3c)*, whereas a large excess converts *(3c)* to the desired *(3f)*. Thus epichlorohydrin functions as both alkylating agent and base. The intermediates *(3d)* and *(3e)* were detected by thin-layer chromatography.

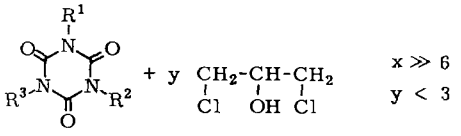
Fractional crystallization of the product *(3f)* gives two stereoisomers α-*(3f)* and β-*(3f)*, which were considered, on account of the chirality of the glycidyl group, to be racemates with the configurations (R,R,R/S,S,S) or (R,R,S/S,S,R) [m.p. 105 °C(α), 156 °C(β)].

In order to assign configurations to α-*(3f)* and β-*(3f)* and to the products therefrom suitable additive and degradative reactions were performed.

Among reagents of the type H^+A^- used for addition, *O*-Aryl, *S*-Aryl, *S*-Alkyl, and NR_2 act as anions. Treatment with aequeous alkali leads to partial or total hydrolysis. The adduct *(4)* is formed in almost quantitative yield on addition of 3 moles of HA to 1 mole of *(3f)*. Presence of a base leads, again almost quantitatively, to the oxazolidone *(5)*, which is also accessible by heating *(4)* with bases. The isomers α-*(3f)* and β-*(3f)* yield different adducts *(4)* but the same oxazolidone *(5)*.



(1) (2)



(3)

(a), $R^1 = R^2 = H$, $R^3 = CH_2\text{-}CHOH\text{-}CH_2Cl$

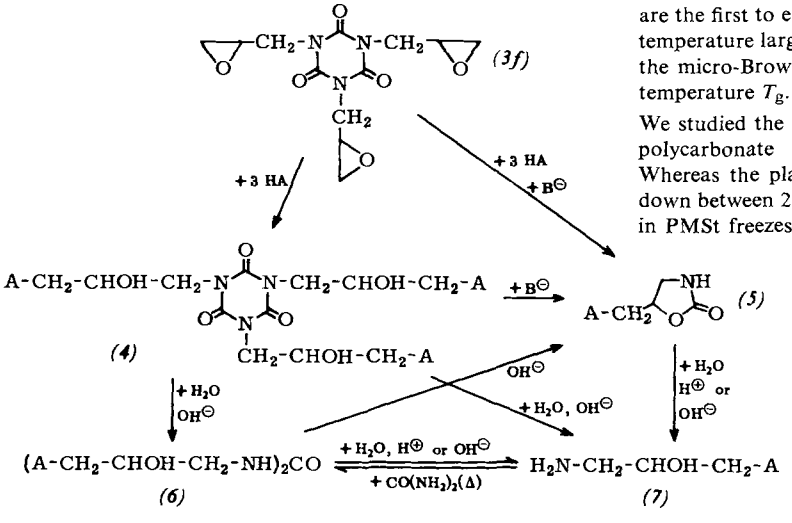
(b), $R^1 = H$, $R^2 = R^3 = CH_2\text{-}CHOH\text{-}CH_2Cl$

(c), $R^1 = R^2 = R^3 = CH_2\text{-}CHOH\text{-}CH_2Cl$

(d), $R^1 = R^2 = CH_2\text{-}CHOH\text{-}CH_2Cl$, $R^3 = CH_2$-(epoxide)

(e), $R^1 = R^2 = CH_2$-(epoxide), $R^3 = CH_2\text{-}CHOH\text{-}CH_2Cl$

(f), $R^1 = R^2 = R^3 = CH_2$-(epoxide)



A = *O*-Aryl, *S*-Aryl, *S*-Alkyl, NR_2

Partial hydrolysis degrades the products *(4)* to the urea derivatives *(6)*, α-*(4)* giving a mixture of two isomers *(6)*, but β-*(4)* giving only one urea derivative *(6)*, namely that formed in lower yield from α-*(4)*.

Total hydrolysis of *(4)*, *(5)*, and *(6)* leads to 1-amino-2-propanol derivatives *(7)*, independently of the isomer *(4)* or *(6)* used. Acylation of *(7)* with urea regenerates both isomers *(6)* in approximately equal yield.

These results identify α-*(3f)* and β-*(3f)* as racemates with the configurations (R,R,S/S,S,R) and (R,R,R/S,S,S) at the asymmetric centers. The ring-opening reactions, which occur with complete retention, require the same assignments of configuration for the adducts *(4)*. For α-*(4)* the three possibilities of ring fission lead to two moles of (*R,S*)-*meso* and one mole of (R,S/S,S)-racemic urea derivative *(6)*. β-*(4)* can give only one racemate for *(6)*. Synthesis of *(6)* from racemic *(7)* and urea yields the *meso*-*(4)* and the *rac*-*(4)* in about equal amounts.

Since the product distribution found for the diastereoisomers approximates to that calculated statistically, intramolecular interaction of the chiral groups is probably small. By variation of the anion in the reactant HA, this method can be modified so as to open new possibilities for preparation of derivatives of the above classes of compound which shall have predetermined configurations.

Lecture at Hamburg (Germany) on July 12, 1968 [VB 165 IE]
German version: Angew. Chem. *80*, 851 (1968)

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Hindered Rotation in Macromolecular Solids, Investigated by Nuclear Magnetic Resonance

By *R. Kosfeld*[*]

Nuclear magnetic resonance and nuclear magnetic relaxation are used as well as the mechanical-dynamic and dielectric methods for the study of molecular movements and their relation with the structure of amorphous and semicrystalline macromolecular solids.

The evaluation of investigations of this type are based on the fact that thermal molecular motion always occurs above absolute zero. These transpositions are strongly temperature-dependent. Owing to the complicated structure of high polymers, different types of movement can take place simultaneously or (depending on the temperature) successively. Thus at low temperatures, smaller groups such as the CH_3 group are the first to exhibit recognizable mobility. With increasing temperature larger parts of the molecule become mobile, and the micro-Brownian movement begins only above the glass temperature T_g.

We studied the freezing-in of the rotation of CH_3 groups in polycarbonate (PC) and poly-α-methylstyrene (PMSt). Whereas the planar rotation of the CH_3 groups in PC die down between 216 and 64 °K, the rotation of the CH_3 groups in PMSt freezes at temperatures between 320 and 80 °K.

If a classical jump process is assumed for the rotation of the CH_3 groups, the activation energies for rotation as found from NMR measurements are 1.2 kcal·mole^{-1} for PC and 1.5 kcal·mole^{-1} for PMSt. The limiting frequencies for this process would then be in the MHz range, *i.e.* they would be too low by a factor of 10^6.

Another model discussed instead of classical movement for the CH_3 groups is a quantum-mechanical rotator with a three-fold axis of symmetry, which can overcome the potential opposing rotation by the tunnel effect. This model gives a low-temperature potential barrier of 5.4–5.5 kcal·mole^{-1} for both polymers. At higher temperatures, the values of the correlation frequencies ν_c, which are equal to the tunnel frequencies for the quantum-mechanical rotator, differ considerably from those expected from the quantum-mechanical model. This is understandable, in view of the fact that the neighboring groups, which are responsible for the hindrance of the CH_3 rotation, also become more mobile with rising temperature. As the temperature rises, therefore, the rotation of the methyl groups approximate more closely to a rotation diffusion capable of being described in the classical theory. This result shows that the movement behavior of the methyl groups on transition from the frozen-in to the "freely mobile" state cannot be described merely by the model of a quantum-mechanical rotator, and points to a correlation spectrum.

Correlation functions are very difficult to determine. The amount N_{ME} of frozen CH_3 groups in relation to the total number N_M was determined as a function of the temperature by separation of the nuclear magnetic absorption curve. Hence it is possible to calculate the number of methyl groups that pass from the frozen state into rotational motion as a result of a temperature increase δT for PC and PMSt.

It is thus possible, from the nuclear magnetic resonance experiment, to find the number of CH_3 groups that are forced by a temperature change δT from a rotational movement below ν_c to a rotational movement above ν_c. This number is related to the number of CH_3 groups found in a frequency range δ_c around a frequency ν_c that is fixed by the temperature.

Lecture at Hamburg (Germany) on June 14, 1968 [VB 166 IE]
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Electrical Excitation of the Axon Membrane as Co-operative Ion Exchange

By *G. Adam* [*]

The widely accepted theory proposed by *Hodgkin* and *Huxley* [1] for nerve stimulation fails to explain the mechanism of regulation of the state of the axon membrane by the membrane potential or the cation activities.

If, on the other hand, the axon membrane is regarded as a two-dimensional cation exchanger interacting with the internal and external electrolyte reservoirs, a physico-chemical mechanism can be advanced for the control of the electrical state of the membrane [2]. In this mechanism, calcium ions are bound in the lattice sites of the cation exchanger in the resting state. On depolarization or on lowering of the calcium activity in the outside medium, the resting state becomes thermodynamically unstable, and calcium is co-operatively displaced from the lattice sites by monovalent cations. The movements of the ions during this cation exchange give rise to an ion current flowing inward, as observed *e.g.* in the voltage-clamp experiment.

This co-operative cation exchange is described as a two-dimensional phase transition. Its kinetics can be theoretically described for small depolarizations on the basis of the concept of nucleation and nuclear growth.

The resulting kinetic theory has been applied to the measurements of *Cole* and *Moore* [3] of the ion current in the voltage clamp experiment. Within the range of validity of the theory, *i.e.* for small depolarizations, the experimentally determined dependence of the ion current on time and on the membrane potential, particularly the threshold behavior that characterizes axon stimulation, is quantitatively described by the equations derived.

Three parameters must be matched. Two of these have simple molecular meanings, and have the following numerical values: $a_o = 21 \times 21$ Å^2 = area per binding site for the co-operatively exchangeable cations; $w = 5.1$ kcal/mole = interaction energy between two binding sites in the two different bonding states.

It is probable, from the order of magnitude of these parameters, that the structural units responsible for the axon stimulation are membrane-bound proteins, as was suggested by *Tasaki et al.* [4].

Lecture at Konstanz (Germany) on June 27, 1968 [VB 167 IE]
German version: Angew. Chem. *80*, 806 (1968)

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[1] *H. L. Hodgkin* and *A. F. Huxley*, J. Physiology *117*, 500 (1952).
[2] *G. Adam*, Z. Naturforsch. *23b*, 181 (1968).
[3] *K. S. Cole* and *J. W. Moore*, J. gen. Physiol. *44*, 123 (1960).
[4] *I. Tasaki*, *I. Singer*, and *K. Takenaka*, J. gen. Physiol. *48*, 1095 (1965).

High-Pressure Properties and Structure of Liquids

By *E. Kuss* [*]

In contrast to solids, compressed gases and liquids can be studied at pressures up to 10 kbar over a wide range of densities and hence valuable information about the intermolecular forces and the structure of liquids, which is still largely unknown, can be obtained from the physical properties. Properties of interest in this connection are the pVT data, the equations of state, the thermal conductivity, the viscosity, the spin-lattice interaction of the nuclear magnetic resonance, and the electric birefringence.

The theoretical calculation of the second, third fourth, and higher virial coefficients from fundamental potential functions leads to very complicated mathematical expressions and in some cases to very different constants for the potential functions. Owing to the mathematical difficulties, the potential $U(r)$ is always taken to be spherically symmetrical, *i.e.* the effect of the shape of the molecule is not yet theoretically expressible.

The effect of the molecular structure on the pVT data of liquids has been studied experimentally up to 2000 atm, and in some cases even up to 5000 atm. A piezometric method and a buoyancy method have been developed for this purpose. Since no suitable material was available for use as a float, the test substance was introduced into a hollow body and the buoyancy was measured in mercury. Measurements that have not yet been completed show that some substances whose viscosities are extremely pressure-dependent have a very low compressibility (*e.g.* 2,4-bis-(1-phenylethyl)methoxybenzene).

The viscosity measurements were carried out in a falling sphere viscometer (accuracy $\pm 2\%$) and a capillary viscometer (accuracy $\pm 1\%$), both of which are suitable for fully automatic operation. The effects of chain length, "degree of branching", and other parameters of the molecular structure on the viscosity-pressure behavior were determined for numerous substances. On the basis of the relationships found, it was possible to synthesize substances whose viscosities at 2000 atm are up to 8×10^6 times as great as at atmospheric pressure [1]. According to *Benedek* and *Purcell* [2], a comparison of measurements of the pressure-dependence of the viscosity and the nuclear magnetic relaxation leads to the conclusion that the translational degrees of freedom are more strongly reduced than the rotational degrees of freedom by rising pressure.

The very small measured effect in the electric birefringence requires the complete elimination of parasite birefringence of the high pressure windows in high-pressure measurements. Benzene showed a marked anomaly in the pressure dependence of the Kerr constant [3], which suggests a modification of the π-electron cloud or an unusual change in the liquid structure under pressure.

Lecture at Berlin (Germany) on July 5, 1968 [VB 170 IE]
German version: Angew. Chem. *80*, 806 (1968)

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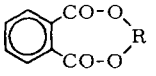
[1] *E. Kuss*, Chemie-Ing.-Techn. *37*, 465 (1965); Angew. Chem. internat. Edit. *4*, 944 (1965).
[2] *G. B. Benedek* and *E. M. Purcell*, J. chem. Physics *22*, 2003 (1954).
[3] *E. Kuss* and *H. H. Heydemann*, Z. physik. Chem. N.F. *43*, 97 (1964).

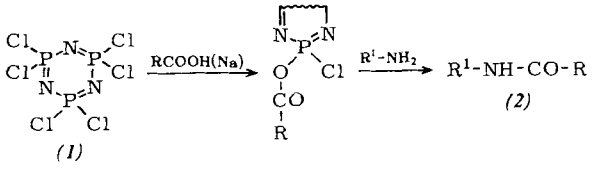
Synthesis of macrocyclic *o*-phthalate esters from the corresponding polyesters is reported by *W. A. Ehrhart*. Esterification of phthalic anhydride with glycols in the presence of catalysts such as tetrabutyl orthotitanate yields polyesters, from which the corresponding macrocyclic *o*-phthalic esters are obtained



(1), R = $-(CH_2)_2-O-(CH_2)_2-$
(2), R = $-(CH_2)_2-O-(CH_2)_2-O-(CH_2)_2-$
(3), R = $-(CH_2)_5-$
(4), R = $-(CH_2)_6-$

by distillation at 220–260 °C/1–4 torr. The polyesters of diethylene and triethylene glycol, as well as those of 1,5-pentanediol and 1,6-hexanediol, yield the macrocyclic compounds *(1)–(4)* in almost quantitative yields. / J. org. Chemistry *33*, 2930 (1968) / –Ma. [Rd 894b IE]

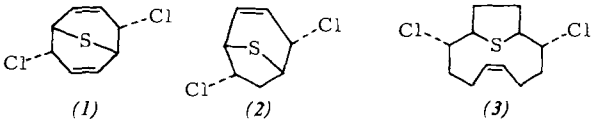
Phosphorus nitride-chloride *(1)* as an activator of carboxylic acids was investigated by *L. Caglioti, M. Poloni* and *G. Rosini*. *(1)* reacts with carboxylic acid salts, and on subsequent treatment with an excess of primary or secondary amine forms the amide *(2)* in yields of 60–83%. The reaction proceeds in benzene, cyclohexane, THF, THF/water, ethyl acetate, *etc.* Amine salts can be used in place of the alkali metal salts. *(1)* is used in amounts of 0.35–1 equivalents, and the amine in 6- to 10-fold excess. Hydrazides are obtainable in the same manner. The reaction takes about 20 min and presumably proceeds as follows:



(1) *(2)*

/ J. org. Chemistry *33*, 2979 (1968) / –Ma. [Rd 895 IE]

The reaction of SCl_2 with cyclic polyolefins was investigated by *F. Lautenschlaeger*. SCl_2 adds with the formation of new S-containing ring systems. 31, 35, and 69% yields of the bicyclic sulfides *(1)*, *(2)*, and *(3)*, m.p. 101–102 °C, 47.5 to

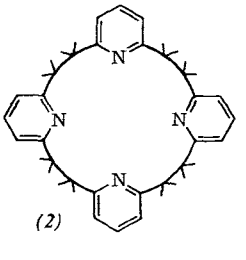


(1) *(2)* *(3)*

49 °C, and 139.5–141.5 °C respectively, were obtained from cyclooctatetraene, cycloheptatriene, and *trans,trans,cis*-1,5,9-cyclodecatriene, in CH_2Cl_2 at –10 to –20 °C. / J. org. Chemistry *33*, 2627 (1968) / –Ma. [Rd 896 IE]

Macrocyclic compounds with 2,6-bridging pyridine rings were synthesized by *W. Jenny* and *H. Holzrichter* by cyclization of 1,2-bis(6-chloromethyl-2-pyridyl)ethane *(1)* with Na and tetraphenylethylene in THF. Tetrameric [2.2.2.2]-(2,6)pyridinophane *(2)*, m.p. 205–206 °C and hexameric [2.2.2.2.2.2]-(2,6)pyridinophane, m.p. 160–161 °C, were isolated chromatographically in 4.2 and 2.1% yields, respectively. The compounds are colorless. The octamer was detected spectroscopically (< 1%). / Experientia *22*, 306 (1968) / –Ma. [Rd 897 IE]

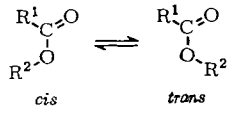
(1)



(2)

The reactions of methyl radicals with ethanol were examined mass-spectroscopically by *P. Gray* and *A. A. Herod*. The methyl radicals were generated by photolysis of acetone ($\lambda > 3000$ Å) and D_6-acetone at 130–250 °C. By comparing the reactions of CH_3CH_2OH, CH_3CD_2OH, and CH_3CH_2OD it was established that at 150 °C 75% of the hydrogen derived from the ethanol originates from the methylene group, 20% from the hydroxyl, and 5% from the methyl group. As the hydroxyl H undergoes an exchange reaction with acetone, D_6-acetone must be used for investigating the reaction of CH_3CH_2OD, as a source of the radicals. / Trans. Faraday Soc. *64*, 1568 (1968) / –Hz. [Rd 898 IE]

The ultrasonic absorption of alkyl esters in the 1–30 MHz region was studied by *J. Bailey* and *A. M. North*. The results were used to obtain an indication of the equilibrium between the isomers



cis *trans*

The activation energy is independent of R^1 and R^2 in the conversion of *trans* into *cis*, 8.8 ± 1.4 kcal/mole; in contrast, the energy content of the *cis*-form depends on the sum of the C-atoms in R^1 and R^2. It was concluded from this that the energy difference between the two isomers depends essentially on the steric interaction of the alkyl groups in the *cis*-form. The higher dipole moment of the *cis*-form or a stabilization of the *trans*-form by hydrogen bridges, on the other hand, are not suitable for the interpretation of the experimental results. / Trans. Faraday Soc. *64*, 1499 (1968) / –Hz. [Rd 899 IE]

Cleavage surfaces of silicon single crystals prepared under a high vacuum exhibit an ESR signal (g = 2.0055, width 6 G) according to *D. Haneman*. This corresponds to a spin density of 8.10^{13} cm^{-2} at the surface, which is not affected by addition of oxygen at 10^{-3} torr·min; with addition of more oxygen (about 10^{-1} torr·min) the spin density increases by some 20%. Hyperfine structure and g-anisotropy are not evident. Comparison with measurements of the electron work-functions and the conductivity in the neighborhood of the surface show that the spins lie in the surface itself. A model is proposed for the silicon surface, which shows the atoms arranged in alternate rows, running in the direction of cleavage. Each alternate row lies at a higher level and has unpaired electrons of preponderantly s-character, which are freely mobile within the row; these are responsible for the ESR signal. The other rows of atoms lie at a lower level, the single electrons have a preponderantly p-character, and overlap with their neighbors within the low-lying series. / Physic. Rev. [2] *170*, 705 (1968) –Hz. [Rd 900 IE]

Kinetics of the ring-opening in liquid cyclooctasulfur were investigated by *T. K. Wiewiorowski, A. Parthasarathy* and *B. L. Slaten*, It is known that an equilibrium is set up in molten sulfur (at a moderate temperature) between S_8 rings and S_8 chains. This reaction was followed by measurement of the freezing point of liquid sulfur in relation to the time of

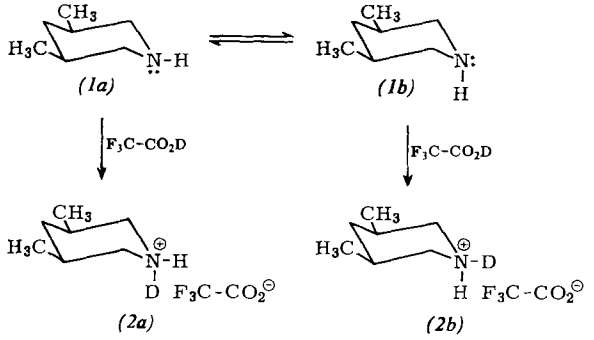
heating and temperature. The S_8 chains "dissolved" in the cyclooctasulfur bring about a freezing point depression. From the freezing point depressions after preheating to 130–150 °C, the rate constants of the ring opening reaction were calculated as 0.5×10^{-2} to 3.34×10^{-2} min^{-1}, and from their temperature dependence, the dissociation enthalpy of the S–S bond in cyclooctasulfur was obtained as 32 kcal/mole. / J. physic. Chem. *72*, 1890 (1968) / –Hz. [Rd 901 IE]

A mechanism for the chlorine dioxide explosion was proposed by *E. T. McHale* and *G. von Elbe*. The reaction is characterized by long induction periods; these were measured in relation to temperature (54–134 °C), pressure (0.2–40 torr), vessel size, irradiation, and addition of foreign gases. The reaction shows chain branching and proceeds *via* a relatively stable intermediate, identified as Cl_2O_3. The results of the measurements and known enthalpy data permit the postulate of the following reaction mechanism:

Start	$2\ ClO_2$	$\xrightarrow{\text{wall}}$	$ClO + ClO_3$
Intermediate product	$ClO_2 + ClO$	$\longrightarrow$	Cl_2O_3
	$ClO + Cl_2O_3$	$\longrightarrow$	$ClOOCl + ClO_2$
Branching	$ClOOCl$	$\longrightarrow$	$ClOO + Cl$
	$ClOO$	$\longrightarrow$	$Cl + O_2$
	$Cl + ClO_2$	$\longrightarrow$	$2\ ClO$
	$Cl + ClO_2$	$\longrightarrow$	$Cl_2 + O_2$
Chain termination	Cl	$\longrightarrow$	$1/2\ Cl_2$

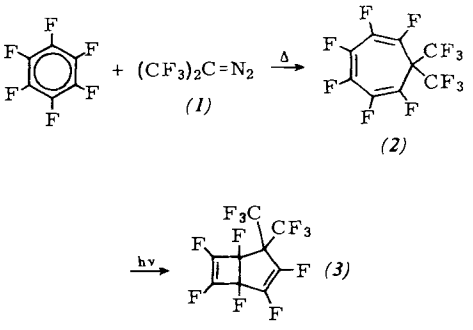
Cl_2O_3 is formed together with Cl_2O_6 by the photolysis of ClO_2 at –45 °C and can be separated readily from Cl_2O_6 because of its substantially greater volatility. The structure $O_2Cl–ClO$ is assigned to it. / J. phys. Chem. *72*, 1849 (1968) / –Hz. [Rd 902 IE]

The conformation equilibrium in *cis*-3,5-dimethylpiperidine *(1)* was examined by *H. Booth* by means of the ^1H–NMR spectra in deuterotrifluoracetic acid and in trifluoracetic acid. The 2,6-axial protons appear as a quartet in the spectrum of *cis*-3,5-dimethylpiperidinium trifluoracetate, *(1)*. CF_3CO_2H, at $\tau = 7.30$. The spectrum of the mixture of *(2a)* and *(2b)* shows a triplet at $\tau = 7.30$, and a quartet (2,6-axial protons of *(2a)* or *(2b)*). Under the conditions of the reaction exceptionally little H^+ or D^+ is split off from *(2a)* and *(2b)*. The spectrum was still unchanged after two days. The ratio of the areas of the triplet and the quartet shows that 54% of *(2a)* and 46%

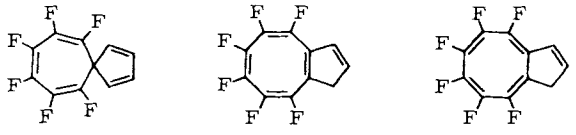


of *(2b)* are present. The energy difference between the two forms is only 0.1 kcal/mole. Obviously the H-atom and the free electron pair on the nitrogen require about the same space. / Chem. Commun. *1968*, 802 / –Kr. [Rd 903 IE]

Carbenes undergo addition to hexafluorobenzene, according to *D. M. Gale* and *M. Jones jr.* As a result hexafluorobenzene cannot be used as an inert solvent for carbene reactions. *Gale* obtained the perfluorinated *(2)* (b.p. ≈ 125 °C) by the

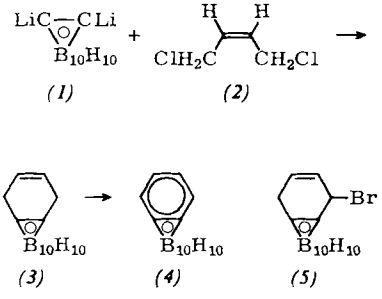


thermolysis of hexafluoro-2-diazopropane *(1)* in C_6F_6, in 20% yield; on irradiation, ($\lambda > 3100$ Å) *(2)* is converted into the bicyclic compound *(3)* (99% yield). *Jones jr.* was



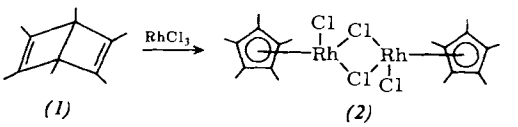
able to isolate the spirane *(4)* after irradiation of diazocyclopentadiene in C_6F_6, the former being converted on heating-probably into *(5)* or *(6)*. / J. org. Chemistry *33*, 2536, 2538 (1968) / –Kr. [Rd 905 IE]

The synthesis of benzo[a]-1,2-dicarba-*closo*-dodecarorane (benzocarborane) *(4)* was successfully carried out by *N. K. Hota* and *D. S. Matteson* by the reaction of 1,2-dilithiocarborane *(1)* with *cis*-1,4-dichloro-2-butene *(2)* and dehydrogenation of the reaction product with *N*-bromosuccinimide to *(4)*.



After chromatography, recrystallization and sublimation, *(4)* is obtained in 30% yield. According to the ^1H–NMR and UV spectra it has a partially aromatic character. It is not attacked by conc. H_2SO_4 at 100 °C, does not react with bromine in CBr_4, but is decomposed by $KMnO_4$ in acetone. The monobromo compound *(5)* may be obtained as a by-product of the dehydrogenation. / J. Amer. chem. Soc. *90*, 3570 (1968) / –Kr. [Rd 906 IE]

A new type of ring contraction was observed by *J. W. Kang* and *P. M. Maitlis*. $RhCl_3 \cdot 3\ H_2O$ in methanol is converted almost quantitatively with excess hexamethyl (Dewar)benzene *(1)* into the dimeric pentamethylcyclopentadienylrhodium-(III)chloride *(2)*, which forms very stable, dark red crystals

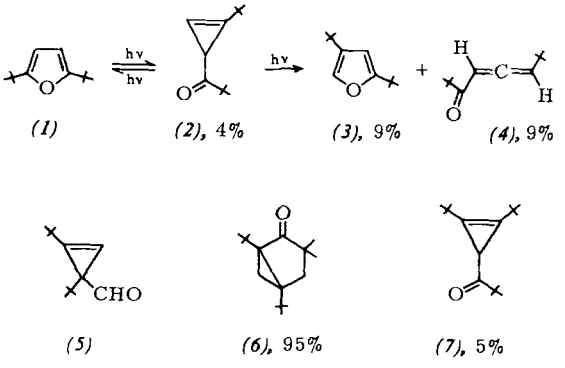


earlier regarded as $[(CH_3)_6C_6RhCl]_2^{4+}$ 4 Cl^- [11]. Hexamethylbenzene is also formed. The structure of *(2)* was checked by mass spectroscopy and other methods. The chlorine bridges

in *(2)* are broken by triphenylphosphine, pyridine, and other reagents. (π-1,5-cyclooctadiene) (π-pentamethylcyclopentadienyl)rhodium(I) is formed with 1,5-cyclooctadiene in the presence of Na_2CO_3. / J. Amer. chem. Soc. *90*, 3259 (1968) / –Kr. [Rd 907 IE]

[1] *B. L. Booth, R. N. Haszeldine,* and *M. Hill,* Chem. Commun. *1967*, 1118.

The photolytic isomerization of poly-*tert*-butylfurans was examined by *E. E. van Tamelen* and *T. H. Whitesides*. After irradiation of *(1)* in pentane (1.2×10^{-3} M) under nitrogen for 1 hour, *i.e.* after about a half of *(1)* had been converted, it was possible to isolate *(2)*, *(3)*, and *(4)* (residue: probably oligomers). *(2)* is converted on irradiation into *(1)*, *(3)*, and

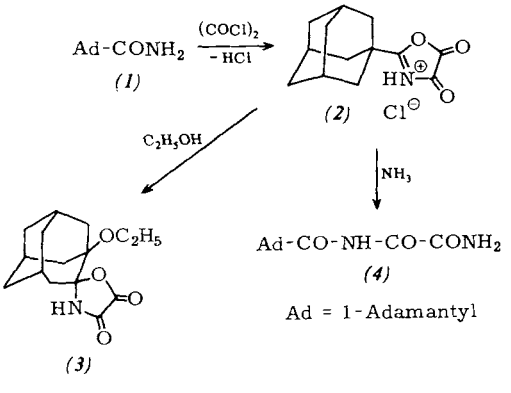


(1) *(2)*, 4% *(3)*, 9% *(4)*, 9%

(5) *(6)*, 95% *(7)*, 5%

(4), while *(3)* forms the cyclopropenecarbaldehyde *(5)*. 2,3,5-Tri-*tert*.butylfuran rearranges under analogous conditions mainly into the bicyclic compound *(6)*, and into the cyclopropyl ketone *(7)*. / J. Amer. chem. Soc. *90*, 3894 (1968) / –Kr. [Rd 908 IE]

A spirohomoadamantane *(3)* has been obtained by *T. Sasaki, S. Eguchi,* and *T. Toru* in the reaction of 1-adamantanecarbonamide *(1)* with oxalyl chloride by treatment of the primary adduct *(2)* with anhydrous ethanol at room temperature. The structure of the rather unstable compound *(2)*,



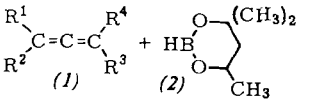
m.p. = 98–100 °C (dec.), yield ≈ 70 %, was determined *inter alia* by its ammonolysis to form *(4)*. The spirane *(3)* forms colorless crystals, m.p. = 194–195 °C (dec.), yield 62 %, which are insoluble in anhydrous ethanol. 1-Adamantane-carbanilide reacts in a similar manner. / Tetrahedron Letters *1968*, 4135 / –Kr. [Rd 909 IE]

Tris(diethylamino)phosphine has been suggested by *D. N. Harpp, J. G. Gleason,* and *J. P. Snyder* for the partial desulfurization of organic disulfides.

$$R^1\text{–S–S–}R^2 + [(C_2H_5)_2N]_3P \rightarrow R^1\text{–S–}R^2 + [(C_2H_5)_2N]_3PS$$

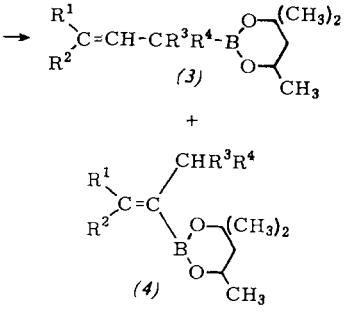
The method can be applied to many organic disulfides. No rearrangements take place. Examples: $R^1 = R^2 = n$-pentyl (yield 63 %); $R^1 = p$-tolyl, R^2 = benzyl (86 %), $R^1\text{–S–S–}R^2$ = 1,2-dithiacyclohexane (100 %). The formation of $R^1\text{–S–}R^1$, $R^2\text{–S–}R^2$, and $R^1\text{–S–}R^2$ in yields of 22, 11, and 38 % on partial desulfurization of $p\text{-Br–}C_6H_4\text{–}CH_2\text{–S–S–}CH_2\text{–}C_6H_5$ has not yet been explained. / J. Amer. chem. Soc. *90*, 4181 (1968) / –Kr. [Rd 910 IE]

The addition of 4,4,6-trimethyl-1,3,2-dioxaborinane *(2)* **to allenes** has been studied by *R. H. Fish*; this reaction, unlike the addition of B_2H_6 to allenes, proceeds in one step. If one of the terminal allene C atoms is unsubstituted, the principal product is the adduct *(3)*; on the other hand, the attack on the middle carbon atom to give *(4)* is favored in the other allenes. Thus allene *(1a)* gives the adducts *(3a)* and *(4a)* in a ratio of



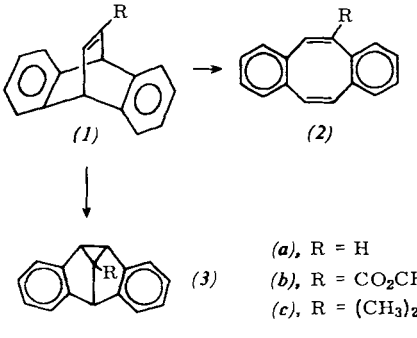
(1) *(2)*

(a), $R^1 = R^2 = R^3 = R^4 = H$
(b), $R^1 = R^2 = CH_3$, $R^3 = R^4 = H$
(c), $R^1 = R^2 = R^3 = R^4 = CH_3$
(d), $R^1 = R^4 = H$, $R^2\text{–}R^3 = -(CH_2)_6-$



86.5:13.5; *(1b)* gives 78 % of *(3b)* and 22 % of *(4b)*, and *(1c)* gives 100 % of *(4c)*. 1,2-Cyclononadiene *(1d)* gives the *cis* and *trans* adducts in a ratio of 85:15. 2,3-Pentadiene [*(1e)*, $R^1 = R^4 = H$, $R^2 = R^3 = CH_3$] forms 81 % of *(4e)*, but unlike the other allenes, it also yields 19 % of 4,4,6-dimethyl-2-(*trans*-3-penten-1-yl)-1,3,2-dioxaborinane, which is not formed by rearrangement from *(3e)*. / J. Amer. chem. Soc. *90*, 4435 (1968) / –Kr. [Rd 917 IE]

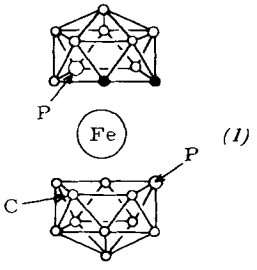
The photoisomerization of mono- and dibenzobarrelene *(1a)* by direct irradiation at 2537 Å is regarded by *P. W. Rabideau, J. B. Hamilton,* and *L. Friedman* as a convenient synthesis of mono- and *sym*-dibenzocyclooctane *(2a)*, which are formed almost without by-products. Irradiation > 3000 Å in the presence of acetophenone, or acetone, on the other hand, leads to semibullvalene *(3a)*, also in high yields.



(a), R = H
(b), R = CO_2CH_3
(c), R = $(CH_3)_2COH$

Direct irradiation of *(1b)* leads only to *(2b)*, whereas *(1c)* rearranges to give only *(3c)*. These results support the view of *Brewer* and *Heaney* that the cyclooctatetraenes are formed *via* the excited singlet state and the semibullvalenes *via* the excited triplet state. / J. Amer. chem. Soc. *90*, 4465 (1968) / –Kr. [Rd 918 IE]

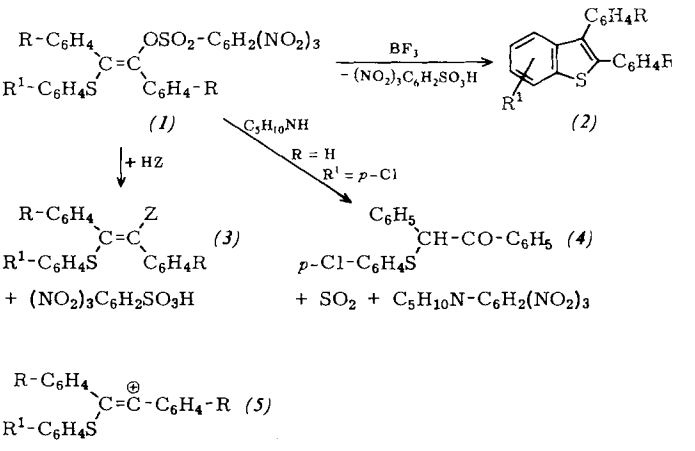
New transition metal complexes with the carbaphosphollide ion (3)-1,7-$B_9H_9CHP(CH_3)^-$ are described by *L. J. Todd, I. C. Paul, J. L. Little, P. S. Welcker*, and *C. R. Peterson*. When 1,7-$B_{10}H_{10}CHP$ is heated in piperidine it forms the piperidinium salt of (3)-1,7-$B_9H_{10}CHP^-$, the tetramethylammonium salt of which reacts with NaH and then with $FeCl_2$ to give the red-violet anion $[(3)\text{-}1,7\text{-}B_9H_9CHP]_2Fe^{2-}$. This anion can be alkylated with CH_3I to give $[(3)\text{-}1,7\text{-}B_9H_9CHP(CH_3)]_2Fe$ *(1)* (brown isomer, m.p. = 239.5–240.5 °C; red isomer, m.p. 233–234 °C). A cocrystallite containing both isomers forms deep red orthorhombic prisms (a = 13.66, b = 13.96, c = 20.36 Å, space group Pbca) on sublimation. The unit cell of the brown form has a = 14.44, b = 13.79, c = 19.51 Å.



(1)

According to the X-ray structural analysis of a cocrystallite of *(1)* (formula shown without substituents), the C atom in one of the polyhedra probably statistically occupies one of the two positions marked in black. Similar complexes are formed with Co^{2+} and Ni^{2+}. / J. Amer. chem. Soc. *90*, 4489 (1968) / –Kr. [Rd 919 IE]

1,2-Diaryl-2-arylthiovinyl-2,4,6-trinitrobenzenesulfonate *(1)* has been obtained by *G. Capozzi, G. Melloni, G. Modena*, and *M. Piscitelli* by addition of arylsulfenyl 2,4,6-trinitrobenzenesulfonates to tolan and 4,4′-dimethyltolan. The arylsulfenyl derivatives were prepared from arylsulfenyl chlorides with silver 2,4,6-trinitrobenzenesulfonate, and were not isolated. Examples of *(1)*: R = R^1 = H, m.p. = 109–110 °C; R=H, R^1 = *p*-Cl, m.p. 139–140 °C; R = R^1 = CH_3,



m.p. = 104–105 °C. *(1)* gives orange-red crystals, which can be recrystallized *e.g.* from chloroform/pentane and decompose in many inert solvents, particularly in the presence of BF_3, to give the free sulfonic acid and a 2,3-diarylbenzo[b]-thiophene *(2)*. Reaction with weak nucleophiles gives products such as *(3)*, while strong nucleophiles form acetophenone derivatives such as *(4)* as well as SO_2 and trinitrophenyl derivatives. The authors believe that a vinylcarbonium ion *(5)* is formed as an intermediate in the decompositions. / Tetrahedron Letters *1968*, 4049 / –Kr. [Rd 920 IE]

BOOK REVIEWS

Chemical Reactions at High Pressures: By *K. E. Weale, E.* and *F. N. Spon* Ltd., London 1967. 1st Edit., xiii, 350 pp., numerous illustrations and tables, 70 s.

The chemistry of reactions at moderately high and very high pressures has developed so vigorously in the last few years that it is now hardly possible for one person to write a really comprehensive monograph covering the whole field. At the same time, the meaning of the term "high pressure" becomes more and more blurred. From this point of view it must be recognized that, in spite of its comprehensive title, the present monograph deals thoroughly with only a part of the field of high-pressure chemistry – reactions in fluid phases at pressures up to 15 kbar.

A short historical introduction is followed by chapters on the influence of high pressures on the physical properties of single-phase systems and on the pressure dependence of phase equilibria. This is followed by a survey of the experimental methods of high-pressure chemistry, including a few sections on the possible sources of danger of work at high pressure.

The main part of the book is made up of chapters on equilibria and reaction rates in liquids at high pressures. After a rather theoretically oriented introduction to reaction kinetics at high pressures, which establishes the concept of activation volumes, many examples of the influence of high pressures on organic reactions are given. Polymerizations are treated particularly thoroughly. This chapter should be stimulating even to the specialist in the field.

Gas reactions at high pressures are also dealt with. The end of the book comprises a 19-page section entitled "Reactions at very high pressures" which deals with pressures above 15 kbar. In a later edition this section should either be omitted entirely or so expanded that the fundamentals of the chemistry of the solid state at very high pressures are at least indicated. In the present form it merely presents a distorted picture.

Weale cites about 1000 references to the literature, some as recent as 1966. In the main chapters, on the high-pressure reactions of organic systems in particular, the recent literature has been considered extensively. The book will be of greatest value to those wishing to familiarize themselves with the fluid state reactions at pressures up to 15 kbar, the basic information on instrumental aspects, theoretical foundations and experimental results. The book also provides a good introduction to the original literature. It will also be of interest to workers already concerned with high-pressure problems. *K.-J. Range* [NB 729 IE]

Aromatic Amine Oxides. By *E. Ochiai*. Elsevier Publishing Company, Amsterdam-London-New York 1967. 1st ed., x, 456 pp., 31 figures, 87 tables, bound Dfl 85.00 / £8.15.0.

The author of this book started his studies on the aromatic amine oxides, which had been discovered in 1925 by *J. Meisenheimer*, as early as 1940. It was only many years later, with the general growth of interest in the mechanism of

nucleophilic reactions and *H. J. den Hertog*'s independent investigations in this field after 1950, that *Ochiai*'s early work became known outside Japan. The literature has greatly increased in volume since then, an important cause of this growth being interest in biological aspects (iodinin had been known since 1938 as a metabolite of micro-organisms). *Ochiai* recognized *e.g.* the difference between the true aromatic amine oxides, *i.e.* the *N*-oxoaza aromatic compounds, and the *N*-oxides of trimethylamine, dimethylamine, *etc.*, and reached certain conclusions concerning the charge distribution in these compounds, which is roughly the reverse of that in the parent bases.

This field was dominated by Japanese workers for many years, and since most of the publications were in Japanese, it was some time before the results became known outside Japan. It is therefore all the more pleasing to find a thorough, competent review of work carried out up to the beginning of 1964 from the pen of the most successful worker and the foremost expert in the field. The book contains over 1100 references. However, the clear layout and style and the intelligent use of formulas ensure that even in the English translation by *D. U. Mizoguchi*, the reader will have no trouble in finding his way through the book.

The introduction is followed by a chapter on preparation, which contains a number of examples. The physico-chemical properties such as dipole moment, polarographic behavior, dissociation constant, NMR, IR and UV spectra, and the electronic structure from the point of view of MO theory are discussed in Chapter 4 (100 pages). Other chapters deal with reactivity, electrophilic and nucleophilic substitution, and the effect of the *N*-oxide groups substituents. The last chapter is devoted to the biological properties of the aromatic amine oxides, such as their antibacterial, carcinogenic, and carcinostatic activities, and reference is made to the possible pharmacological uses, which are still in their infancy.

Despite the broad picture presented by the book, the greatest care has been taken with details. In view of the rapid growth of knowledge in every field of organic chemistry really reliable monographs of this type are invaluable.

F. Kröhnke [NB 739 IE]

Ullmanns Encyklopädie der technischen Chemie (Ullman's Encyclopedia of Industrial Chemistry). Vol. 18: Uranium (continued) to Rayon Staple (Zellwolle). Chief editor *W. Foerst*, editor: *Hertha Buchholz-Meisenheimer*. Verlag Urban & Schwarzenberg, München-Berlin 1967. 3rd, completely revised Edit., xii, 792 pp., 261 figures, DM 182.– per volume (sold only as the complete work).

The penultimate volume of the encyclopedia [*] contains long articles on water (100 pp.), washing and detergents (95 pp.), vitamins (79 pp.), viscose rayon, fibers, and sponges (46 pp.), wine (46 pp.), uranium (continued) (45 pp.), wax (44 pp.), cellulose (41 pp.), and hydrogen (39 pp.). Of the shorter articles, mention should be made of viruses, growth factors spices, plasticizers, wool, bismuth, and tungsten.

The article on water is a condensed monograph. Nine authors from universities, industry, the Ministry of Health, the Vereinigung der Grosskesselbesitzer, and other institutions deal with structure, physical properties (with comprehensive tables), drinking water and water for industry (with good water consumption statistics and quality standards), boiler feed water, cooling water, demineralization of sea water (technical and economic comparison of the methods), general aspects of water supply, water legislation, and finally the production of heavy water (processes and economic comparison). The article shows an excellent combination of expert and editorial co-operation.

The article on cellulose gives a clear picture of modern digestion and purification processes. Many of the articles in this volume refer back to earlier articles, and efforts have been made in the treatment of new key words to include further information on topics discussed earlier. Thus the article on washing and detergents is closely related, *via* detergent raw materials, to the surfactants (Vol. 16). The question of biological degradation and tolerance by fish is considered at some length. The article also contains a good theory of washing, as well as a description of modern washing machines and the demands that they place on detergents and washing. In the article on wine, one is impressed by the progress in the field of foods and beverages. Total analyses of wines, listing more than 200 constituents, are given. We learn from the article on hydrogen that the liquid hydrogen consumption for rockets in the USA was 60000 t in 1966. The growing experience of the editorial staff becomes increasingly evident with each new volume of the encyclopedia that appears. We therefore look forward eagerly to the final volume, which will contain the general index.

H. Sachsse [NB 731 IE]

[*] Cf. Angew. Chem. *79*, 695 (1967); Angew. Chem. internat. Edit. *6*, 719 (1967).

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Oligophenyls, Oligophenylenes, and Polyphenyls, a Class of Thermally Very Stable Compounds

BY W. RIED AND D. FREITAG[*]

Dedicated to Professor W. Schultheis on the occasion of his 65th birthday

The classical and modern syntheses of oligophenyls and polyphenyls are compared to illustrate the value and the range of applications of the preparation methods described. The investigations showed a relationship between the number, arrangement, and substitution of the aromatic rings and the physical properties of the products. The melting point of the p-polyphenyls rises with increasing degree of condensation. Methylation, and linkage in the m-positions lowers the melting point and at the same time improves the solubility. o-Oligophenyls melt at lower temperatures than the p-isomers. The highest-melting substance in this class is p-septiphenyl, which melts at 545 °C.

1. Introduction

Modern industry and space research in particular require new, and, above all, heat-resistant materials. The rapid development[1–3] of macromolecular organic chemistry has resulted in the development of innumerable new organic constructional and manufacturing materials. It has become possible to improve the natural properties of many polymers, *e.g.* their thermal and electrical insulating properties and their elasticity. Important progress has been made in particular in the synthesis of heat-resistant polymers, and products of this type with melting points[1] above 900 °C are no longer uncommon.

The laborious preparation of the starting materials, which often requires several costly reaction steps, has hindered the wide application of these substances. For this reason the strenuous efforts that have been made in recent years, particularly in the USA[4], to obtain thermally stable polyphenyl directly from benzene seem very promising.

The nature and number of linkages formed between rings in the polymerization of benzene are largely known from model reactions. The methods for the synthesis of oligo- and polyphenyls will now be described with special reference to their physical properties and the relation between the arrangement of the benzene units and the thermal stability of the products.

2. *p*-Oligophenyls

2.1. Nomenclature

The oligomeric lower members of the series benzene, biphenyl, *p*-terphenyl, *etc.* were referred to by *Kern* and *Wirth*[5] as "*p*-oligophenylenes". These compounds are now named in accordance with IUPAC Rule A-54[6], according to which the prefix for the number of linked rings (ter-, quater-, quinque-, sexi-, septi-, octi-, novi-, deci-, *etc.*) is placed in front of the radical name "phenyl". Substances of this class must therefore be named *p*-oligophenyls. An ex-

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[1] *F. T. Wallenberger*, Angew. Chem. *76*, 484 (1964); Angew. Chem. internat. Edit. *3*, 460 (1964).

[2] *G. Greber*, Umschau *67*, 60 (1967).

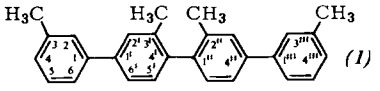
[3] *C. L. Segal*: High-temperature Polymers. Dekker, New York 1967.

[4] *H. F. Mark*, Lecture at Farbwerke Hoechst AG on Oct. 26, 1967.

[5] *W. Kern* and *H. O. Wirth*, Kunststoffe-Plastics (Solothurn) *6*, 12 (1959).

[6] a) International Union of Pure and Applied Chemistry: Nomenclature of Organic Chemistry. Definitive Rules for Section A and B. 2nd Edit., Butterworths, London 1966, p. 44; b) see also *R. Pummerer* and *K. Bittner*, Ber. dtsch. chem. Ges. *57*, 84 (1924).

ample of the numbering of the carbon atoms is given in formula *(1)* [6a,7] (for other suggestions see [8]).



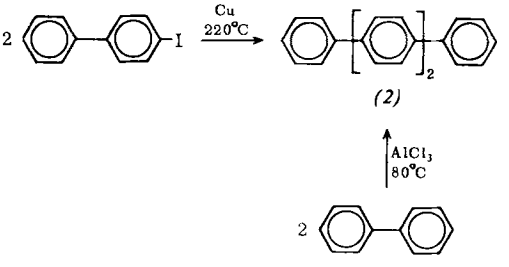
(1)

3,3′,2″,3‴-Tetramethyl-*p*-quaterphenyl

2.2. Syntheses

The Gattermann [9] synthesis of biphenyl is well known. A modification [10] of this reaction, the reduction of the diazonium salt with 78.5 % formic acid followed by decomposition with copper powder, led in 1924 not only to biphenyl, but also to ter-, quater, and the previously unknown quinquephenyl, with predominance of *p*-linkages.

Ullmann [11] prepared *p*-quaterphenyl *(2)* by reaction of *p*-iodobiphenyl with copper powder at 220 °C. *Dayal* and *Rao* [12] very recently discovered a simpler synthesis in which *p*-quaterphenyl is obtained in good yields from biphenyl and $AlCl_3$ in nitrobenzene at 80 °C.



(2)

p-Sexiphenyl [6b] has been obtained by a reaction similar to the Ullmann reaction from *p*-iodoterphenyl and silver powder at 330 °C. *Busch* and *Weber* [13] obtained *p*-oligophenyls with degrees of condensation up to $p = 7$ (Table 1) by hydrogenation of *p*-dibromobenzene under pressure with hydrazine hydrate as the source of hydrogen and palladium as the catalyst. The structure of *p*-septiphenyl could not be verified because of its poor solubility.

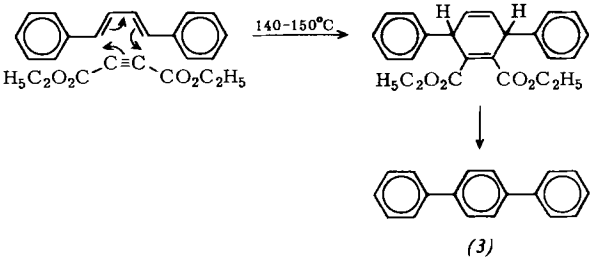
Table 1. Properties of the *p*-oligophenyls.

Degree of condensation *p*	Yield (%) [13]	M.p. (°C) [13]	Solubility (g/l) toluene 20 °C [22]	λ_{max} (nm) calc. [a]	λ_{max} (nm) found [24] [b]	$\varepsilon_{max} \cdot 10^{-3}$
2	21	70	440	251.7	251.5	18.3
3	14	210	8.5	280.0	280.0	25.0
4	10	320	0.22	298.0	300.0	39.0
5	2	395	<0.1	309.7	310.0	62.5
6	0.7	475	<0.01	317.6	317.5	>56.0
7	0.2 [c]	545		323.1		
∞				343.8		

[a] The absorption bands were calculated by *Kuhn*'s root law [23].
[b] In chloroform. [c] Molecular weight not yet determined.

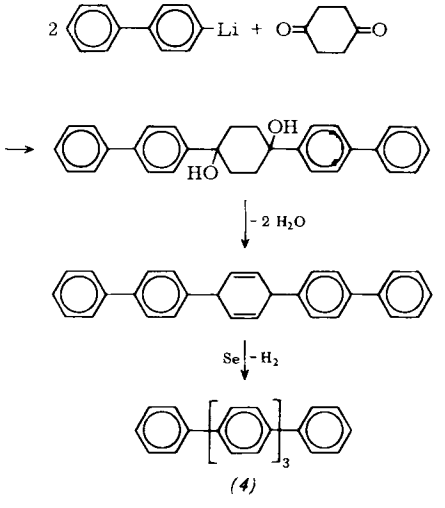
Most of the syntheses described so far are not very specific. They very often yield a mixture of several products, which can be separated only with difficulty and with considerable loss of material by fractional sublimation and crystallization.

A rather laborious, but specific, synthesis of *p*-terphenyl *(3)* was devised by *Lohaus* [14]. The intermediate product was hydrolyzed, decarboxylated, and oxidized.



(3)

An equally specific synthesis of *p*-terphenyl, the organometallic-carbonyl reaction [15], was first used by *Mayer* and *Schiffner* [16]; this method was later used by *Müller* and *Töpel* [17] for the preparation of *p*-quinquephenyl *(4)*.



(4)

Kern et al. [18] were able to obtain a large number of substituted *p*-oligophenyls having specific constitutions in yields of 40–50 % by a mixed Ullmann reaction. The organometallic-carbonyl reaction, which involves several steps, rarely gives higher yields than this process, in which a monofunctional aromatic halogen

$$n\,A\text{–}X + m\,ArX_2 \xrightarrow{Cu} \sum_{q=0}^{q=\infty} \nu_i\,A\text{–}[\text{–}Ar\text{–}]_q\text{–}A \qquad (1)$$
$$(q=0,1,2,3\ldots)$$

[7] *J. v. Braun, G. Irmisch,* and *J. Nelles,* Ber. dtsch. chem. Ges. *66,* 1471 (1933), footnote 8 therein.

[8] *W. Kern, M. Seibel,* and *H. O. Wirth,* Makromolekulare Chem. *29,* 164 (1959).

[9] *L. Gattermann* and *R. Ehrhardt,* Ber. dtsch. chem. Ges. *23,* 1226 (1890).

[10] *O. Gerngross* and *M. Dunkel,* Ber. dtsch. chem. Ges. *57,* 739 (1924).

[11] *F. Ullmann,* Liebigs Ann. Chem. *332,* 38 (1904).

[12] *S. K. Dayal* and *K. N. Rao,* Indian J. Chem. *5,* 122 (1967).

[13] *M. Busch* and *W. Weber,* J. prakt. Chem. *146,* 1 (1936).

[14] *H. Lohaus,* Liebigs Ann. Chem. *516,* 295 (1935).

[15] Terminology taken from *W. Kern* and *H. O. Wirth* [5].

[16] *F. Mayer* and *R. Schiffner,* Ber. dtsch. chem. Ges. *65,* 1337 (1932).

[17] *E. Müller* and *T. Töpel,* Ber. dtsch. chem. Ges. *72,* 273 (1939).

[18] *H. O. Wirth, K. H. Gönner, R. Stück,* and *W. Kern,* Makromolekulare Chem. *63,* 30 (1963).

compound (A–X) is allowed to react with a bifunctional aromatic halogen compound (ArX_2) in accordance with eq. (1). The degree of polymerization q is determined by the molar ratio of the starting materials. When A–X is present in a sufficiently large excess, practically the only products are the first two members of the series with $q = 0$ and $q = 1$. The optimum molar ratio AX: ArX_2 found by *Kern et al.* [18] for the compound having $q = 1$, which is of considerable preparative interest, is about 10:1.

2.3. Properties

Owing to the linear arrangement of the *p*-phenylene units, the *p*-oligophenyls have rod-shaped molecules [5]; like the cumulenes, they differ in this respect from the linear aliphatic compounds. The single bonds allow free rotation of the rings about the longitudinal axis of the molecule, but no change in shape [19]. As can be seen from Table 1, the solubility of the *p*-oligophenyls decreases rapidly with increasing degree of condensation p, while the melting point rises very rapidly. Even the members with $p = 5$, 6, and 7 exhibit an unusually high thermal stability for organic molecules. It is even thought [1] that *p*-polyphenyl whose crystal lattice is free from defects could be infusible and stable up to 800 or 900 °C.

Dissolution and melting are strongly dependent on the lattice energy, since both processes involve the destruction of the lattice. In a search for a relationship between solubility and thermal stability in *p*-oligophenyls, *Kern et al.* [5, 18, 19a] synthesized 29 methylated *p*-oligophenyls with degrees of condensation up to $p = 12$ resp. 16 [19b] as models. It was found that the solubility of the *p*-oligophenyls is considerably improved by methylation, but the melting point is simultaneously lowered. The only exceptions to this rule are the initial members of the durene series with $p = 2$ and $p = 3$ [20]. *Kern et al.* [21] attribute this effect mainly to the disturbance of the molecular symmetry. Owing to the possibility of rotation of the substituted rings about the longitudinal axis of the molecule, it becomes fully evident in the *p*-oligophenyls only beyond $p = 3$.

The electronic spectra of the members from biphenyl to *p*-sexiphenyl, unlike that of benzene, show no fine structure splitting. The absorption maximum is displaced toward red with increasing degree of condensation p, and the intensity simultaneously increases.

The values calculated in accordance with *Kuhn*'s root law [23] (see eq. (2)) agree well with those found experimentally.

$$\lambda = \frac{2.08 \times 10^3}{\sqrt{1 - 0.634 \cos \frac{\pi}{p+1}}} \quad (2)$$

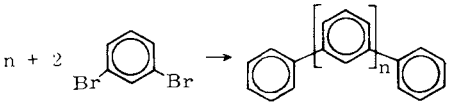
In 1939, *Gillam* and *Hey* [24] concluded from their measurements that all the nuclei of the *p*-oligophenyls are coplanar and that the entire molecule is in a state of resonance. These authors used the continuous conjugation, as a result of which quinoid formulations also contribute to the structure, to explain their observed electronic spectra. It was later shown by *Dale* [25], however, that biphenyl is not planar either in solution or in the crystalline state. As was found from an MO calculation by *Murrel* and *Longuet-Higgins* [26], the angle of twist between the ring units and the conjugation need not be considered in the interpretation of the electronic spectra of the *p*-oligophenyls. The formula used for the calculation of the excitation energies is simply based on π-electron repulsion between adjacent rings.

Special mention should be made of the fluorescence properties of the methyl-substituted *p*-oligophenyls. For example, 3,3′,2‴,3‴′-tetramethyl-*p*-quinquephenyl and 3,3′,2‴′,3‴′′-tetramethyl-*p*-sexiphenyl [5] fluoresce so strongly that their solutions must be described as blue. *p*-Oligophenyls, and particularly the methyl-substituted members, are used as scintillators [27].

3. Acyclic *m*-Oligophenyls

3.1. Syntheses

Mention has already been made of the linear linking of benzene rings into chains by hydrogenation of *p*-dihalogenoaromatic compounds under pressure [13], which leads to products up to *p*-septiphenyl. Using a



n = 1,3,7-14

Table 2. Properties o the acyclic *m*-oligophenyls.

Degree of condensation p	M.p. (°C)	Ref.	λ_{max} (nm) found	$\varepsilon_{max} \cdot 10^{-3}$
3	85	[13]	251.5 [a]	44.0
4	85–86	[29]	247 [b]	61
5	112	[13]	249 [c]	79.5
6	147–148	[31]	248 [b]	105
8	129–131 [d]	[31]	248 [b]	142
9	166	[13]	253 [a]	184
10	184	[13]	253 [a]	213
11	202	[13]	253 [a]	215
12	223	[13]	253 [a]	233
13	245	[13]	253 [a]	252
14	270	[13]	253 [a]	283
15 [e]	292	[13]	254 [a]	309
16 [e]	321	[13]	255 [a]	320 [f]

[a] Recorded in chloroform by *Gillam* and *Hey* [24].
[b] Recorded in isooctane by *Woods et al.* [30].
[c] Recorded in cyclohexane by *Alexander* [31].
[d] The melting point is probably slightly too low.
[e] Molecular weight not yet determined.
[f] Estimated.

[19] *S. Claesson, R. Gehm,* and *W. Kern,* Makromolekulare Chem. *7,* 46 (1951).

[19a] *H. Weitz* and *R. Ullrich,* Makromolekulare Chem. *98,* 29 (1966).

[19b] Personal communication from Prof. Dr. *W. Kern.*

[20] *H. O. Wirth, F. U. Herrmann,* and *W. Kern,* Makromolekulare Chem *80,* 120 (1964).

[21] *H. O. Wirth, K. H Gönner,* and *W. Kern,* Makromolekulare Chem. *63,* 53 (1963).

[22] *W. Kern, H. W. Ebersbach,* and *I. Ziegler,* Makromolekulare Chem. *31,* 154 (1959).

[23] *W. Kuhn,* Helv. chim. Acta *31,* 1780 (1948).

[24] *A. E. Gillam* and *D. E. Hey.* J. chem. Soc. (London) *1939,* 1170.

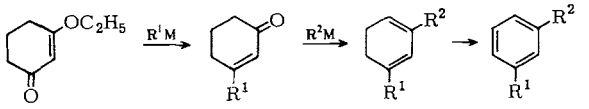
[25] *J. Dale,* Acta chem. scand. *11,* 640, 650 (1957).

[26] *J. N. Murrel* and *H. C. Longuet-Higgins,* J. chem. Soc. (London) *1955,* 2552.

[27] *U. Nay, H.-J. Eichhoff, G. Herrmann,* and *H. O. Wirth,* Z. Elektrochem., Ber. Bunsenges. physik. Chem. *64,* 1098 (1960).

modified process (Pd/hydrazine hydrate, methanolic potassium hydroxide solution, 140 °C, 10 atm, 2.5 hours), *Busch* and *Weber*[13] condensed the rings in the *m*-position to give products up to *m*-sedeciphenyl ($p = 16$). The reaction led to ten acyclic *m*-oligophenyls in a total yield of 86 %. These were separated by fractional distillation and fractional dissolution and crystallization.

Woods et al. described the first specific synthesis of *m*-terphenyl, *m*-quaterphenyl, and *m*-quinquephenyl[28,29]. This is a two-step method involving the reaction of 3-ethoxy-2-cyclohexen-1-one *(5)* (the monoethyl ether of dihydroresorcinol) with organometallic compounds (R–M) to give the dihydroaromatic compounds, which are then dehydrogenated with palladium/animal charcoal.

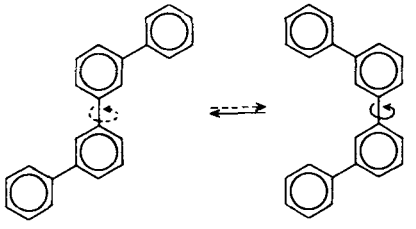


(5) R^1, R^2 = Aryl

Alexander[31] prepared *m*-sexiphenyl and *m*-octiphenyl by a similar method, and so completed the acyclic series of *m*-phenyls up to a degree of condensation $p = 16$, with the exception of *m*-septiphenyl.

3.2. Properties

Owing to the angular arrangement of the benzene rings, acyclic *m*-oligophenyls do not have a rigid molecular shape. Thus for *m*-quaterphenyl, rotation about the bond between the middle rings leads to an extended transoid form *(6)* and a ring-like cisoid form *(7)*.



(6) *(7)*

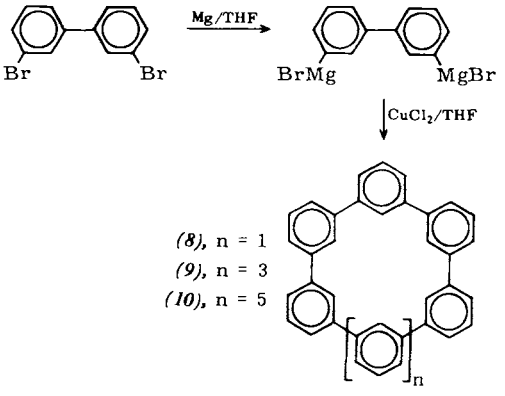
The disturbance of the molecular symmetry by rotation, like the substituent effect (cf. Section 2.3), results in a marked improvement in solubility and a considerable depression of the melting point in relation to those of the *p*-oligophenyls. This difference is very clear from a comparison of members of the *p*- and *m*-series (cf. Tables 1 and 2).

The UV spectra of the acyclic *m*-oligophenyls, in contrast to those of the *p*-oligophenyls, contain a practically constant absorption maximum at 250 nm. However, the molar extinction steadily increases with the number of units in the chain.

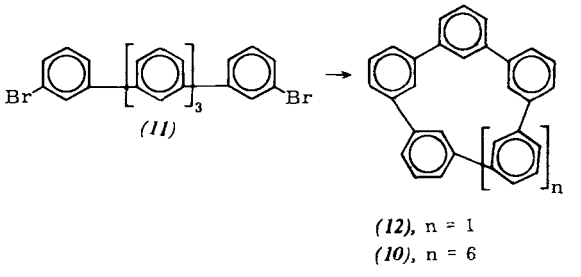
4. Cyclic *m*-Oligophenylenes[*]

4.1. Syntheses

On reaction of the di-Grignard compound of 3,3′-dibromobiphenyl in tetrahydrofuran with anhydrous copper(II) chloride, *Staab* and *Binnig*[32] obtained the cyclic *m*-oligophenylenes *(8)* (11 %), *(9)* (1.8 %), and *(10)* (≈0.1 %), which were separated by fractional precipitation and crystallization. Mass-spectrometric examination of the products showed that higher acyclic oligophenyls had also been formed.



3,3′′′′-Dibromo-*m*-quinquephenyl *(11)* was obtained by the organometallic-carbonyl reaction principle[33]. Conversion into the di-Grignard compound and reaction with copper(II) chloride gave *(12)* (3.2 %) and *(10)* (2.5 %).



(11)

(12), n = 1
(10), n = 6

4.2. Properties

Staab and *Binnig*[32,33] gained considerable information from investigations on the properties of the cyclic *m*-oligophenylenes and presented an interpretation of the results of physical measurements.

It is known from the structural analyses carried out so far that, at least in *m*-hexaphenylene *(8)* and *m*-octa-

[28] *G. F. Woods* and *I. W. Tucker*, J. Amer. chem. Soc. *70*, 2174 (1948).

[29] *G. F. Woods* and *F. Reed*, J. Amer. chem. Soc. *71*, 1348 (1949).

[30] *M. Bennett, N. B. Sunshine*, and *G. F. Woods*, J. org. Chemistry *28*, 2514 (1963).

[31] *R. L. Alexander*, J. org. Chemistry *21*, 1464 (1956).

[*] For the nomenclature of cyclic oligophenylenes see IUPAC Rule A-21 (International Union of Pure and Applied Chemistry: Nomenclature of Organic Chemistry. Definitive Rules for Section A and B. 2nd ed., Butterworths, London 1966, p. 22); cf. *G. Wittig* and *G. Lehmann*, Chem. Ber. *90*, 875 (1957), ref. [11].

[32] *H. A. Staab* and *F. Binnig*, Chem. Ber. *100*, 293 (1967).

[33] *H. A. Staab* and *F. Binnig*, Chem. Ber *100*, 889 (1967)

phenylene *(9)*, the rings are turned through about 30° with respect to one another. On the other hand, the NMR spectrum of *m*-pentaphenylene *(12)* shows that the inside five protons are equivalent, from which it may be assumed that all the nuclei in *(12)* should be coplanar. However, a planar arrangement of the rings would give an H–H distance of 1.5 Å, for which no analogy is known. Information on this point should be provided by an X-ray structural analysis that has now been started.

The melting points of the cyclic *m*-oligophenylenes are much higher than those of the open-chain *m*-oligophenyls. In addition to its thermal stability, *m*-hexaphenylene has a remarkable stability to radiation, no change in physical properties being detected after exposure to extreme doses. The electronic spectra contain an absorption maximum at about 251 nm (except in the case of *m*-octaphenylene, the maximum of which is situated at 243 nm), comparable to that of biphenyl. The molar extinction increases with the number of nuclei.

Table 3. Properties of the cyclic *m*-oligophenylenes.

Degree of condensation *p*	M.p. (°C) corr.	λ_{max} (nm)	$\varepsilon_{max} \cdot 10^{-3}$
5	344	250 [b]	89.25
6	510–511	251 [c]	119
8	449–451	243 [b]	125
10	385–386 [a]	251 [c]	187

[a] According to mass-spectrometric analysis, the compound is not completely free from solvent and open-chain *m*-polyphenyls.

[b] In cyclohexane. [c] In tetrahydrofuran.

5. Acyclic *o*-Oligophenyls

5.1. Syntheses

Bachmann and *Clarke* [34] obtained *o*-terphenyl and *o*-quaterphenyl in low yields by the action of sodium on boiling chlorobenzene. To verify their structures, the two substances were prepared under the conditions of the Ullmann reaction from *o*-iodobiphenyl and iodobenzene with natural copper C and from *o*-iodobiphenyl with natural copper C. Two more recent methods giving higher yields of *o*-terphenyl have been described by *Kern et al.* [35]. *Wittig* and *Lehmann* [36] obtained *o*-sexiphenyl and *o*-octiphenyl by the decomposition of organometallic compounds.

5.2. Properties

A comparison of the acyclic terphenyls having different types of linkage shows that the melting point decreases in the order $p > m > o$. For the quater-, sexi-, and octiphenyls, on the other hand, the melting point changes in the order $p > o > m$ (cf. Tables 1, 2, and 4, and Fig. 1). The differences in thermal stability are undoubtedly due to the linearity or angularity of the structure. Stuart-Briegleb models of *o*-oligophenyls show [36] that no stereoisomers can be formulated for *o*-quaterphenyl, two for *o*-sexiphenyl, and more for *o*-octiphenyl. The observation that *o*-octiphenyl has a melting range of 8 °C (312–320 °C), whereas the lower homologs melt within 1–2 °C, agrees with the assumption that *o*-octiphenyl is a mixture of isomers.

The UV spectrum of *o*-terphenyl contains an absorption maximum [37] at 233 nm. The hypsochromic effect observed in relation to *m*-terphenyl is the more remarkable in that conjugation should occur more readily in *o*-terphenyl than in *m*-terphenyl. The relatively short distance between the two *o*-hydrogen atoms of the phenyl rings leads to twisting [38] of the rings, so that the conjugation extends over a shorter distance in *o*-terphenyl than in *p*-terphenyl. The absorption maximum for oligophenyls in the UV resulting from the energy difference between the ground state and the excited state can thus hardly be explained purely by the conjugation effect (cf. Section 2.3.).

Table 4. Properties of the acyclic *o*-oligophenyls.

Degree of condensation *p*	M.p. (°C)	λ_{max} (nm)	$\varepsilon_{max} \cdot 10^{-3}$
3	57	233 [a]	29
4	118	[b] [39]	
6	216–217	[b] [36]	
8	312–320		

[a] In cyclohexane. [b] No pronounced maximum.

6. Cyclic *o*-Oligophenylenes

6.1. Syntheses

Mannich [40] obtained dodecahydrotriphenylene on condensation of cyclohexane with methanolic sulfuric acid; subsequent dehydrogenation yielded triphenylene. The theoretically interesting biphenylene was first prepared by *Lothrop* [41] by dehalogenation of 2,2'-

Table 5. Melting points of the cyclic *o*-oligophenylenes.

Degree of condensation *p*	M.p. (°C)
2	110
3	196
4	233
6	334–335
8	424–425

[34] *W. E. Bachmann* and *H. T. Clarke*, J. Amer. chem. Soc. *49*, 2089 (1927).

[35] *W. Kern*, *W. Heitz*, and *H. O. Wirth*, Makromolekulare Chem. *42*, 177 (1960).

[36] *G. Wittig* and *G. Lehmann*, Chem. Ber. *90*. 875 (1957); see also *G. Wittig* and *G. Klar*, Liebigs Ann. Chem. *704*, 91 (1967).

[37] *G. F. Woods*, *A. L. Van Artsdale*, and *F. T. Reed*, J. Amer. chem. Soc. *72*, 3221 (1950).

[38] *C. J. B. Clews* and *K. Lonsdale*, Proc. Roy. Soc. (London), Ser. A *161*, 493 (1937).

[39] *W. S. Rapson*, *H. M. Schwartz*, and *E. T. Stewart*, J. chem. Soc. (London) *1944*, 73.

[40] *C. Mannich*, Ber. dtsch. chem. Ges. *40*, 153, 159 (1906); see also *E. Bergmann* and *O. Blum-Bergmann*, J. Amer. chem. Soc. *59*, 1441 (1937); *T. Sato*, *Y. Goto*, and *K. Hata*, Bull. chem. Soc. Japan *40*, 1994 (1967).

[41] *W. C. Lothrop*, J. Amer. chem. Soc. *63*, 1187 (1941); see also *G. Wittig* and *W. Herwig*, Chem. Ber. *87*, 1511 (1954).

dibromobiphenyl with copper oxide. *Rapson et al.*[42] synthesized *o*-tetraphenylene by reaction of the di-Grignard compound of 2,2′-dibromobiphenyl with anhydrous copper chloride. *o*-Hexaphenylene and *o*-octaphenylene were first synthesized by *Wittig* and *Lehmann*[36] from 2,2′-dilithiumbiphenyl with metal chlorides *via* the organometallic complexes.

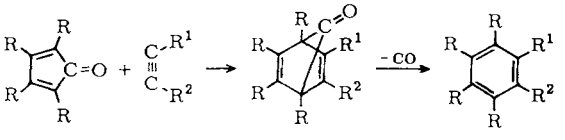
6.2. Properties

On the basis of models, *Wittig* and *Lehmann*[36] were able to show that the cyclic *o*-oligophenylenes have no stereoisomers. *o*-Hexaphenylene and *o*-octaphenylene have tube-like structures. In contrast to *o*-triphenylene, in which the outer rings are coplanar, the inner ring is not planar in *o*-tetra-, *o*-hexa-, and *o*-octaphenylene. (The conformations were deduced from the UV spectra[36, 39].) The relatively high melting points of the cyclic *o*-oligophenylenes are remarkable in comparison with those of the open-chain analogs. The melting point increases with increasing molecular size, while the solubility decreases.

7. Highly Arylated Oligophenyls

7.1. Synthesis from Monoalkynes with Mono- and Biscyclopentadienones

A simple, specific method for the preparation of branched oligophenyls is based on the Diels-Alder reaction. In this way *Dilthey et al.*[43] obtained arylated oligophenyls of the terphenyl series from tetracyclone and acetylene, phenylacetylene, or tolan.



R = C_6H_5
R^1, R^2 = H or C_6H_5

Whereas the double bonds of butadiene each react with a tetracyclone molecule to give hexaphenyl-*p*-quaterphenyl[44], only one of the triple bonds in compounds of the diphenyldiacetylene type reacts under the usual conditions[44, 45]. It was later found[46] that the reaction of two moles of tetracyclone with one mole of diphenyldiacetylene to give octaphenyl-*p*-quaterphenyl *(16a)* could be brought about under much more forcing conditions (bomb tube, 315 °C).

Becker et al.[46, 47] synthesized ten of the deeply colored "bistetracyclones" *(13a)–(13i)* and *(15)*, which react with tolan[46, 47] to give the analogs of hexaphenylbenzene *(14a)–(14i)* and *(16b)* (see Table 6).

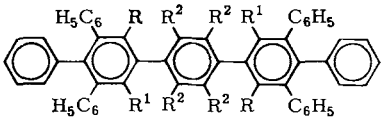
Table 6. Properties of the *p*-ter-, *p*-quater-, *p*-quinque-, and *p*-sexiphenyl derivatives *(14)* and *(16)*.

Compound	R	M.p. (°C)	λ_{max} [a] (nm)	$\varepsilon_{max} \cdot 10^{-3}$ (nm) [46]	λ_{max} [b] (nm)	$\varepsilon_{max} \cdot 10^{-3}$
(14a)	$-CH_2-$	440–444	247	102.8	267	50.7
(14b)	$-(CH_2)_2-$	422–424	247	97.8	266	54.6
(14c)	$-(CH_2)_3-$	404–406	247	93.0	268	51.3
(14d)	$-(CH_2)_4-$	398–400	247	98.3	268	53.2
(14e)	$-(CH_2)_5-$	337–340	248	99.0	267	62.8
(14f)	$-(CH_2)_6-$	356–358	247	99.3	268	58.5
(14g)	–O–	456–459	248	95.4	270	59.0
(14h)	–S–	442–446	248	96.3	268	63.3
(14i)	–	440–442	247	78.5	279	54.2
(16a)	–	322–324	254	63.5	272	49.0
(16b) [c]	*p*-C_6H_4	468–470	252	77.7	278	53.0
Hexaphenylbenzene		465	247	56.8	266	34.7

[a] In 1,2-dichloroethane. [b] Shoulder. [c] Prepared earlier by *Ried* and *Bönnighausen* [45] from tetracyclone and 1,4-bis(phenylethynyl)-benzene.

7.2. Synthesis from Dialkynes and Trialkynes with Mono- and Biscyclopentadienones

By heating one mole of aromatic diethynyl compound[48–50] with two moles of substituted cyclopentadienone in the high-boiling inert solvent β-decalol, we obtained[45] the products *(17)–(20)* in very good yields.



(17)

(a) R = C_6H_5; $R^1 = R^2$ = H; m.p. = 417–418 °C
(b) R = CH_3; $R^1 = R^2$ = H; m.p. = 311–312 °C
(c) R = $R^1 = C_6H_5$; R^2 = H; m.p. = 478–479 °C (sinters above 448 °C)
(d) R = $R^1 = C_6H_5$; R^2 = Cl; m.p. = 492–495 °C (sinters above 480 °C)

The *o*- and *m*-diethynylaromatic compounds also react to give the compounds *(21)–(24)*.

The constitution of the compounds *(17)–(24)* was readily verified by elementary analysis and from the IR spectra[52]. The formulation was based on the most favorable steric arrangement of the rings as found from models.

(17c) and *(17d)* have no stereoisomers while several conformations are conceivable for *(17a)* and *(17b)* as well as

[42] *W. S. Rapson, R. G. Shuttleworth,* and *J. N. Niekerk,* J. chem. Soc. (London) *1943*, 326.

[43] *W. Dilthey, W. Schommer,* and *O. Trösken,* Ber. dtsch. chem. Ges. *66*, 1627 (1933).

[44] *W. Dilthey, W. Schommer, W. Höschen,* and *H. Dierichs,* Ber. dtsch. chem. Ges. *68*, 1159 (1935).

[45] *W. Ried* and *K. H. Bönnighausen,* Chem. Ber. *93*, 1769 (1960).

[46] *M. A. Ogliaruso* and *E. I. Becker,* J. org. Chemistry *30*, 3354 (1965).

[47] *M. A. Ogliaruso, L. A. Shadoff,* and *E. I. Becker,* J. org. Chemistry *28*, 2725 (1963).

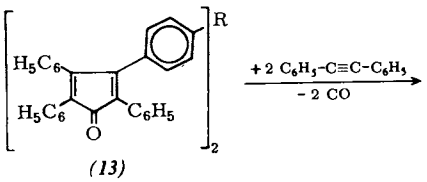
[48] *W. Ried, H.-J. Schmidt,* and *A. Urschel,* Chem. Ber. *91*, 2472 (1958).

[49] *W. Ried* and *K. Wesselborg,* Naturwissenschaften *46*, 142 (1959).

[50] See also *W. Ried,* Angew. Chem. *76*, 933, 973 (1964).

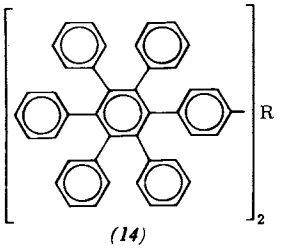
[51] *W. Ried* and *V. B. Saxena,* Angew. Chem. *80*, 366 (1968); Angew. Chem. internat. Edit. *7*, 378 (1968).

[52] *K. H. Bönnighausen,* Dissertation, Universität Frankfurt/M., 1959.

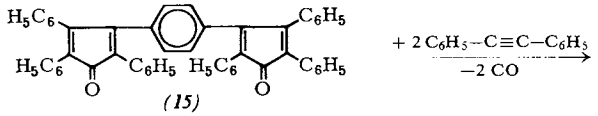


(13)

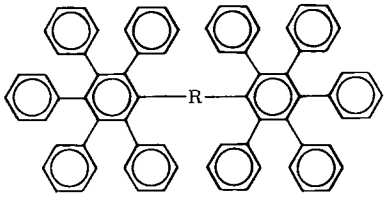
	R
(13a)	$-CH_2-$
(13b)	$-(CH_2)_2-$
(13c)	$-(CH_2)_3-$
(13d)	$-(CH_2)_4-$
(13e)	$-(CH_2)_5-$
(13f)	$-(CH_2)_6-$
(13g)	$-O-$
(13h)	$-S-$
(13i)	—



(14)

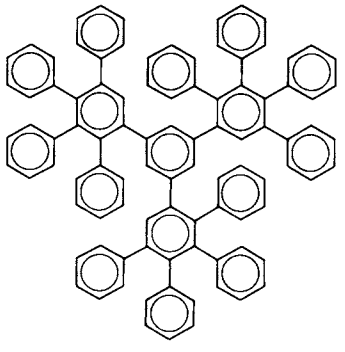


(15)

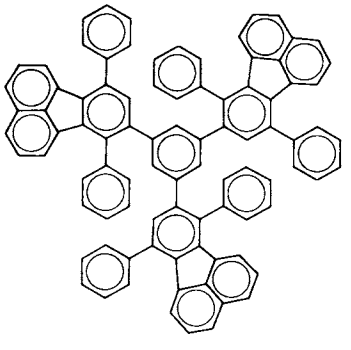


(16), R = *p*-C_6H_4

for *(18)–(24)*. However, the differences are evident only if rotation is restricted. An X-ray analysis[53] that has been started for *(17c)* and *(25)* should provide information about the steric arrangement.

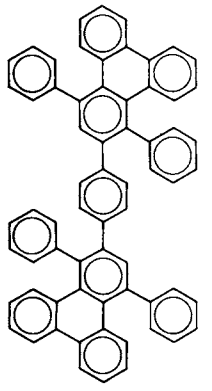


(25), m.p. = 374-375°C

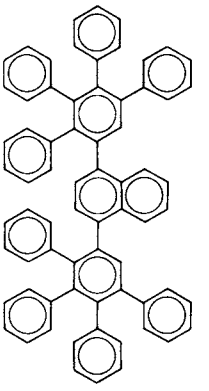


(26), m.p. = 296-301°C

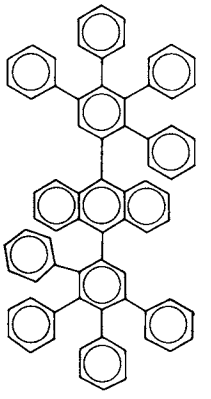
[53] *G. Habermehl*, Organisch-chemisches Institut der Technischen Hochschule Darmstadt.



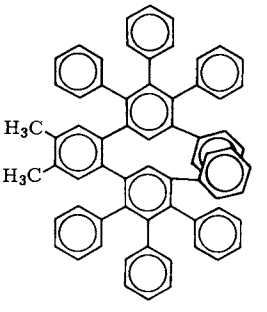
(18), m.p. = 411-413°C



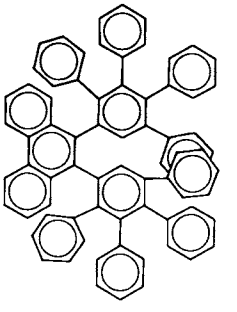
(19), m.p. = 368-370°C



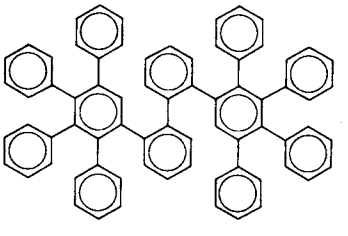
(20), m.p. = 404-406°C



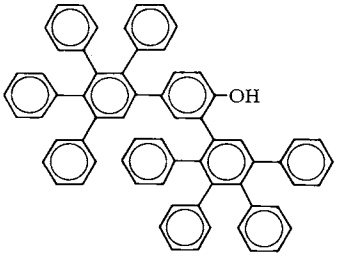
(21), m.p. = 377-379°C



(22), m.p. = 295-296°C



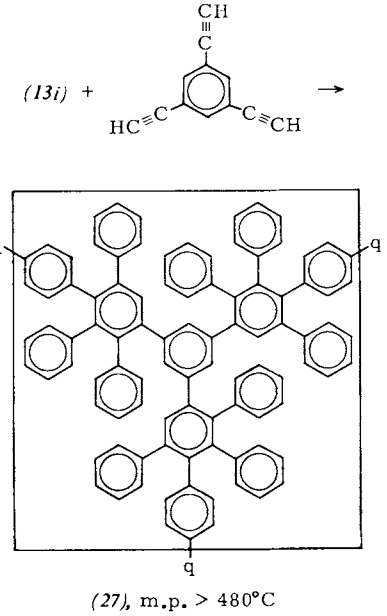
(23) [51], m.p. = 238-240°C



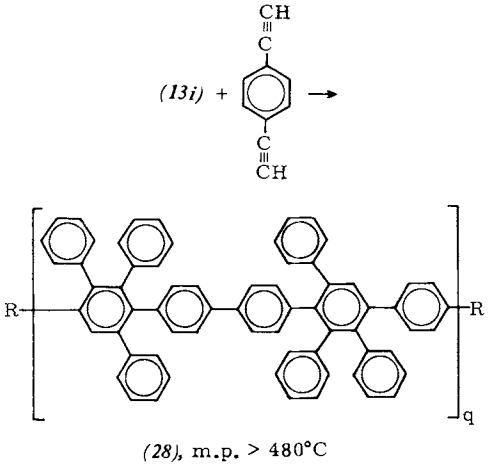
(24), m.p. = 393-396°C

Kern et al. [54] have already reported the preparation of branched oligophenyls by cyclotrimerization. We obtained the oligophenyls *(25)* and *(26)* quantitatively by Diels-Alder reactions of 1,3,5-triethynylbenzene [55] with cyclopentadienones. Both products [56] have a specific, star-shaped structure. The structures indicated are verified by elementary analysis, molecular weight determinations, and their IR spectra.

2,2′,4,4′,5,5′-Hexaphenyl-3,3′-bicyclopentadienyl-1,1′-dione *(13i)* reacts with diethynylbenzene and triethynylbenzene with elimination of CO and formation of the oligo- and polyphenyls respectively [56] *(28)* and *(27)*.



(27), m.p. > 480°C

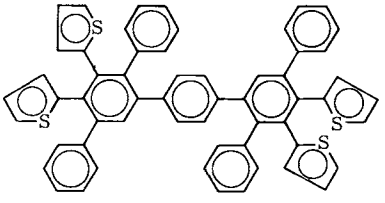


(28), m.p. > 480°C

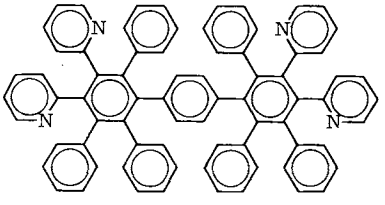
The IR spectrum of *(28)* still shows a weak carbonyl band at 1689 cm^{-1}, but no C≡C band at ≈2200 cm^{-1}; the end groups are therefore assumed to be *(13i)* groups. Nonlinear linkage of the benzene rings in *(28)* is thought to be unlikely because of its extremely high melting point (> 480 °C). *Stille et al.* [56a] have also synthesized *(28)* and found the molecular weight of the polymer to be ≈40000. Clear films, which are stable in air up to 550 °C, were prepared from *(28)*. The good agreement of the IR spectra of *(25)* and *(27)* supports the formulation *(27)*, particularly since the constitution of the model substance *(25)* has been definitely established. Further methods for the preparation of polyphenyls will be discussed in Section 8.

7.3. Preparation of Oligophenyls with Hetero Atoms

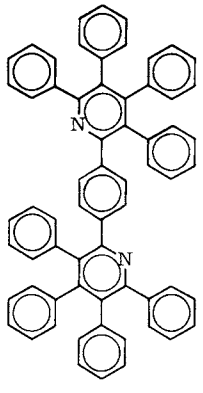
The oligophenyls *(29)* [57] and *(30)* [58], which contain hetero atoms, have recently been prepared by classical diene syntheses from heterocyclically substituted cyclopentadienones or their hydrates.



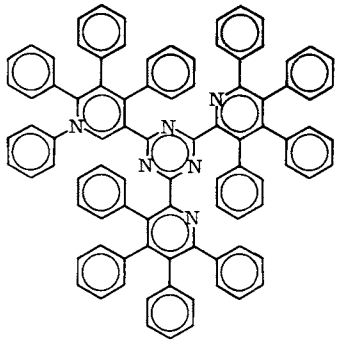
(29), m.p. = 395-397°C



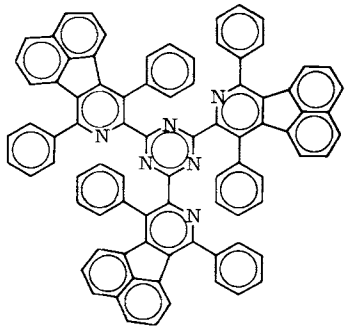
(30), m.p. = 488-490°C



(31), m.p. = 366-369°C



(32), m.p. = 208-213°C



(33), m.p. = 472°C (decomp.)

[54] *H. O. Wirth, W. Kern*, and *E. Schmitz*, Makromolekulare Chem. *68*, 69 (1963).

[55] *W. Hübel* and *R. Merényi*, Angew. Chem. *74*, 781 (1962); Angew. Chem. internat. Edit. *1*, 781 (1962).

[56] *W. Ried* and *D. Freitag*, Naturwissenschaften *53*, 305, 306 (1966); *D. Freitag*, Dissertation, Universität Frankfurt/M., 1967.

[56a] *J. K. Stille, F. W. Harris, R. D. Rakutis*, and *H. Mukamal*, J. Polymer Sci., Part B *4*, 791 (1966); *H. Mukamal, F. W. Harris*, and *J. K. Stille, ibid.* Part A *1*, 2721 (1967).

[57] *W. Ried* and *A. Göbel*, Chem. Ber. *100*, 3405 (1967).

[58] *P. Bergmann* and *H. Paul*, Chem. Ber. *100*, 828 (1967).

Tetracyclone reacts in the same manner[59] with terephthalodinitrile to give *(31)* and with tricyano-*s*-triazine to give *(32)*. *(33)* has been prepared from acecyclone (diphenylnaphthopentalenone) and tricyano-*s*-triazine[59].

7.4. Properties

As expected, the melting point decreases with increasing aliphatic content in the series of highly arylated systems *(14a)–(14f)*. The compound *(16a)*, in which the rotation of the outer rings is largely blocked by the substituents, has a particularly low melting point. The electronic spectra of the oligophenyls *(14a)–(14h)* show no fine-structure splitting, and like the spectrum of hexaphenylbenzene, they have a principal absorption band at 247 nm. The molar extinction coefficient of the oligophenyls is about double that of hexaphenylbenzene. These observations[46] show that the spectral properties of the molecules *(14a)–(14h)* are almost additively those of two unconjugated hexaphenyl units.

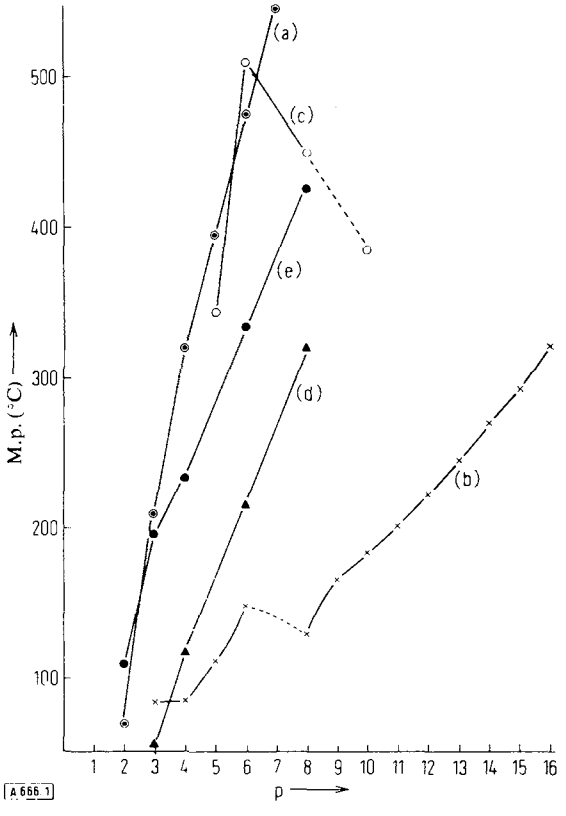


Fig. 1. Melting points of the oligophenyls and oligophenylenes as a function of the degree of condensation *p*.

(a) *p*-oligophenyls; (b) acyclic *m*-oligophenyls; (c) cyclic *m*-oligophenylenes; (d) acyclic *o*-oligophenyls; (e) cyclic *o*-oligophenylenes.

It can be seen from Figure 1 that the melting points of the oligophenyls and oligophenylenes depend mainly on the nature of the linkage, and less on the number of rings. The highest values are found for the *p*-oligophenyls.

An additional increase is obtained by symmetrical arylation, as is shown by a comparison of the melting points of hexaphenyl- and octaphenyl-*p*-quinquephenyl *(17a)* and *(17c)* (417–418 and 478–479 °C respectively) and of *p*-quinquephenyl (395 °C). A further, though small, improvement is achieved by halogenation [tetrachlorooctaphenyl-*p*-quinquephenyl *(17d)* melts at 492–495 °C].

With increasing steric hindrance [cf. octaphenyl-*p*-quaterphenyl *(16a)* and hexaphenyl-*p*-quinquephenyl *(17a)*], the increased bulk of the molecule leads to a decrease in the packing density in the lattice, and hence to a decrease in the enthalpy of fusion $(\Delta H)_f$, so that the melting point is lower. The relationship[20] between the melting point T_f, the enthalpy of fusion $(\Delta H)_f$, and the entropy of fusion $(\Delta S)_f$ can be expressed by equation (3):

$$T_f = (\Delta H)_f/(\Delta S)_f \qquad (3)$$

This equation shows that a disturbance of symmetry due to substitution [compare *(17a)* with *(29)* and *(31)*, *(17c)* with *(30)*, *(25)* with *(32)*, and *(26)* with *(33)*] results in an increase in entropy $(\Delta S)_f$ and hence to depression of the melting point at constant $(\Delta H)_f$. However, since $(\Delta H)_f$ changes, the melting point can be predicted only if the enthalpy and entropy terms are accurately known.

The oligo- and polyphenyls *(27)* and *(28)* are extremely heat-resistant for organic molecules (m.p. > 480 °C). The ready solubility of *(28)* in benzene is also interesting.

The UV spectra of the compounds *(17a)*, *(23)*, and *(25)* (in 1,2-dichloroethane) show a hypsochromic shift of the absorption bands from 255 through 248 to 244 nm. *(28)* has two absorption maxima at 250 and 310 nm, which probably result from the superposition of the electronic spectra of the hexaphenyl-*p*-quinquephenyl unit and the end groups R.

The arylated oligophenyls have proved to be very useful in gas chromatography[60]. Separating columns with solid (*e.g.* graphitized carbon black) as the stationary phase, when coated with less than a unimolecular layer of octaphenyl-*p*-quinquephenyl *(17c)*, are more reliable and more efficient than uncoated graphitized carbon black for the separation of gas mixtures. Strongly polar substances such as aniline derivatives and esters of fatty acids can also be separated at much lower temperatures. The thermal stability of the resulting columns is extremely good. Their properties were unchanged after a long test period (more than two months) at an analysis temperature of 450–480 °C.

8. *p*-Polyphenyls

It can be seen from Figure 1 that *p*-polyphenyls should be very suitable where maximum thermal stability is required. This conclusion has led to attempts to synthesize them in various ways.

Edwards and *Goldfinger*[61] obtained a "*p*-polyphenyl" having a molecular weight of 2700–2800 by condensation of *p*-dichlorobenzene in the presence of a liquid sodium-potassium alloy (KNa_2); however, the physical properties of the polymer showed that the rings were linked only predominantly, but not entirely, in the *p*-position. Despite these defects, the polyphenyl does not melt below 550 °C.

Kern et al. tried to obtain methyl-substituted *p*-polyphenyls having uniform structures from methylated

[59] *A. Göbel*, Dissertation, Universität Frankfurt/M., 1967.

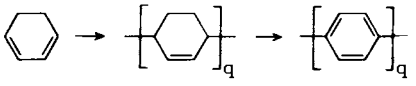
[60] *F. A. Holdinghausen, D. Freitag, W. Ried*, and *I. Halász*, Angew. Chem. *80*, 754 (1968); Angew. Chem. internat. Edit. *7*, 724 (1968).

[61] *G. A. Edwards* and *G. Goldfinger*, J. Polymer Sci. *16*, 589 (1955).

dihalogenoaromatic compounds by the Ullmann synthesis with copper [62], by the Wurtz-Fittig synthesis with sodium [19], and by the Kharasch synthesis with magnesium and anhydrous heavy metal chlorides [63].

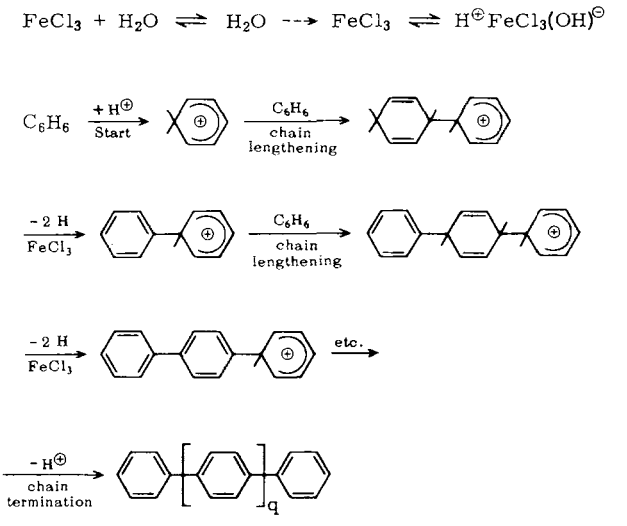
The reactions led [64] to soluble macromolecular products, but in addition to the desired *p*-linkages these also contained other linkages and exhibited branching. The methylated polyphenyls obtained by the Ullmann method had the highest melting point (290–310 °C).

Marvel et al. [65, 66] obtained polycyclohexene by polymerization of 1,3-cyclohexadiene with Ziegler catalysts or with cationic initiators; treatment with chloranil or halogenation followed by pyrolysis then gave *p*-polyphenyl (molecular weight 7000–8000) containing some incompletely aromatized units.



The polymeric products are dark brown to black (depending on the experimental conditions), infusible, and stable up to about 530 °C.

Kovacic and *Koch* [67] obtained a *p*-polyphenyl having similar properties in a single reaction step by oxidative cationic polymerization of benzene. The authors assumed that the reaction proceeds in accordance with Scheme 1.



A very recent method [4] that has proved a convenient route to *p*-polyphenyls is the oxidative coupling of benzene with chlorine. Natta-Ziegler catalysts react with benzene in this process to give a complex. The subsequent treatment with chlorine gas yields a yellow-brown *p*-polyphenyl having a softening point higher than 500 °C. Investigations on the stabilization of the complex with suitable co-catalysts and on the processing of the polymeric products are being carried out at present.

The author is grateful to the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft, Farbwerke Hoechst AG, Farbenfabriken Bayer AG, and Badische Anilin- und Soda-Fabrik for their support of his work in this field.

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Translated by Express Translation Service, London

[62] *W. Kern* and *R. Gehm*, Angew. Chem. *62*, 337 (1950).

[63] *W. Kern*, *R. Gehm*, and *M. Seibel*, Makromolekulare Chem. *15*, 170 (1955).

[64] *R. Gehm*, Acta chem. scand. *5*, 270 (1951).

[65] *C. S. Marvel* and *G. E. Hartzell*, J. Amer. chem. Soc. *81*, 448 (1959).

[66] *D. A. Frey*, *M. Hasegawa*, and *C. S. Marvel*, J. Polymer Sci., [Part A *1*, 2057 (1963).

[67] *P. Kovacic* and *F. W. Koch*, J. org. Chemistry *28*, 1864 (1963).

Trends in Radiation Polymerization

BY R. C. POTTER, CHRISTEL SCHNEIDER, M. RYSKA, AND D. O. HUMMEL[*]

Dedicated to Professor K. Ziegler on the occasion of his 70th birthday

Previously it was generally assumed that high energy radiation could only initiate radical polymerization in solutions of monomers. However, examples of radiation-induced polymerization have recently become known that proceed via an ionic mechanism. Thus, solutions of a monomer can be polymerized ionically, preferably in the presence of a solid, at low temperatures. Surprisingly, this may also be accomplished with ultra-pure, mainly anhydrous systems, even at room temperature. The nature of the ions has not yet been fully elucidated.

1. Introduction

Probably going largely unnoticed by the community of polymer chemists has been the progression of the startling and exciting developments over the last ten years in the area of radiation-initiated polymerization. New instruments, refined techniques, inspired research, and an occasional sprinkling of serendipity have produced a renaissance in what was once thought to be a thoroughly explored field.

By 1957, most of the common monomers had been polymerized using high energy radiation. In order to determine the mechanism of reaction, the kinetics of radiation-initiated processes were compared with the kinetics of conventionally initiated free radical and ionic polymerization. For instance, since the dose rate of radiation, (I), is exactly analogous to catalyst concentration, (C), one would expect that for a radiation-induced free radical mechanism, the rate (R_p) and the average degree of polymerization ($\overline{DP}$) would obey the following relationships.

$$R_p \sim I^{0.5}$$

$$\overline{DP} \sim I^{-0.5}$$

Indeed it was observed that such was the case. Furthermore, experimentally determined temperature coefficients conformed to those predicted for a free radical process in which the formation of active species in the initiation step was independent of temperature. Additional evidence favoring a radical mechanism was obtained from scavenger studies and copolymerization experiments. Without exception, it appeared that a free radical mechanism could be ascribed universally to radiation polymerizable monomers.

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Throughout the course of these studies, there gradually developed a picture of the events which take place in the interaction of ionizing radiation with covalently bonded molecules. This scheme of events remains valid today, although the importance of some of the reactions has had to be re-evaluated. Bearing this in mind, let us now consider this chain of reaction events.

2. Introduction to Radiation-Chemical Mechanisms

An incident photon may cause either ionization or excitation of a molecule AB.

$$AB + h\nu \rightarrow AB^+ + e^- + h\nu' \quad (1)$$

$$AB + h\nu \rightarrow AB^+ + e^- \quad (2)$$

$$AB + h\nu \rightarrow AB^* + h\nu'' \quad (3)$$

Equation (1) depicts classical Compton scattering, wherein the photon imparts sufficient kinetic energy to an orbital electron so that it is ejected from the molecule. Emerging from this encounter with a somewhat longer wavelength and a different direction of travel, the photon may interact further with AB by either additional Compton scattering or photoelectric absorption [eq. (2)]. In the case of photoelectric absorption, the energy of the photon is so low that it is all imparted to the electron. However, most experimental work utilizes γ rays from ^{60}Co, and since these transfer their energy [*] primarily by Compton scattering (in materials of low atomic number), reaction (2) is of relatively little importance as a primary process. Also the dimensions of experimental samples are usually smaller than the mean free path of a 1 MeV γ ray [as, for instance, might result from reaction (1)], which is of the order of 15 cm in material of unit density. Therefore, multiple interactions of a given γ ray within the sample are rather improbable.

[*] 1.33 and 1.17 MeV.

In some cases the energy transferred by the incident photon is insufficient to cause the ejection of an electron. Instead, the energy level of the molecule is raised above the equilibrium level to an excited state [eq. (3)]. However, since the reaction can involve no more than 3 to 4 eV per reaction step without rupturing covalent bonds, as contrasted with energies of the order of MeV involved in reaction (1), it is relatively unimportant as a means of depositing energy in the sample.

Compton "recoil electrons" usually possess sufficient energy to cause further ionization and excitation, according to the following reaction scheme:

$$AB + e_i^- \rightarrow AB^+ + e_{i'}^- + e_j^- \quad (4)$$

$$AB + e_i^- \rightarrow AB^* + e_{i''}^- \quad (5)$$

e_i^- is an incident, high energy electron formed in reaction (1); $e_{i'}^-$ is the same electron now of lower energy owing to ionization of the substrate molecule AB; e_j^- is the electron ejected in the ionization process; and $e_{i''}^-$ is also a lower energy state of the incident electron e_i^- resulting from an inelastic collision with a substrate molecule, and forming an excited molecule AB*.

If electrons $e_{i'}^-$, $e_{i''}^-$, or e_j^- have sufficient kinetic energy to escape Coulombic interaction with AB^+, they may produce further ionization and excitation, their energy approaching the thermal level more closely on each interaction. On the other hand, a scattered or ejected electron of low energy will be captured by AB^+. Thus, depending on the environment of the electron when it reaches thermal energy and on other factors, such as electron affinity of the substrate molecule, the following processes are possible:

$$AB^+ + e_{thermal}^- \rightarrow AB^{**} \quad (6)$$

$$AB + e_{thermal}^- \rightarrow AB^- \quad (7)$$

The absorption coefficients of γ rays and electrons of about the same energy are in the approximate ratio of 1:100 to 1:1000. When this fact is considered in conjunction with reactions (1) through (7), it may be seen that the vast majority of the energy deposited by γ rays from ^{60}Co in a small sample of almost unit density and low atomic number will result from reactions (4) and (5), which in turn are initiated by reaction (1).

The excited molecules produced by the above reactions are unstable and may decompose into molecular species, normal (or excited) radicals, or ions (AB* and AB** now being equally depicted as AB*):

$$AB^* \rightarrow A^\cdot + B^\cdot \quad (8)$$

$$AB^* \rightarrow A + B \quad (9)$$

$$AB^* \begin{cases} \nearrow A^+ + B^- \\ \searrow A^- + B^+ \end{cases} \quad (10)$$

However, reactions (8) and (9) are favored because less energy is required for homolytic scission [eq. (8)] than for heterolytic scission [eq. (10)]. Also the available energy is usually insufficient to prevent immediate recombination of the ion pair generated by reaction (10).

In summary, then, ions may be produced both directly and indirectly by radiation. However, free radicals are strictly an indirect product from the interaction of radiation with matter.

The very earliest theoretical arguments[1] supported a free radical mechanism of polymerization by advancing the view that large ions would probably be unstable and, further, by emphasizing that free radicals are an important by-product from the decay of excited molecules. The observation that thermalized recoil electrons [from reactions (1) and (4)] do not, on the average, escape recombination with positive ions, even in a solvent of such high dielectric constant as water[2] not only seemed to preclude the formation of free ions by reactions (1) and (4), but also minimized the formation of free ions by reactions due to electron solvation [eq. (7)]. Furthermore, calculations showed that the time required for thermalization followed by charge neutralization is short (*ca.* 10^{-13} seconds in water[2]). Thus, after a primary radiation event a population of excited molecules arises rapidly and exclusively through charge neutralization and direct excitation. As has already been mentioned, these excited molecules preferentially decay into free radicals.

Seemingly, then, there was no fundamental question in the field of radiation polymerization remaining to be investigated. An indication of the prevailing consensus is conveyed very well by *Chapiro*. He notes in the preface to his volume on the radiation chemistry of polymeric systems that his original manuscript contained a detailed argument which "not only showed that ionic processes had never been observed under irradiation but also conclusively demonstrated why radiations could not initiate ionic polymerization"[3].

3. Low-Temperature Polymerization

In 1957, *Magat* commented on the paradox that "ionizing" radiation seemed to be incapable of initiating ionic polymerization[4]. He challenged the idea that electron-neutralization times would be as short as 10^{-13} sec, especially if the irradiation were to be conducted at low temperature. Employing the Platzman-Frohlich model[5, 6], he calculated that a reduction in temperature from 300 to 100 °K corresponds to a thirty-fold increase in the distance between the parent ion and its thermalized electron. The increased ion-lifetimes under such conditions were deemed sufficient to sustain long-chain ionic propagation.

At just this time, the radiation-induced cationic polymerization of isobutene at low temperature[7] was

[1] *H. Eyring, J. O. Hirschfelder*, and *H. J. Taylor*, J. chem. Physics *4*, 479 (1936).

[2] *A. H. Samuel* and *J. L. Magee*, J. chem. Physics *21*, 1080 (1953).

[3] *A. Chapiro*: Radiation Chemistry of Polymeric Systems. Interscience, New York 1962.

[4] *M. Magat*, Collect. czechoslov. chem. Commun. *22*, 141 (1957).

[5] *R. L. Platzman* and *H. Frohlich*, Physic Rev. *92*, 1151 (1953).

[6] *R. L. Platzman*: Basic Mechanisms in Radiobiology. Nat. Res. Council Publication 305, Washington 1953, p. 22.

[7] *W. H. T. Davison, S. H. Pinner*, and *R. Worrall*, Chem. and Ind. *1957*, 1274.

discovered. A great deal of evidence was amassed in support of an ionic mechanism, including a linear dose rate dependence[8], ionic copolymerizations[9,10], and inhibition by diisobutene[11] (which also inhibits the conventional ionic reaction). Although other scavenger studies did lead to some conflicting results (*e.g.*, retardation by benzoquinone[12]), these results were, nevertheless, reconcilable with an ionic reaction.

Magat also predicted that the presence of electrophilic solvents and/or inorganic solids in a reaction system would further facilitate ion propagation[4,13]. Thus he necessarily emphasized the importance of reaction (7) (electron solvation with monomer or solvent molecules) and the possibility of electron entrapment in a crystal defect:

$$e_{thermal} + \text{Solid} \rightarrow \text{F-center} \qquad (11)$$

Such strategems did, indeed, enhance the low-temperature polymerization rate (R_p) of isobutene[3]. The addition of zinc oxide to the system was especially successful in increasing R_p[14,15]. When the same reasoning was extended to styrene, similar results were obtained. For instance, when styrene was irradiated at −78 °C, it polymerized rapidly in methylene chloride[16,18], ethyl chloride[9], and 1,1- or 1,2-dichloroethane[17]. The polymerization rate was directly proportional to the dose rate ($R_p \sim I^{1.0}$) and the presence of oxygen or benzoquinone did not affect the reaction[17,18]. In addition, the reaction was accelerated by the presence of such solid additives as silica or zinc oxide[19].

Since these initial discoveries, the same techniques have been used to ionically polymerize and copolymerize some fifty monomers. In most cases, the investigators were content to merely establish the fact that one could induce an ionic mechanism in a certain monomer. Thus, one frequently encounters the statement in the literature that "monomer X polymerizes by an ionic mechanism at low temperature in the liquid phase but the normal free radical mechanism predominates at room temperature". Typically such

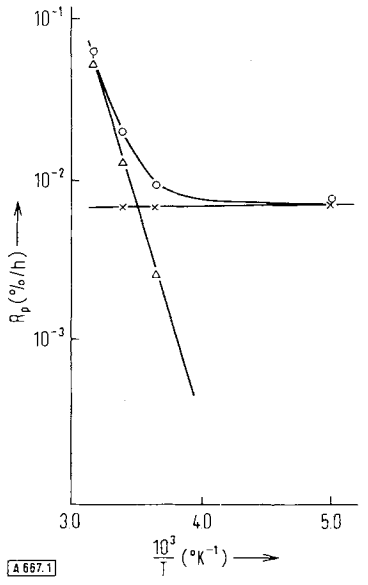


Fig. 1. Radiation polymerization of isoprene [20]: Radical and ionic contributions to the rate were distinguished by means of diphenyl picryl hydrazyl (DPPH): × — × experiments with DPPH; ○ — ○ experiments without DPPH; Δ — Δ experiments with pyridine. In this system radical polymerization is faster than ionic polymerization.

behavior is illustrated by a two-segment Arrhenius diagram (*e.g.*, see Fig. 1). Another frequent illustration is provided by the difference in copolymerization parameters between −78 and 0 °C (*e.g.*, see Table 1).

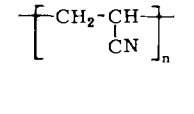
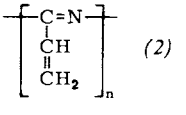
Table 1. Monomer reactivity ratios in copolymerization of isobutene (r_1) and vinylidene chloride (r_2) [9].

T (°C)	r_1	r_2
−78	25	0
−40	1.27	0.21
0	0.03	1.3

With few exceptions little has been done in the way of truly enlightening kinetic studies.

On γ-irradiation of the novel system of acrylonitrile in liquid ethylene at −78 °C[21,22], a maximum in R_p was observed at the highest acrylonitrile concentration and the reaction is completely inhibited by a radical scavenger such as pyrogallol.

The infrared spectrum of the resultant polymer corresponds to a reaction through the vinyl group as in *(1)*. The reaction

(1)   *(2)*

rate passes through a minimum at the equimolar concentration of the monomers and then reaches a second maximum at a very low concentration of acrylonitrile. In this region of low acrylonitrile concentration, pyrogallol has no appreciable effect on the reaction, the acrylonitrile polymerizing through the nitrile group to yield *(2)*.

[8] *W. H. T. Davison, S. H. Pinner,* and *R. Worrall,* Proc. Roy. Soc. (London), Ser. A *252,* 187 (1959).

[9] *A. P. Sheinker et al.,* Doklady Akad. Nauk SSSR *124,* 632 (1959).

[10] *A. D. Abkin, A. P. Sheinker,* and *L. P. Mezhirova,* Russ. J. physic. Chem. (English translation of Ž. fiz. Chim.) *33,* 2636 (1959).

[11] *C. P. Brown* and *A. R. Mathieson,* J. chem. Soc. (London) *1959,* 3612.

[12] *E. Collinson, F. S. Dainton,* and *H. A. Gillis,* J. physic. Chem. 63, 909 (1959).

[13] *M. Magat,* Makromolekulare Chem. *35,* 159 (1960).

[14] *R. Worrall* and *A. Charlesby,* Int. J. appl. Radiat. Isotopes *4,* 84 (1959).

[15] *R. Worrall* and *S. H. Pinner,* J. Polymer Sci. *34,* 229 (1959).

[16] *S. Okamura* and *S. Futami,* Int. J. appl. Radiat. Isotopes *8,* 46 (1960).

[17] *A. Chapiro* and *V. Stannett,* J. Chim. physique Physico-Chim. biol. *56,* 830 (1959).

[18] *S. Okamura, T. Higashimura,* and *S. Futami,* Isotopes and Radiation (Japan) *1,* 216 (1958).

[19] *A. Charlesby,* Lecture at Miller-Conference, North Wales 1961.

[20] *Y. Tabata, R. Shimozowa,* and *S. Hitoshi,* J. Polymer Sci. *54,* 201 (1961).

[21] *Y. Tabata, K. Hara,* and *H. Sobue,* J. Polymer Sci., Part A *2,* 4077 (1964).

[22] *Y. Tabata* and *H. Sobue,* Ann. Rep. JARRP (Japanese Association for Radiation Research on Polymers) *2,* 303 (1960).

Although the role of ethylene (mere solvent or reactive component) and the extent to which it influences the reaction is not clear, it is apparent that the presence of ethylene facilitates a changeover in reaction mechanism. Thus, it is believed that at low acrylonitrile concentration the reaction proceeds by an anionic mechanism. As the concentration increases, however, the reaction becomes progressively free-radical in character.

Despite the implications of *Magat*'s reasoning, many workers have assumed that the propagating ions in these systems are associated with some type of gegenion as in a normal catalytic polymerization. However, *Geymer* has suggested that free ions are the participating species [23]. He points out that a carbonium ion-electron pair in close proximity would be rapidly neutralized by quantum mechanical tunneling. It is then inconceivable that the lifetime of such a pair would permit a DP of 10^5, as has been observed for isobutene [8]. Furthermore this is an irreversible reaction since the neutralization of a polymeric carbonium ion releases about 5 eV of energy.

In another study relating to free ions, the effect of a strong electric field has been examined for the low-temperature cationic polymerization of styrene in methylene chloride [24]. It was found that the electric field increases R_p and has no effect on DP, which seemed to indicate that the number of initiating sites is increased. This phenomenon was explained by assuming a free ion mechanism wherein the population of stable propagating carbonium ions is increased because of the comparatively easy migration of electrons or solvated electrons towards the anode. On the other hand, the radiation-initiated anionic polymerization of methyl methacrylate in isopropylamine and acrylonitrile in triethylamine (at $-78\,^{\circ}C$) is retarded by the application of an electric field. Since the formation of propagating anions would depend upon electron solvation, this result gives further indication that there are fewer electrons available for reaction.

These studies have provided more evidence for the existence of ions in radiation polymerization. Also, on the basis of subsequent conductivity measurements it has been estimated that the lifetime of the styryl cation in the system is from 10^{-1} to 10^{-2} sec, which is quite sufficient for a long chain reaction to take place [25].

Some work has been done to investigate the role of solid additives. It has been found that during irradiation the conductivity of zinc oxide increases when isobutene is adsorbed on its surface [26]. This is believed to be due to the formation of positive "holes" within the zinc oxide as a consequence of irradiation. By means of the semiconductor effect these holes can then travel to the surface of the solid and abstract electrons from the isobutene molecules. Contrary to this idea, *Charlesby* has suggested that the carbonium ions are formed in the liquid phase and then become propagation sites by adsorption on the zinc oxide surface [27]. There is also the third possibility of electron trapping, which was the original proposal of *Magat*.

Interestingly, the addition of nickel oxide or magnesium oxide (which, just as zinc oxide, are p-type semiconductors) sharply increases R_p for the low-temperature anionic polymerization systems of methyl methacrylate and acrylonitrile [28]. Also, the rate of copolymerization of acrylonitrile with methyl methacrylate at $-50\,^{\circ}C$ is increased by about an order of magnitude by addition of magnesium oxide. The explanation of such results would require yet another hypothesis regarding the working of solid additives.

As might be expected, the use of various solvents in these ionic polymerizations yields varying results. Thus the rate of acrylonitrile polymerization is much higher in electron donating solvents than in electron withdrawing solvents [29]. However, the results are not always so predictable. For example, an equimolar feedstock of styrene and methyl methacrylate yields an equimolar copolymer in bromoethane, while one containing 91 mole-% styrene was obtained in dichloromethane [30]. Also the copolymerization of formaldehyde and styrene takes place in bulk and in dichloromethane, whereas in diethyl ether there is only homopolymerization of the formaldehyde [31].

4. Ultra-pure Systems

Without exception, the ionic polymerizations mentioned in Section 3 were carried out under "extreme" conditions. That is, they were performed at very low temperature (to favor ionic over free radical propagation), and sometimes with an added second phase (to act as an electron trap) or a homogeneously distributed second component of reasonably high dielectric constant (to promote ion stabilization). At normal temperatures, one could always rely upon the species of propagation as being free radicals.

However, in 1960 even this inviolable rule was put to rest by a remarkable discovery made at Brookhaven National Laboratory. *Metz*, having need of very pure polystyrene, turned to the catalyst-free technique of radiation preparation. In particular, special precautions were taken so that the monomer was extremely pure and dry before irradiation. The subsequent polymerization gave the astounding indications of proceeding, not by a radical mechanism, but by an ionic mechanism at *room temperature*, as evidenced by enhanced rates of reaction (as high as thirty times the previously observed free radical reaction rate), independence of molecular weight of dose rate, and extreme sensitivity to impurities, especially traces of water [32, 33].

[23] *D. O. Geymer*, Polymer Preprints *5* No. 2, 942 (1964).

[24] *M. Sakamoto*, *K. Hayashi*, and *S. Okamura*, Ann. Rep. JARRP (Japanese Association for Radiation Research on Polymers) *5* (1963–1964), AEC-tr-6565, p. 199.

[25] *I. Sakurada*, *N. Ise*, and *S. Kawabata*, Makromolekulare Chem. *97*, 17 (1966).

[26] *T. I. Barry* and *K. Klier*, Discuss. Faraday Soc. *31*, 219 (1961).

[27] *A. Charlesby* and *J. Morries*, Proc. Roy. Soc. (London), Ser. A *273*, 387 (1963).

[28] *L. P. Mezhirova*, *A. P. Sheinker*, and *A. D. Abkin*, Doklady Akad. Nauk SSSR *158*, 1159 (1964).

[29] *A. D. Abkin*, *A. P. Sheinker*, and *L. P. Tolstovkhova* in *J. Dobo* and *P. Hedvig*: Proceedings of the Second Tihany Symposium on Radiation Chemistry. Akademiai Kiado, Budapest 1967, pp. 463–9.

[30] *Y. Tsuda*, J. Polymer Sci. *54*, 193 (1961).

[31] *Y. P. Castille* and *V. Stannett*, J. Polymer Sci., Part A-1 *4*, 2063 (1966).

[32] *C. L. Johnson* and *D. J. Metz*, Polymer Preprints *4*, 440 (1963).

[33] *D. J. Metz*: Trans. Amer. nuclear Soc. *7*, 313 (1964).

During the early 1960's *Metz*[34], *Williams*[35,36,38], and *Hirota*[37] independently investigated pure, anhydrous α-methylstyrene, which was believed to polymerize conventionally only by an ionic mechanism. Normally under irradiation at room temperature, this monomer had polymerized very slowly and yielded a low molecular weight polymer. However, under the conditions of extreme purity the rate increased considerably and a material of much higher molecular weight was formed.

Only in the last two years has this field truly matured. The schools of *Metz*, *Williams*, and *Okamura* have provided the literature with a great outpouring of papers which have probed the subject at depth. The most detailed research efforts have been concerned with the further investigation of styrene[39–46,60]. However, a number of other highly purified monomers have been shown to be susceptible to ionic polymerization at room temperature, including β-pinene[35,36,38], isobutyl vinyl ether[47], 1,2-epoxycyclohexane[48,67], nitroethylene[49,51], and molten trioxane[50,66].

4.1. Techniques of Purification

Generally, the various purification schemes for preparing these ultrapure monomers have four steps in common, all of which are performed in a vacuum environment: distillation of monomer; vacuum bake-out of apparatus; degassing of monomer; and contacting of monomer with a drying agent such as activated silica gel, Na-K alloy, or barium oxide. As might be anticipated for an ionic polymerization these elaborate schemes do not always yield reproducible results. However, for the styrene and α-methylstyrene systems, reproducibility has ultimately been attained[41–45,60]. For this case, it is interesting to note that styrene at 0 °C, when exposed to ^{60}Co γ-rays at a dose rate of 1 Megarad/h, polymerizes at a rate of 940 %/h, compared to the classical free radical value of 0.2 %/h for these conditions (see Fig. 2).

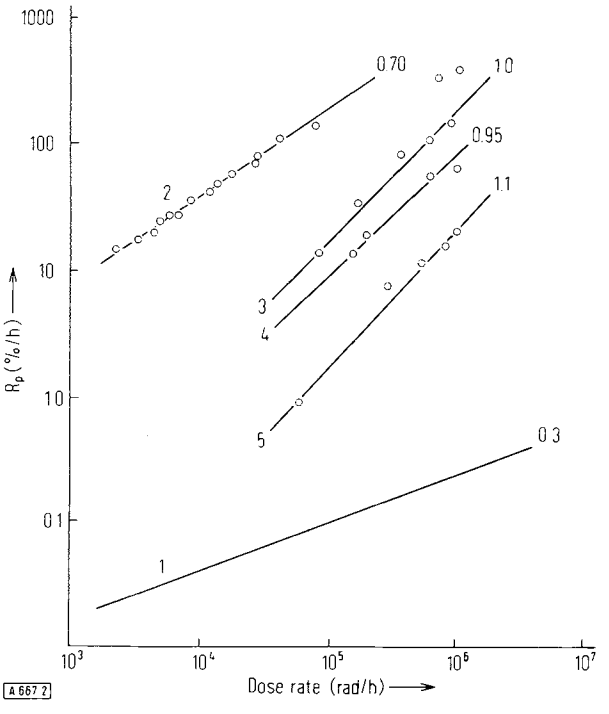


Fig. 2. γ-Induced polymerization of styrene at 0 °C. Curve 1: classical inverse-power radical polymerization (calculated); curve 2: reproducible results from four independent dilatometer determinations [41]; curves 3–5: previous non-reproducible results from three independent dilatometer determinations [40]. Values of x for the relation $R_p \sim I^x$ are given on the right-hand side of each curve.

4.2. Evidence for the Formation of Ions

At this point, it is worthwhile to conjecture as to the reasons for the sudden appearance of such enormous and unsuspected ionic activity. Certainly, the relatively recent discovery of the hydrated electron[52,53] forces a re-evaluation of the importance of electron solvation. The production of hydrated electrons during the radiolysis of water demonstrates that some electrons are not only capable of avoiding recapture [eq. (6)], but during the thermalization process may undergo solvation [eq. (7)].

Other recent evidence supporting a high degree of charge separation has been obtained by *Allen et*

[34] *C. G. Baumann* and *D. J. Metz*, J. Polymer Sci. *62*, 141 (1962).

[35] *T. H. Bates, J. V. F. Best*, and *T. F. Williams*, Nature (London) *188*, 469 (1960).

[36] *T. H. Bates, J. V. F. Best*, and *T. F. Williams*, Trans. Faraday Soc. *58*, 192 (1962).

[37] *K. Hirota* and *F. Takemura*, Bull. chem. Soc. Japan *35*, 1037 (1962).

[38] *T. H. Bates, J. V. F. Best*, and *F. Williams*, J. chem. Soc. (London) *1962*, 1531.

[39] *K. Ueno, K. Hayashi*, and *S. Okamura*, J. Polymer Sci., Part B *3*, 363 (1965).

[40] *R. C. Potter, C. L. Johnson, D. J. Metz*, and *R. H. Bretton*, J. Polymer Sci., Part A-1 *4*, 419 (1966).

[41] *R. C. Potter, R. H. Bretton*, and *D. J. Metz*, J. Polymer Sci., Part A-1 *4*, 2295 (1966).

[42] *R. C. Potter*, Dissertation, Yale University, 1966.

[43] *D. J. Metz, C. L. Johnson*, and *R. C. Potter*, Abstracts of Papers, 151st Meeting Amer. chem. Soc. G *42*, March 1966.

[44] *R. C. Potter, R. H. Bretton*, and *D. J. Metz*, J. Polymer Sci., in press.

[45] *R. C. Potter* and *D. J. Metz*, Paper read to the Deutsche Bunsen-Gesellschaft für physikalische Chemie, Köln, May 1967.

[46] *K. Ueno, K. Hayashi*, and *S. Okamura*, Polymer (London) *7*, 43 (1966).

[47] *M. A. Bonin, M. S. Calvert, W. L. Miller*, and *F. Williams*, J. Polymer Sci., Part B *2*, 143 (1964).

[48] *D. Cordischi, M. Lenzi*, and *A. Mele*, J. Polymer Sci., Part A-3 *3*, 342 (1965).

[49] *H. Yamaoka, F. Williams*, and *K. Hayashi*, Trans. Faraday Soc. *63*, 376 (1967).

[50] *K. Ueno, K. Hayashi*, and *S. Okamura*, Paper presented at First Joint Japanese-American Conference on Radiation Polymerization, Honolulu, May 1966.

[51] *D. Vofsi* and *A. Katchalsky*, Ric. sci., Parte II, Sez. B *25*, 165 (1955).

[52] *E. J. Hart* and *J. W. Boag*, J. Amer. chem. Soc. *84*, 4090 (1962).

[53] *J. P. Keene*, Nature (London) *197*, 47 (1963).

al.[54,55] from measurements in irradiated media of low dielectric constant. Yields of free ions have been determined from the ion mobilities and zero-field conductivity induced by irradiation of insulating liquids with either X-rays or fast electrons. Surprisingly, although these yields [from reaction (1), (4), and (7)] are small, they are not negligible as had been supposed previously. For example, for "normal" purity hexane at 23 °C the yield of ion pairs was found to be 0.10 per 100 eV of absorbed radiation[54]. Using this value, it was then shown that an electron of 57 eV could travel a mean distance of 87 Å from its parent ion[55]. It had previously been estimated that the range of such an electron was only 9 Å[56]. Since the values of dielectric constants for hexane and for many monomers are similar, it would not be unusual to encounter a small but measurable yield of ions in an irradiated monomer. In fact, the low temperature ionic polymerization of cyclopentadiene (again, a "normal" purity system) has been shown to have an ion yield of 0.2 pairs per 100 eV[57]. It can be concluded, then, that the ionic contribution to a "normal" purity monomer had been overlooked because most of the growing chains are terminated as oligomers (or monomers) by means of a very efficient reaction with water and any other ion-inhibiting substances that might be present. The elimination of ions thus allows the free radicals generated [from reaction (8)] to act as the chain-sustaining species. It would follow that as the water concentration was reduced the contribution of the ionic species to the over-all polymerization would steadily increase.

4.3. The Influence of Water

It has already been mentioned that, for styrene, the earliest (and, thus, the least refined) drying and purification techniques of *Metz* produced reaction rate increases above the free-radical values by a factor of about one order of magnitude. Later work by *Metz*[40] and *Okamura*[39] resulted in an increase of about two orders of magnitude. Finally, *Metz et al.* reached the limiting and reproducible rates which correspond to an increase of approximately three orders of magnitude over the dose rate range studied[41]. Both groups have conclusively demonstrated that the re-introduction of small amounts of water into the ultra-pure reaction system results in an immediate reduction of rate to the free-radical level[43,46].

In view of this situation, it might seem paradoxical that for many conventional cationic polymerizations there can be no reaction at all without water being present as a co-catalyst. It must be remembered, though, that in a highly purified monomer system there is no chemical catalyst present with which the water can form an active complex:

$$BF_3 + H_2O \rightarrow [BF_3OH]^-H$$

Thus all the highly polar water molecules are free to act as ionic scavengers. *Pinner* has speculated that this reaction – in the case of carbonium ions – may consist of abstraction of a proton to form a hydrated hydronium ion[61] ($H_3O^+ \cdot n\,H_2O$). From a thermodynamic standpoint, such a reaction should occur spontaneously. Whatever the nature of this scavenging process, it must account for the regeneration of water, since no acceleration of rate corresponding to a depletion of water has ever been observed. As this reaction has a fundamental bearing on the course of polymerization, it should be included in our reaction scheme. Therefore, in lieu of additional data, this reaction will, for a monomer ion, be written simply as:

$$MH^+ + H_2O \rightarrow M + H_3O^+ \qquad (12)$$

(Any water of hydration has been omitted.) An analogous scheme can be written for the reaction of a polymer cation with water.

As yet, no one has reliably determined the maximum value of water concentration that still allows a detectable ionic propagation. Although *Okamura* has attempted quantitative measurements in this area[46], he failed to allow for the adsorption of deliberately-added water by the baked glass surface of the apparatus. It is known, however, that the critical water concentration lies below the limits detectable by Karl Fischer analysis (5 ppm)[58]. The maximum allowable water concentration may well be in the $1:10^9$ range.

Williams has pointed out that the phenomenon of low-temperature ionic polymerization may be intimately connected with a reduced activity of water[59], that arises from increased aggregation under the conditions of reaction. Further, the effects arising from the addition of "electron-trapping" substances in low temperature experiments may have been observed solely because of the adsorbing power of these substances. To put it somewhat differently, the low-temperature polymerization proceeded ionically because of conditions reducing the efficiency of reaction (12).

4.4. Radicals in Ultra-pure Systems

Another point of interest can be raised: namely, is the role of the free radical species during the irradiation of a monomer affected by removal of impurities? (Assuming, of course, that the monomer is susceptible to free-radical radiation polymerization in the first place.) An *a priori* conclusion would be that the ionic contribution is simply superimposed on the free-radical contribution. That is, increased purity merely serves to introduce ionic species and has no effect on the normal production of free radicals. This would

[54] *A. Hummel* and *A. O. Allen*, J. chem. Physics *44*, 3426 (1966).

[55] *A. Hummel*, *A. O. Allen*, and *F. H. Watson*, J. chem. Physics *44*, 3431 (1966).

[56] *J. L. Magee*, *K. Funabashi*, and *A. Mozumder*, US AEC Document No. COO-38-378 (1964).

[57] *W. R. Busler*, *D. H. Martin*, and *F. Williams*, Discuss. Faraday Soc. *36*, 102 (1963).

[58] *D. J. Metz*, unpublished.

[59] *F. Williams*, paper presented at 7th Japan Conference on Radioisotopes (May 1966); USAEC Document No. ORO-2968-21.

[60] *D. J. Metz*, Advances Chem. Ser. *66*, 170 (1967).

[61] *S. H. Pinner* in *P. H. Plesch*: The Chemistry of Cationic Polymerization. Pergamon Press, London 1963, p. 613ff.

imply, however, that on a graph of R_p versus I there is a critical dose rate at the intersection of the classical free radical curve with the ionic curve, and below which there would only be free radical behavior. For the case of styrene, at least, there are some data which may refute this idea [41].

A dilatometer assembly was prepared of just sufficient purity to show a slight deviation ($R_p \sim I^{0.60}$) from the square root line. Thus, there was a definite, albeit small, ionic contribution. At dose rates below the point of intersection, the order dependency did not suddenly revert to 0.5 but, instead, remained constant. This can only occur if the free radical contribution has been reduced. Most of the styryl cations which are initially formed in a "wet" system are either destined to ultimately become free radicals [reaction (6) followed by reaction (8)] or else are inactivated as a consequence of eq. (12). Thus, the implication is that whenever some propagating ions are stabilized in a "dry" system, the result is the net loss of some potential free radicals.

4.5. Polymeric Ions

As already mentioned, it is clear that free ions are active in the systems rather than the "paired" ions prevailing in a conventional ionic system. An experimental argument supporting this comes from the observation that the propagation rate constants which have so far been determined for these radiation ionic reactions are very much higher than those for the corresponding catalytic ionic reactions [62]. The idea of the enhanced reactivity of a free ion over a paired ion is not only in accord with absolute rate theory, but also finds agreement with *Szwarc*'s work on "living" polystyrene [63].

Generally these ions are believed to be cationic, although there is no real evidence indicating whether they are carbonium ions or carbonium radical ions. An exception occurs in the radiation polymerization of ultra-pure nitroethylene at room temperature, which is believed to proceed by an anionic mechanism [49, 51]. This is not surprising, considering the well-known polymerizability of this monomer by basic reagents. Furthermore, it has been shown that nitroethylene polymerizes anionically in low-temperature systems [68].

The "cationic *status quo*" may have a much more intriguing exception in the case of styrene. Factors such as reaction retardation by ammonia [39], the observed relations $R_p \sim I^{1.0}$ [33, 40] and $\overline{DP} \sim I^0$ [43, 44], copolymerization results (see Fig. 3) [46], and previous results from low temperature polymerization combine to make a strong argument favoring a simple cationic polymerization mechanism. However, at the very highest rates of polymerization of styrene the relation $R_p \sim I^{0.70}$ holds (see Fig. 2). At these high

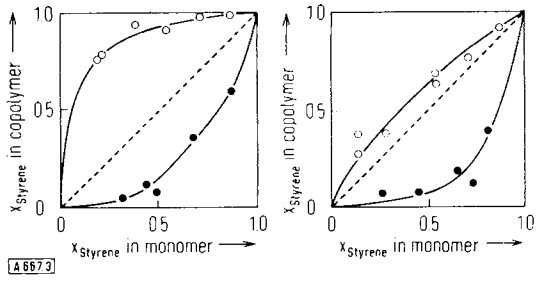


Fig. 3. a) Copolymerization of styrene and isobutyl vinyl ether, temperature 30 °C, dose rate 3800 rad/min; ○ normal purity r_1 (St) = 17.0 ± 8.0, r_2 (VE) = 0.1 ± 0.1, • anhydrous, r_1 (St) = 0.3 ± 0.3, r_2 (VE) = 10.0 ± 4.0 [46].
b) Copolymerization of styrene and α-methylstyrene, temperature 30 °C, dose rate 3800 rad/min, ○ normal purity r_1 (St) = 2.2 ± 0.2, r_2 (αMST) = 0.6 ± 0.2; • anhydrous r_1 (St) = 0.25 ± 0.25, r_2 (αMST) = 8.5 ± 4.0 [46].

rates (or, put another way, at this level of purity), species which are unusually sensitive to any protonic impurity, such as water, would begin to emerge. The styrene anion is such a species. Further, the propagation of the anion in addition to the cation would introduce the possibility of a remarkable mode of termination: termination by combination of oppositely charged polymeric ions. If this bimolecular termination occurred to an appreciable extent then a square-root dependency would be competing with the already established linear dependency. The result would be a dose rate dependence intermediate between these two extremes, which may account for the observed value of 0.70. Similar behavior has also been noted for α-methylstyrene [43, 60].

4.6. Influence of Temperature

Except for the thoroughly studied case of styrene, the influence of temperature in any of these systems has hardly been investigated. For styrene of a purity corresponding to a first order termination process ($R_p \sim I^{1.0}$), parallel isotherms have been obtained which correspond to a slightly negative overall temperature coefficient, E, on an Arrhenius diagram (*e.g.*, −1.5 kcal/mole) [43, 44]. It has also been shown that at higher purity levels the higher values of R_p result in isotherms corresponding to lower values of E (*e.g.*, −4 kcal/mole) [43, 44]. Such values of E are not in disagreement with those which would be predicted for ionic radiation polymerization. Interestingly, the isotherms obtained for the highest purity styrene ($R_p \sim I^{0.70}$) are skewed and therefore cross over one another [43, 44]. This behavior may be a consequence of the appearance of a second species (see Section 4.5.).

Other temperature investigations reveal a slight inverse relationship between temperature and $\overline{DP}$ [43, 44]. Again this is the theoretical expectation for an ionic polymerization initiated by radiation.

4.7. Chain Transfer

One further deduction may be made concerning the kinetics of these ionic systems. Simple calculations show that chain transfer occurs to a great extent dur-

[62] *F. Williams* [50].

[63] *D. R. Bhattacharyya, C. L. Lee, J. Smid,* and *M. Szwarc,* Polymer (London) *5*, 54 (1964); J. physic. Chem. *69*, 612 (1965).

ing the irradiation of ultra-pure monomers. To begin with, the values of $G_{(-m)}$ which are encountered are extraordinarily large[*]. For instance, in the case of styrene, values of $G_{(-m)}$ in the order of 10^5 are typical (as compared to free radical values of approximately 10^3). Assuming an ionic mode of termination and the total absence of chain transfer, the yield of chains initiated is given by:

$$G_i = G_{(-m)}/\overline{DP}$$

Since the $\overline{DP}$ for styrene is in the order of 10^3, the resulting value of G_i is in the order of 10^2. However, about 32 eV are required to form one ion pair in the gas phase, which corresponds to a G_i of about 3. For a condensed system, the corresponding result should be similar. In fact we have already made mention of the low G_i values ($\approx 10^{-1}$) for cyclopentadiene and hexane. A G_i of 10^2 is unreasonably high, and thus the presence of chain transfer is necessitated. When chain transfer occurs, the calculated value of G_i is reduced to a more reasonable value according to:

$$G_i = [k_t/(k_t + k_{tr})] \cdot [G_{(-m)}/\overline{DP}]$$

where k_t is the rate constant for termination and k_{tr} is the rate constant for transfer.

4.8. Synopsis on Ultra-pure Systems

Upon irradiation of an ultra-pure monomer, free ions arise immediately, primarily as a consequence of reactions such as (4) and (7). Provided that the concentration of water is low enough to preclude a substantial contribution from reaction (12), these ions permit rapid propagation of a relatively small number of kinetic chains. The primary mode of termination of the polymeric ions is effected by chain transfer to monomer. Transfer maintains R_p at a constant value and creates a distribution of low average molecular weight, while the termination of a kinetic chain by neutralization, although a relatively rare event, determines the dose rate dependency of the reaction. Under such conditions, the population of radical species is probably diminished to some extent, but, in any event, these free radicals propagate so slowly, that they make no appreciable contribution to the overall polymerization. For certain monomers, such as styrene, one may encounter the simultaneous propagation of carbonium ions [eq. (4)], carbanions [eq. (7)], and free radicals [eq. (8)]. The relative concentration of each chain-sustaining species is determined by the purity of the system.

One definite area of interest is the re-investigation of those monomers which previously exhibited a free radical mechanism, or even a total absence of polymerization, under irradiation. The polymerization of methyl methacrylate[44, 64] and acrylonitrile[65] have not yet responded to ultra-purification. Possibly, more stringent drying techniques are required for the complete removal of water from such highly polar monomers. Copolymerization results for styrene-methyl methacrylate tend to confirm this idea[64].

The primary source of impurities in a monomer system is the water adsorbed on the surfaces of the preparative and reaction apparatus[41, 46]. Since the thorough vacuum baking of apparatus has produced so many new developments in radiation polymerization, one might well ponder the impact of ultra-purity on other areas of chemistry. Studies on conventionally initiated ultra-pure styrene have, however, failed to produce any revolutionary findings (see Fig. 4).

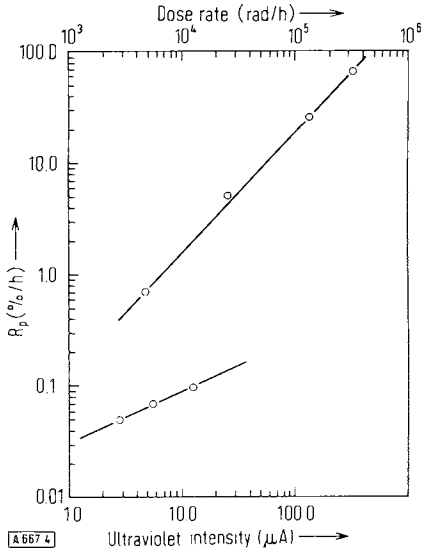


Fig. 4. Polymerization of styrene at 0 °C. Both curves represent the same dilatometer. The upper curve corresponds to γ-initiation, slope 1.1. The lower curve is the result of UV-initiation (using a solar cell to determine relative UV intensities) [40], slope 0.45.

A dilatometer assembly which exhibited the characteristics of the ionic reaction unter γ irradiation exhibited the characteristics of a free radical polymerization[40] when exposed to UV light. The same system also polymerized by a free radical mechanism when initiated thermally.

5. Pulse Radiolysis

Over the last few years, techniques have been perfected for the detection of transient species formed after a high current, microsecond burst of electrons. This analog of flash photolysis, aptly dubbed pulse radiolysis, has proved to be an immensely powerful method for studying the excited molecules, ionic species, and free radicals that are produced in irradiated aqueous solutions and organic systems[69]. Indeed the existence of the hydrated electron was revealed by this method[52, 53].

In all our previous remarks, the arguments for the existence of ions in radiation polymerization have

[*] $G_{(-m)}$ is the number of monomer units consumed per 100 eV of absorbed energy.

[64] *R. C. Potter* and *D. O. Hummel*, unpublished.

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been predicated upon indirect inferences from kinetics. However, pulse radiolysis has recently provided direct evidence for the existence of ions. The technique was first applied by *Burrell*[70] in 1964 to investigate the original example of ionic radiation polymerization: isobutene at low temperature. Using ultraviolet absorption spectroscopy, he observed a species absorbing at 297 nm which disappeared by a first order process. This species was identified as a carbonium ion, possibly the trimethylcarbonium ion.

Styrene and α-methylstyrene have also been examined. Three research groups, each of them using optical methods for the detection of transients, have made independent studies. *Katayama* briefly reported on the pulse radiolysis of anhydrous α-methylstyrene[71]. A transient was observed having absorption maxima at 366 and 546 nm, which was ascribed to the α-methylstyrene radical anion. The absorption disappeared by a first order process with a half-life of ~25 μsec.

Metz applied the pulse technique to ultra-pure styrene[72]. The absorption spectrum obtained after a 1 μsec pulse of 15 MeV electrons showed the existence of at least three species. While two of the absorptions had long lifetimes and were suggested to be due to a radical species and a relatively stable permanent product, the third species, which exhibited an absorption maximum at 370 nm, decayed according to first order kinetics with a half-life of about 4 μsec. This species is very sensitive to traces of water. Also, the addition of oxygen reduced the initial height of the absorption maximum. (Oxygen had already been shown to be an inhibitor for the γ-initiated polymerization of ultra-pure styrene[42, 44].) The authors tentatively identified this short-lived species with the styrene radical anion formed through electron capture by styrene monomer [eq. (7)]. Thus, a comparison of the effect of water and oxygen on R_p with their effect on the 370-nm absorption reinforces the previous suggestion that anions are partially responsible for the polymerization kinetics of ultra-pure styrene. Similar conclusions, based on similar observations, have been made for α-methylstyrene[43, 60].

A disturbing point raised by previous remarks concerns the failure to observe a cationic styryl species with pulse radiolysis? The simple constraint of overall charge neutrality assures the presence of a positively charged species. Moreover, there are reasons to believe that the carbonium ion-radical may absorb in the 600-nm region, which has not yet been investigated because of technical obstacles[72]. There is also the distinct possibility that the carbonium ion absorption overlaps that of the anion radical.

The most serious criticism which can be raised in this area is that intermittent high dose rate studies may not, perhaps, be validly compared with continuous irradiation, low dose rate studies. Unfortunately, there is as yet no answer to this question, although there is an encouraging shred of evidence that the same kinetic processes are operative under both modes of irradiation. R_p was determined for a dilatometer with ultra-pure styrene which had been polymerized by repetitive pulsing. By the admittedly hazardous expedient of extrapolating the limiting data of Fig. 2 across several orders of magnitude, the value of R_p from intermittent irradiation was within a factor of three of the continuous irradiation value[76].

Schneider has applied pulse radiolysis to monomers purified under normal conditions, without taking special precautions to remove traces of water[73–75]. Investigation of the polymerization rate and of the molecular weight of the polymer formed in experiments with repetitive pulsing showed that, under these conditions, the polymerization is caused by radicals. Unstable species were observed on irradiation of styrene and α-methylstyrene in bulk and in solutions of these monomers in benzene, cyclohexane, hexane, carbon tetrachloride, aliphatic alcohols, and water. While the absorption of the propagating styryl radical can be observed in each of these solutions, an additional, very short lived absorption with a maximum at about 390 nm appears in the bulk monomers and in solutions in hexane and cyclohexane (Fig. 5). The species responsible for this

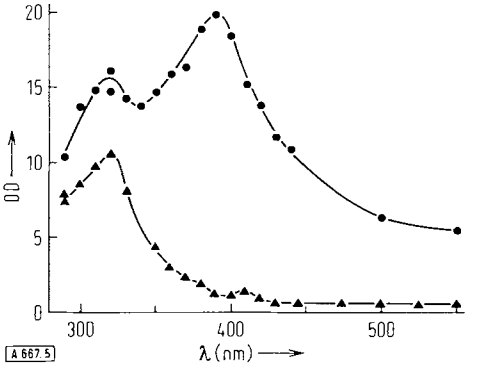

Fig. 5. Absorption spectra of a de-aerated solution of styrene (10^{-3} M) in cyclohexane. Upper curve: immediately after a 2 μsec pulse of 4 MeV electrons. Lower curve: 50 μsec later. Dose rate: 5000 rad/pulse. The free-radical species (left-hand peak) is relatively stable compared to the short-lived ionic species (right-hand peak) [75].

absorption was shown to be very sensitive to electron scavengers such as N_2O and halogen compounds. Water also had a strong effect on the 390 nm absorption. Contrary to the results obtained by *Metz*, the decay of this species was found to obey second-order kinetics, with a termination constant of about 10^{11} l mole^{-1} sec^{-1} and a first half-life of 3 μsec. Because of the effect of additives and the high decay

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constant, it was concluded, in agreement with *Katayama* and *Metz*, that the 390 nm absorption is due to the styrene and α-methylstyrene radical anion. There also seems to be some evidence that the cation indeed absorbs in the same region of wavelength as the anion. A 30 % decrease in the absorption intensity at 390 nm was observed after a small amount of *n*-butylamine had been introduced into a dilute solution of styrene in cyclohexane [77]. In solutions of the monomers in aliphatic alcohols and in water, the solvated electron again reacts with the monomer to form the styrene anion, but due to rapid protonation no absorption at 390 nm can be observed. Certainly these findings are in accord with the previous remark that ions are probably always produced in substantial number under irradiation, regardless of the purity of the monomers, but that the successful propagation of these ions requires extreme purity.

Although there is still uncertainty and even contradiction in some of the pulse radiolysis results obtained so far, the results nevertheless indicate that the technique can provide direct information about the role of ions in polymerization processes. Now that the "second generation" of pulse radiolysis apparatus has arrived, in the guise of nanosecond machines, we may confidently look forward to further contributions toward the elucidation of radiation-induced ionic polymerization.

6. Solid-State Polymerization

Fidelity to theme requires a concluding section on ionic polymerization in the solid state. It is with considerable hesitation that such a section is included, since there has been so much confusion and controversy as to the mechanisms involved. Indeed, radiation polymerization constitutes one of the few areas of science in which the liquid phase is better understood than the solid phase.

One of the earliest expectations was that solid state polymerization for monomers at low temperature would be initiated by ionic species. Unfortunately, this *a priori* attitude did much to becloud the early literature. Contrary to fluid-phase kinetics, it has turned out to be extremely difficult to find clear-cut criteria for identifying the mechanism of the solid-state reaction.

The usual kinetic criteria are simply not unrestrictedly applicable to the solid state, and for several reasons: diffusion processes have a strong influence on the reaction, inhibitors will either act exclusively on the crystal surface or else produce defects in the crystal lattice, and copolymerization parameters are certainly more strongly affected by crystal structure than by monomer reactivity. Also, it is not possible to draw an analogy between radiation and catalytically initiated solid-state polymerization because the effect of the catalyst is confined to the crystal surface, whereas irradiation produces a uniform distribution of active species throughout the entire sample. In considering the mechanism of radiation-induced solid-state polymerization, then, one must use great caution in making statements about the role of ions or radicals. It has been known for some time that crystal structure plays a decisive part in these reactions. Until this influence of morphology is more clearly defined it is clear that any postulated mechanisms are highly speculative.

In the solid state classification scheme of *Chapiro* [78], the Group II monomers are those which are radiation polymerizable only in the solid state. Numbered among these monomers are 1,3,5-trioxane [*], the corresponding eight-membered ring, diketene, β-propiolactone, and 3,3-bis(chloromethyl)oxetane [*], which can be conventionally polymerized only by cationic catalysts. For the radiation initiated polymerization of these monomers, the temperature coefficient is small and the resulting polymer is highly crystalline. Thus, a cationic mechanism has been proposed [79]. This view is further supported by the findings of *Naruse* for trioxane, wherein the rate of reaction is increased by electron acceptors [83]. According to a recent theory, however, the trioxane reaction proceeds by a "radical-initiated ionic mechanism" [54].

The occurrence of post-polymerization introduces additional difficulties in the interpretation of these systems. This phenomenon has been thoroughly investigated for trioxane [80]. If oxygen is present during the in-source irradiation, then peroxides are formed which can initiate post-polymerization. However, post-polymerization occurs even in the absence of oxygen, and this may be due to the presence of trapped ions or radicals. However, little work has been performed *in vacuo* and this second possibility has been largely ignored.

Other investigations have shown that the presence of oxygen has no effect on the in-source polymerization, but that it greatly accelerates the rate of post-polymerization (a consequence of the above-mentioned peroxy radicals [79]). The in-source temperature coefficient has been found to be only 5 kcal/mole, whereas the post-polymerization temperature coefficient is more than 40 kcal/mole (near the value for the decomposition of peroxides). In addition, the reaction can be inhibited by the addition of a radical scavenger such as hydroquinone [82].

Trioxane that has been irradiated at low temperatures exhibits thermoluminescence with rising temperature, which is due to the release of trapped electrons. Also on the basis of ESR studies it has been suggested that the initiating species arises from a radical ion formed by irradiation, and that the polymerization probably proceeds by a cationic mechanism [100, 101].

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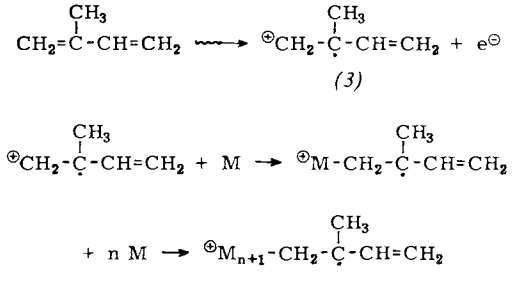
Clearly no consensus has been reached in this area. Thus, the identity of the long-lived species (*ca.* 10^4 to 10^5 sec [81]) participating in post-polymerization remains a mystery, waiting to be solved.

A cationic mechanism has also been proposed for the solid-state polymerization of 1,2-epoxycyclohexane [84]. The presence of water has been shown to drastically reduce the yield. Likewise, cations seem to be the initiators for 1,2,3,4-diepoxybutane [85]. Supporting evidence comes from a low temperature coefficient (0.4 kcal/mole) and a linear dependence of reaction rate on the dose rate.

Dienes have also been assumed to polymerize by an ionic mechanism, although free radicals have been detected *e.g.* by *Hirschberger* for isoprene [86]. Additional investigations have been made to clarify this anomaly, utilizing the low-temperature solid-state polymerization of isoprene, 1,3-pentadiene, and 2,3-dimethyl-1,3-butadiene [98]. The ESR-detected radicals (from electron irradiation) seemed to be of the propagating type attributable to addition of an alkyl radical to the terminal carbon atom of diene monomers. In order to confirm this assignment, several different types of radicals were generated by using ultraviolet irradiation: hydroxyl radicals were produced by the addition of *tert*-butyl hydroperoxide, methyl radicals were produced from methyl iodide, and radicals of undetermined structure were produced in the pure monomers. However, none of these radicals was capable of adding to an unsaturated bond. For instance, isoprene suffered abstraction of a hydrogen atom from its methyl group. Consequently, it seems unlikely that the free radicals from electron irradiation participate in the polymerization. Probably, the reaction proceeds *via* a radical ion *(3)* that reacts further with the monomer. (The sites chosen for the positive charge and for the unpaired electron are arbitrary.)



(3)

The chain would grow only from the ionic terminus, whereas the radical terminus is resonance-stabilized and inactive at low temperature. Similar mechanisms have been ascribed to the other dienes.

A few monomers are believed to polymerize by anionic mechanisms. Included among these are acrylonitrile [87–90] and methacrylonitrile [91], neither of which are polymerizable by cationic initiators. The temperature coefficient for acrylonitrile is −3 kcal/mole; that for methacrylonitrile, 0.3 kcal/mole. *Hardy* has proposed an anionic mechanism for cetyl methacrylate, although radical scavengers hinder the reaction [92]. In this connection it must be pointed out that methyl methacrylate undergoes almost negligible polymerization in the solid state. Nevertheless, mixtures of methyl methacrylate and paraffin oil yield large amounts of polymer by a reaction which is believed to be free radical in nature [99]. Since cetyl methacrylate, which, because of its long side-chain, may be considered analogous to a mixture of methyl methacrylate and paraffin oil, one should approach an anionic assignment with circumspection.

There have been several theories over the last few years proposing mechanisms which involve neither ionic nor radical species and which, in fairness, must be presented here. *Tabata* claims that the polymerizations of acrylonitrile, methacrylonitrile, isoprene, butadiene, and acetylene proceed according to an "electronic" mechanism [93]. Whereas the polymerization of acetylene in the liquid state leads to a *cis* structure by a cationic mechanism, the irradiation of solid acetylene results in a *trans* polymer [94]. This effect cannot be satisfactorily explained in terms of any of the usual theories. According to the "electronic" mechanism, the excitation of a single monomer entity collectively excites its neighboring molecules in the crystalline state. The corresponding polymer then forms spontaneously. The mechanism finds support in the fact that so many solid-state polymerizations have such extraordinarily small temperature coefficients. The mechanism is also in accord with the observation that, at low temperature, polymerization rates are controlled by crystal structure and that, in many instances, stereoregular polymers have been obtained.

A similar mechanism had been proposed earlier by *Semenov* [95] and was further elaborated upon by *Barkalov* [96]. According to the "hot" mechanism of *Semenov*, a highly excited monomer molecule attacks an adjacent molecule and the reaction then proceeds by stepwise excitation from molecule to molecule. This theory was applied by *Barkalov* to explain the polymerization of acrylonitrile, formaldehyde, isobutene, and phenylacetylene. In his view, along the tracks of primary and secondary electrons one would encounter molecular recoil from electron impact, de-freezing of rotation, and excitation of vibration. All these processes create excited species, which are much more reactive than radicals or ions [97]. The polymerization could begin in the "hot" zone of a spur and proceed either along the electron track or along a crystal axis. The excited

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molecules would at first form metastable polymer molecules. These intermediate species may then either undergo "depolymerization" or be transformed into stable polymer. Perhaps this type of mechanism may be extended to explain the phenomenon of post-polymerization. It has been noted that the application of pressure before the post-polymerization of trioxane completely inhibits the reaction [102]. This effect may be due to the destruction of trapped, unstable intermediates, such as excited molecules.

This type of theory is gaining wide support and helps to cast even more doubt on previous discussions of ionic mechanisms in the solid state. Indeed, if these excitation theories are substantially correct, one can no longer consider ions as playing any significant part in solid-state polymerization.

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New Methods of Preparative Organic Chemistry [**]

Preparation, Properties, and Reactions of Polychloroamine Derivatives

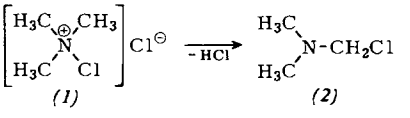
BY H. HOLTSCHMIDT, E. DEGENER, H.-G. SCHMELZER, H. TARNOW, AND W. ZECHER [*]

Highly chlorinated amine derivatives can be prepared by the high-temperature chlorination of amines and amine derivatives. Essential for the success of this reaction is an adequate temperature control suited to the constitution of the amines. In many cases the chlorination products achieve stability by cleavage reactions with formation of the imidic acid chloride or isocyanide dichloride grouping. Cyclic compounds are formed under special conditions. The chlorination process described can be used to obtain e.g. polychloroaryl and polychloroalkyl isocyanide dichlorides, polychloroaryl and polychloroalkyl imidic acid chlorides, and polychloroheterocyclic compounds.

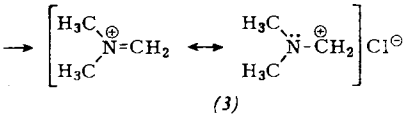
1. Introduction

1.1. Chlorination of Amines at Low Temperatures

The early chlorinations of amines and amine derivatives were all characterized by low reaction temperatures. The products were mostly very unstable, and sometimes decomposed very violently when heated. Primary and secondary amines yield the unstable and explosive *N*-chloro compounds [1]. Tertiary aliphatic amines give thermally unstable salt-like adducts. The product *(1)* obtained from trimethylamine and chlorine, for example, decomposes very vigorously and often explosively when heated above 35 °C [2]. The salt-like adducts of the type *(1)* give, with formal elimination of hydrogen chloride and migration of a chlorine cation, α-halogenated amines *(2)*, which are not stable as free bases, but quaternize with themselves.



(1) *(2)*



(3)

The α-halogenated amines may be regarded as resonance-stabilized immonium-carbonium salts *(3)*.

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[**] Earlier contributions to this series are collected in five volumes, available in English and German, published by Verlag Chemie, Weinheim/Bergstr.

[1] *R. Stroh* in *Houben-Weyl-Müller*: Methoden der organischen Chemie. 4th Edit., Thieme-Verlag, Stuttgart 1962, Vol. V/3, p. 796.

[2] *H. Böhme* and *W. Krause*, Chem. Ber. *84*, 170 (1951).

They are among the most reactive of all electrophiles, and smoothly alkylate *e.g.* aromatic compounds [3].

An elegant route to the aliphatic α-halogenoamines *(2)* in solution, *i.e.* the chlorination of methylenediamines *(4)*, was discovered by *Böhme* [4].

$$\underset{(4)}{(CH_3)_2N{-}CH_2{-}N(CH_3)_2} \xrightarrow{Cl_2} \underset{(2)}{(CH_3)_2N{-}CH_2Cl} + Cl{-}N(CH_3)_2$$

Ammundsen and *Pitts* [5] obtained a mixture of β- and γ-monochloroalkylamines on chlorination of dimethylpropylammonium chloride at −75 °C with UV irradiation. No further chlorination was observed under these conditions.

1.2. High-Temperature Chlorination of Amines

The high-temperature chlorination of aliphatic amines was for a long time ignored by investigators, since such reactions were regarded as dangerous and without utility, as amine salts were reputed to be very resistant to further chlorination [6].

Consequently the observation [7] that amines and amine derivatives can be smoothly chlorinated in the alkyl and aryl residues at high temperatures, such as are normally used in the chlorination of hydrocarbons, came as quite a surprise. The success of the high-temperature chlorination was due to the development of specific techniques that avoided the formation of explosive halogen adducts and resin-forming intermediates. Careful temperature control is essential, particularly in the first phase of the reaction, owing to the high reactivity of the primary products. The basicity of the amine nitrogen and the reactivity of the chlorine atoms in the products decrease with increasing extent of chlorination. The products therefore gain thermal stability and get more resistant to resinification, so that the temperature can be continuously raised to complete the reaction, and can ultimately be elevated very rapidly to the level of 190–250 °C that is often necessary.

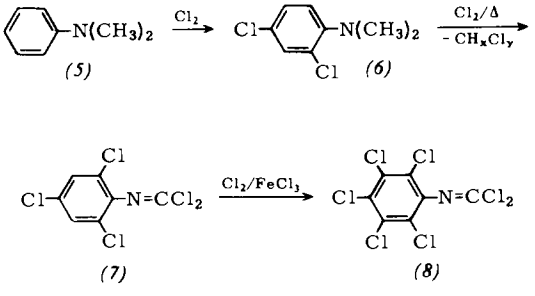
1.3. High-Temperature Chlorination with Dealkylation and Deacylation

During the chlorination of tertiary amines containing at least two suitable aliphatic groups and of disubstituted amides containing at least one alkyl group, a characteristic degradation takes place at high temperatures. Compounds of both classes achieve stability by formation of isocyanide dichlorides [*] or imidic acid chlorides, an alkyl residue being split off as the polychloroalkane in the case of the tertiary amines (high-temperature chlorination with dealkylation) and an acyl residue as the acyl chloride in the case of the amides (high temperature chlorination with deacylation).

2. High-Temperature Chlorination of Tertiary Amines

2.1. *N,N*-Dimethylaniline

The possibility of obtaining polychloroamine derivatives by chlorination of tertiary amines was first realized in 1962 [7]. A typical example is the chlorination of *N,N*-dimethylaniline *(5)*. The procedure found to be best is one in which the temperature is raised by approximately 10 °C per hour. At the same time an adequate supply of chlorine must be provided at all times. The chlorination of *(5)* begins with substitution of the benzene ring in the *o* and *p* positions [*(6)*] [8]. As the temperature is raised, the methyl groups are also chlorinated. The dealkylation with elimination of polychloromethane then begins above 180 °C, and 2,4,6-trichlorophenyl isocyanide dichloride *(7)* is formed at 200–230 °C in 90 % yield. On addition of a catalytic quantity of iron(III) chloride to *(7)*, the remaining hydrogen atoms can also be replaced by chlorine to give pentachlorophenyl isocyanide dichloride *(8)*.



Many derivatives of dimethylaniline and dimethylaminonaphthalene can be converted into highly chlorinated isocyanide dichlorides by the same method [9].

2.2. Intermediates in the High-Temperature Chlorination of *N,N*-Dimethylaniline

N-Dichloromethyl-*N*-trichloromethyl-2,4,6-trichloroaniline *(9)* has been isolated in substance as an intermediate in the high-temperature chlorination of *N,N*-dimethylaniline *(5)* [10]. Rather surprisingly, *(9)* is stable for long periods even at 240–250 °C.

---

[3] *H. Böhme, E. Mundlos, W. Lehners,* and *O.-E. Herboth,* Chem. Ber. *90,* 2008 (1957).

[4] *H. Böhme, E. Mundlos,* and *O.-E. Herboth,* Chem. Ber. *90,* 2003 (1957).

[5] *L. H. Amundsen* and *L. S. Pitts,* J. Amer. chem. Soc. *73,* 1494 (1951).

[6] *C. W. Crane, J. Forrest, O. Stephenson,* and *W. A. Waters,* J. chem. Soc. (London) *1946,* 827.

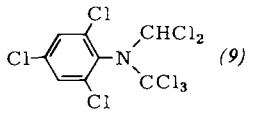
[7] *H. Holtschmidt,* Angew. Chem. *74,* 848 (1962); Angew. Chem. internat. Edit. *1,* 632 (1962).

[*] The isocyanide dichlorides can, strictly speaking, also be referred to as imidic acid chlorides, *i.e.* as *N*-substituted chloroformimidoyl chlorides.

[8] *T. H. Chao* and *L. P. Cipriani,* J. org. Chemistry *26,* 1079 (1961).

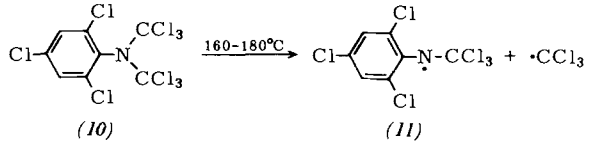
[9] *H. Holtschmidt* and *W. Zecher,* German Pat. 1221212 (Nov. 9, 1961) = Belg. Pat. 622382 (Sept. 12, 1962), Farbenfabriken Bayer AG; Chem. Abstr. *59,* 11534f (1963).

[10] *K. Grohe,* unpublished.

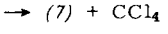


(9)

If the temperature is not allowed to exceed 140 °C, *N,N*-bis-(trichloromethyl)-2,4,6-trichloroaniline *(10)* can be obtained in good yields as the end product of the chlorination of *(5)* [11]. *(10)* decomposes at 160–180 °C into *(7)* and carbon tetrachloride. According to ESR-spectroscopic results, this decomposition proceeds *via* the nitrogen radical *(11)* and a trichloromethyl radical.



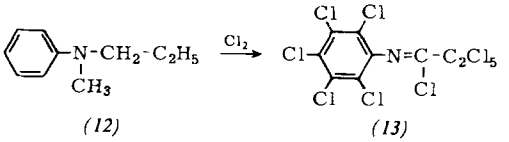
(10) *(11)*



(7)

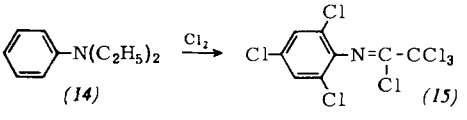
2.3. *N,N*-Dialkylarylamines

If the nitrogen carries higher alkyl residues, the chlorination leads to highly chlorinated imidoyl chlorides. In the case of the *N*-methyl-*N*-alkylanilines, the methyl group is predominantly eliminated as polychloromethane. *N*-Pentachlorophenylpentachloropropionimidoyl chloride *(13)* is formed in 62 % yield from *N*-methyl-*N*-propylaniline *(12)*.



(12) *(13)*

High alkyl groups can also be split off as polychloroalkanes during the high-temperature chlorination. For example, the chlorination of diethylaniline *(14)* results in the elimination of hexachloroethane and formation of 2,4,6-trichlorophenyltrichloroacetimidoyl chloride *(15)*.



(14) *(15)*

Cyclization of the alkyl groups occurs as a side reaction (cf. Section 10.3.3.).

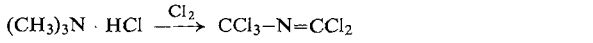
Aromatic substituents on aromatic rings are also chlorinated in the high-temperature chlorination, while nitro groups and bromine atoms are largely replaced by chlorine.

2.4. Trialkylamines

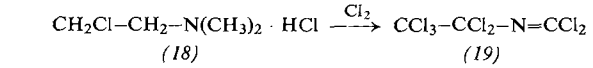
In the aliphatic series, the high-temperature chlorination of tertiary amines also leads to polychlorinated imidoyl chlorides, that of *N*-alkyldimethylamines yielding polychlorinated isocyanide dichlorides. In this case, however, the chlorination often proceeds less uniformly than in the aromatic series, since none of the N–C bonds is preferentially cleaved, and the side reactions of partly chlorinated intermediates are enhanced. This is understandable, since the ease of transition to the mesomeric immonium structure increases with the basicity of the nitrogen atom.

The aliphatic tertiary amines can also be chlorinated as hydrochlorides and ammonium chlorides, preferably suspended in trichlorobenzene, to give the imidoyl chlorides or isocyanide dichlorides. Owing to the heterogeneous nature of the reaction, the reaction times are very long and the yields are not particularly good.

Trimethylammonium chloride *(16)* gives moderate yields of trichloromethyl isocyanide dichloride *(17)*. *N*-(2-Chloroethyl)dimethylammonium chloride *(18)* is chlorinated to pentachloroethyl isocyanide dichloride *(19)*.

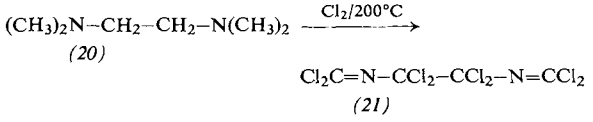


(16) *(17)*



(18) *(19)*

The most successful chlorination observed so far is that of tetramethylethylenediamine *(20)* which leads to tetrachloroethylene-1,2-bis(isocyanide dichloride) *(21)* (yield 30–71 %).



(20) *(21)*

3. High-Temperature Chlorination of Acyl Derivatives of Secondary Amines

The high-temperature chlorination of acyl derivatives of secondary amines is another generally applicable method for the preparation of polychloroamine derivatives. This reaction is also accompanied by a characteristic cleavage. The most suitable acyl derivatives are *N*-chlorocarbonyl compounds and amides of carboxylic acids, though amides of phosphoric and sulfuric acids may also be used.

The aliphatic and aromatic residues are chlorinated first. At higher temperatures the *N*-acyl bond is broken and the acyl residue eliminated as acyl chloride, with formation of an imidoyl chloride grouping [12]. Dialkylamides containing at least one methyl group give isocyanide dichlorides, while higher *N*-alkylamides give polychlorinated imidoyl chlorides.

The chlorination of acyl derivatives of secondary amines has certain advantages over the chlorination of tertiary amines. The reaction solution is homogeneous, since no sparingly soluble hydrochlorides precipitate out. The amide nitrogen is much less basic than the nitrogen of the tertiary amines, so that optimum reaction conditions can be reached more readily, and resinification reactions become less important.

[11] *K. Grohe, E. Klauke,* and *H. Holtschmidt,* German Pat. Appl. F 48901 Vb/qu (April 7, 1966), Farbenfabriken Bayer AG.

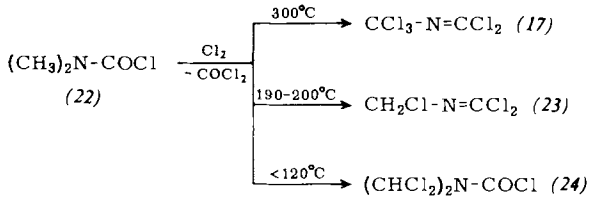
[12] *H. Holtschmidt* and *W. Zecher,* Belg. Pat. 622381 (Sept. 12, 1962), Farbenfabriken Bayer AG; Chem. Abstr. *59,* 11526c (1963).

Moreover, the reaction products are more uniform, since cleavage is almost totally confined to the *N*-acyl bond. The deacylation can be catalyzed by Lewis acids.

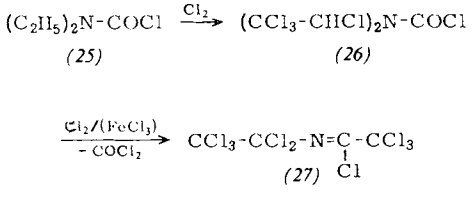
3.1. Chlorocarbonyl Derivatives of Secondary Amines

The use of chlorocarbonyl compounds is particularly advantageous, since the acyl chloride split off in this case is a gas and no chlorine is lost by chlorination of the acyl residue. Low-boiling chlorocarbonyl compounds can be readily chlorinated in the gas phase (preferably on catalysts such as activated charcoal) to give polychloroalkyl isocyanide dichlorides and polychloroalkyl imidoyl chlorides.

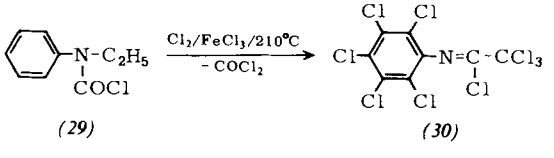
Whereas the gas-phase chlorination of dimethylcarbamoyl chloride *(22)* [13] gives trichloromethyl isocyanide dichloride *(17)* in 87 % yield, monochloromethyl isocyanide dichloride *(23)* can be obtained in 62 % yield by chlorination at 190 to 200 °C with simultaneous distillation [14]. If the reaction is carried out below 120 °C, no deacylation takes place, and bis(dichloromethyl)carbamoyl chloride *(24)* is formed in good yields.



Diethylcarbamoyl chloride *(25)* is first chlorinated to bis(tetrachloroethyl)carbamoyl chloride *(26)* which, at high temperatures, slowly loses phosgene in a current of chlorine to form *N*-pentachloroethyltrichloroacetimidoyl chloride *(27)*. To obtain *(27)* in preparative quantities, the deacylation is best catalyzed with iron(III) chloride.



The high-temperature chlorination proceeds particularly smoothly in the case of the *N*-alkyl-*N*-arylcarbamoyl chlorides, *e.g. (29)*, which gives *N*-pentachlorophenyltrichloroacetimidoyl chloride *(30)* [15].



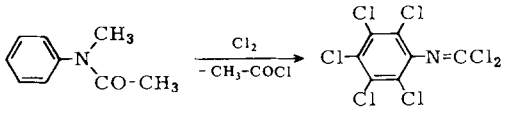
[13] *W. Zecher* and *H. Holtschmidt*, German Pat. 1222917 (Aug. 14, 1963) = Netherlands Pat. Appl. 6409122 (Feb. 15, 1965), Farbenfabriken Bayer AG; Chem. Abstr. *63*, 8327d (1965).

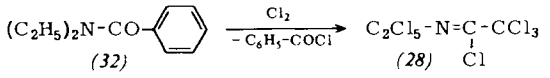
[14] *H. Holtschmidt*, German Pat. 1141278 (May 10, 1961), Farbenfabriken Bayer AG; Chem. Zbl. *1964*, 1–2415.

[15] *H. Tarnow*, *H. Holtschmidt*, and *G. Unterstenhöfer*, German Pat. 1197078 (Nov. 27, 1963), Farbenfabriken Bayer AG; Chem. Abstr. *63*, 14774c (1965).

3.2. *N,N*-Disubstituted Carbonamides

N,N-Disubstituted carbonamides behave in the same way as the chlorocarbonyl compounds on high-temperature chlorination. The acyl residues are split off in the chlorinated form. For example, *N*-methylacetanilide *(31)* gives pentachlorophenyl isocyanide dichloride *(8)*, and *N,N*-diethylbenzamide *(32)* gives *N*-pentachloroethyltrichloroacetimidoyl chloride *(28)* [16]. The chlorination of cyclic amides is discussed in Section 10.2.

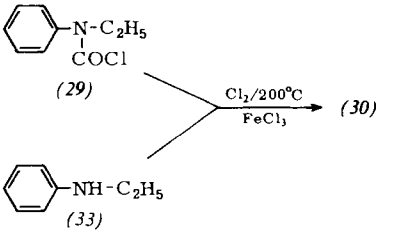




4. High-Temperature Chlorination of Secondary Amines

Instead of the acyl derivatives of secondary amines it is possible to chlorinate the secondary amines themselves [17]. It is surprisingly found that no *N*-chloro compounds accumulate under the conditions of the high-temperature chlorination. Since the secondary amines, as strong bases, form hydrochlorides exothermally at the beginning of the reaction, and in some cases even react with the less chlorinated alkyl residues, it is recommended that the hydrochlorides should be used from the outset to avoid side reactions. The end products are again polychloroamine derivatives containing the stable imidoyl chloride grouping. This grouping is formed even at 80 °C, *i.e.* under much milder conditions than are required for the dealkylation and deacylation. One disadvantage of this process, however, is that the reaction mixtures are inhomogeneous at the beginning of the chlorination because of the low solubility of the amine hydrochlorides.

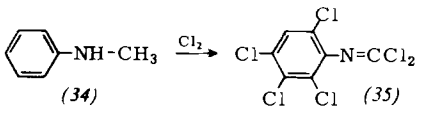
The compounds formed are generally the same as in the chlorination of the corresponding *N,N*-disubstituted carbonamides. Thus *N*-ethylaniline *(33)* like its chlorocarbonyl derivative *(29)*, reacts at 200 °C in the presence of iron(III) chloride to give *N*-pentachlorophenyltrichloroacetimidoyl chloride *(30)* in 85 % yield.



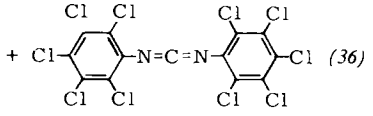
[16] *G. Dankert*, unpublished.

[17] *W. Zecher*, *H. Tarnow*, and *H. Holtschmidt*, German Pat. 1222918 (Dec. 21, 1964), Farbenfabriken Bayer AG.

A special case is the high-temperature chlorination of *N*-methylaniline *(34)*, in which considerable quantities of bis-(pentachlorophenyl)carbodiimide *(36)* and polymeric highly chlorinated diphenylcarbodiimides are obtained as well as 2,3,4,6-tetrachlorophenyl isocyanide dichloride *(35)*.

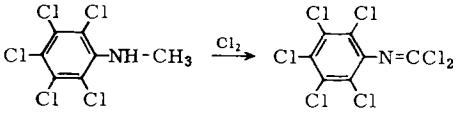


(34) *(35)*



(36)

The high-temperature chlorination of the less basic *N*-methylpentachloroaniline *(37)*, on the other hand, leads almost exclusively to the isocyanide dichloride *(8)* in very good yield [18].



(37) *(8)*

5. High-Temperature Chlorination of Derivatives of Primary Amines

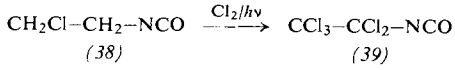
The chlorination of aryl and alkyl isocyanates, *N*-alkylcarbonamides, isocyanide dichlorides, and imidoyl chlorides, as well as of Schiff bases of aromatic and aliphatic amines, have been investigated. The alkyl and aryl residues can be readily polychlorinated in every case. The imidoyl chloride grouping is often formed either by rearrangement, dehydrochlorination, or chlorination of the azomethine group.

5.1. Alkyl Isocyanates and *N*-Alkylcarbamoyl Chlorides

The chlorination of alkyl isocyanates results in substitution in the alkyl chain. The alkyl residues of longer-chain alkyl isocyanates are largely randomly chlorinated, but the first chlorine atom is preferentially attached in an exothermic reaction to the α position with respect to the isocyanate group [19].

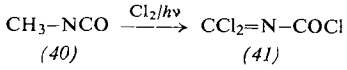
The complete chlorination of longer alkyl chains requires relatively high temperatures and long reaction times. Good yields are generally obtained only when the reaction is carried out in an inert solvent, since intramolecular condensation otherwise often leads to resinification.

The perchlorination of ethyl isocyanate or 2-chloroethyl isocyanate *(38)* leads to a product whose IR spectrum indicates that it consists mainly of pentachloroethyl isocyanate *(39)*.

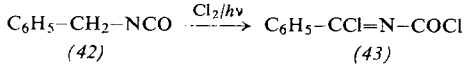


(38) *(39)*

Methyl isocyanate *(40)* and benzyl isocyanate *(42)*, on the other hand, give, not the expected chlorinated isocyanates, but the isomeric chloroalkylidenecarbamoyl chlorides *(41)* and *(43)* [7].



(40) *(41)*



(42) *(43)*

Instead of the alkyl isocyanates, the corresponding alkylcarbamoyl chlorides may also be chlorinated. The chlorinations of alkyl isocyanates and of alkylcarbamoyl chlorides are practically indistinguishable, since the hydrogen chloride formed adds to the isocyanate group to form the carbamoyl chloride. To avoid this exothermic reaction, it is often advantageous to convert the isocyanates into the carbamoyl chlorides before the chlorination. The fact that the carbamoyl chlorides boil at higher temperatures than the isocyanates is frequently also an advantage in the high-temperature chlorination.

5.2. Aryl Isocyanates and *N*-Arylcarbamoyl Chlorides

The chlorination of phenyl isocyanate in the cold, which has been known for a long time, leads to single or multiple ring chlorination, the hydrogen chloride formed adding to the isocyanate group to form the carbamoyl chloride [20].

Difficulties were encountered in the preparation of perchlorinated aryl isocyanates, since the use of high temperatures and metal catalysts is necessary for the substitution of the less active ring hydrogen atoms. Considerable losses result in this case from Friedel-Crafts condensations and carbodiimide formation. Perchlorinated aryl isocyanates such as pentachlorophenyl isocyanate can, however, be obtained in good yield by a two-step process [21]. The aryl ring is first chlorinated at or slightly above room temperature in the absence of metal catalysts to give a mixture of mono-, di-, and trichloro compounds. In the second step the chlorination is continued in the presence of *e.g.* iron(III) chloride at 210–250 °C, the perchlorinated aryl isocyanate ultimately being formed in very good yields.

Aromatic mono- and polyisocyanates with alkyl side chains can be chlorinated in the ring and/or in the side chain [22]. The chlorination of the side chain can be stimulated by light, free radical generators, or by

[18] *G. Beck*, unpublished.

[19] *H. Holtschmidt* and *E. Degener*, DAS 1122058 (Aug. 26, 1960), Farbenfabriken Bayer AG; Chem. Zbl. *1962*, 13945.

[20] *F. Gumpert*, J. prakt. Chem. *32*, 278 (1885).

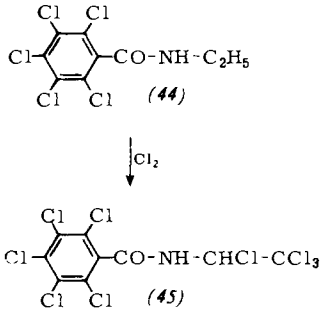
[21] *H. Holtschmidt*, *O. Bayer*, and *E. Degener*, German Pat. 1157601 (May 10, 1962), Farbenfabriken Bayer AG; Chem. Zbl. *1965*, 35–2659.

[22] *H. Holtschmidt*, German Pat. 947470 (April 9, 1953), Farbenfabriken Bayer AG; Chem. Zbl. *1957*, 3664.

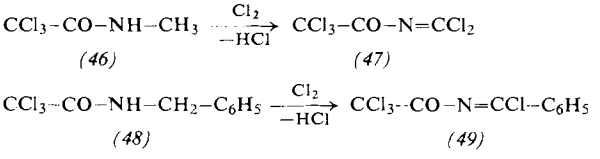
heat. The normal Friedel-Crafts catalysts are used for the ring chlorination. The aliphatic side chains can be chlorinated stepwise in a fairly uniform manner.

5.3. *N*-Alkylcarbonamides

The chlorination of *N*-alkylcarbonamides proceeds first with progressive substitution in the alkyl residue. At 160 °C, for example, *N*-ethylpentachlorobenzamide *(44)* gives *N*-(1,2,2,2-tetrachloroethyl)pentachlorobenzamide *(45)* [10, 18].



As in the chlorination of secondary amines, hydrogen chloride is frequently eliminated and acyl isocyanide dichlorides [such as *(47)*] or acylimidoyl chlorides [such as *(49)*] are formed [10]. Thus the chlorination of *N*-methyltrichloroacetamide *(46)* leads to very good yields of *N*-dichloromethylenetrichloroacetamide *(47)*, and that of *N*-benzyltrichloroacetamide *(48)* to *N*-(α-chlorobenzylidene)trichloroacetamide *(49)*.

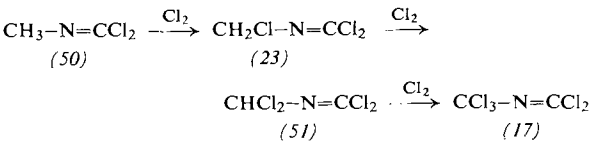


5.4. Isocyanide Dichlorides and Imidoyl Chlorides

The high-temperature chlorination of isocyanide dichlorides and imidoyl chlorides [23,24] proceeds particularly smoothly, since the energetically favored functional groups are already present in these cases. Aromatic isocyanide dichlorides and *N*-arylimidoyl chlorides behave in the same way as aryl isocyanates on chlorination. Partly chlorinated isocyanide dichlorides and imidoyl chlorides are intermediates in some of the high-temperature chlorinations described already.

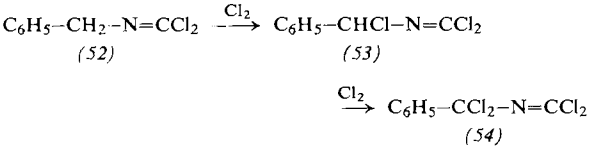
5.4.1. Alkyl Isocyanide Dichlorides

Methyl isocyanide dichloride *(50)* can be chlorinated in steps to give mono-, di-, and trichloromethyl isocyanide dichloride *(23)*, *(51)*, and *(17)*. However, this chlorination is very slow, even in the light. Rapid perchlorination in 80 % yield can be achieved in the gas



phase by passing methyl isocyanide dichloride or methyl isothiocyanate over activated charcoal in a current of chlorine and nitrogen at 350–390 °C.

The activated α-hydrogen atoms in benzyl isocyanide dichloride *(52)* are particularly readily replaced with formation first of α-chlorobenzyl isocyanide dichloride *(53)* and then of α,α-dichlorobenzyl isocyanide dichloride *(54)* in very good yields. With very long chlorination times the phenyl ring is also perchlorinated [18].

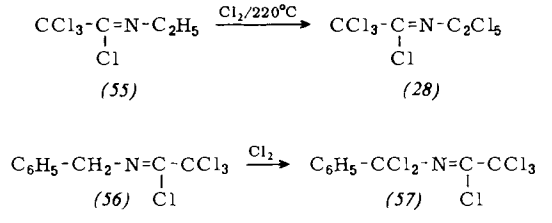


The isothiocyanates [25] and the formimidoyl chlorides [24, 26], which can be obtained from the formamides, can also be chlorinated directly. The primary product in both cases is the isocyanide dichloride, which need not be isolated (for the desulfurization of the isothiocyanates, see Section 9.1.).

5.4.2. *N*-Alkylimidoyl Chlorides

The *N*-alkyltrichloroacetimidoyl chlorides [23, 24], which are readily obtainable from *N*-alkylacetamides with phosphorus pentachloride, are particularly suitable for chlorination.

The chlorination of *N*-ethyltrichloroacetimidoyl chloride *(55)* at temperatures rising to 220 °C gives a 96 % yield of *N*-pentachloroethyltrichloroacetimidoyl chloride *(28)*, the same compound as is obtained on high-temperature chlorination of *(25)* and *(32)* with deacylation. *N*-Benzyltrichloroacetimidoyl chloride *(56)* leads, again in almost quantitative yield, to *N*-(α,α-dichlorobenzyl)trichloroacetimidoyl chloride *(57)*.



The chlorinations can also be applied to bifunctional imidoyl chlorides and to trichloroacrylimidoyl chlorides.

[23] *H. Holtschmidt, E. Degener*, and *H.-G. Schmelzer*, Liebigs Ann. Chem. *701*, 107 (1967).

[24] *E. Degener, H.-G. Schmelzer*, and *H. Holtschmidt*, German Pat. 1193033 (April 25, 1963), Farbenfabriken Bayer AG; Chem. Zbl. *1965*, 50–2453.

[25] *E. Degener, H. Holtschmidt*, and *H.G. Schmelzer*, German Pat. 1163803 (Dec. 14, 1962), Farbenfabriken Bayer AG; Chem. Zbl. *1965*, 5-2424.

[26] *E. Kühle*, Angew. Chem. *74*, 861 (1962); Angew. Chem. internat. Edit. *1*, 647 (1962).

5.4.3. Rearrangement of the N=C Double Bond

The N=C double bond of the imidoyl chlorides can rearrange during the high-temperature chlorination, as was observed in the case of *N*-alkylbenzimidoyl chlorides. The chlorinations of *N*-methyl- and *N*-ethylbenzimidoyl chloride *(58)* and *(59)* lead to the products *(54)* and *(57)*, which are also formed on chlorination of the isocyanide dichloride *(52)* and the imidoyl chloride *(56)*. The constitution of *(54)* is confirmed by independent synthesis from benzoyl isocyanide dichloride *(60)* and phosphorus pentachloride [27] and by the formation of benzoyl isocyanide dichloride *(60)* on partial hydrolysis with formic acid [23].

$$C_6H_5\text{-}\underset{Cl}{C}\text{=}N\text{-}CH_3 \xrightarrow{Cl_2} C_6H_5\text{-}CCl_2\text{-}N\text{=}CCl_2$$
(58) *(54)*

$$C_6H_5\text{-}\underset{Cl}{C}\text{=}N\text{-}C_2H_5 \xrightarrow{Cl_2} C_6H_5\text{-}CCl_2\text{-}N\text{=}\underset{Cl}{C}\text{-}CCl_3$$
(59) *(57)*

$$C_6H_5\text{-}CO\text{-}N\text{=}CCl_2 \underset{HCOOH}{\overset{PCl_5}{\rightleftharpoons}} \textit{(54)}$$
(60)

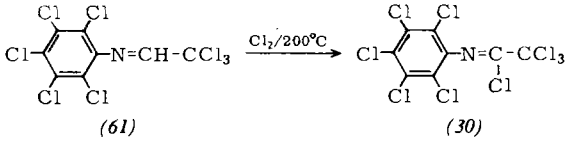
The IR spectrum of *(54)* also contains the characteristic absorptions of an isocyanide dichloride. The corresponding bands are absent from the spectrum of the chlorination product of *N*-methylpentachlorobenzimidoyl chloride, so that it is possible that the benzimidoyl chloride structure is retained in this case [28]. Steric factors appear to play some part in determining the position of the double bond.

5.4.4. Schiff Bases

The chlorination of Schiff bases generally begins with the hydrogen atom of the azomethine group. This yields imidoyl chlorides, so that the further chlorination proceeds as in these compounds.

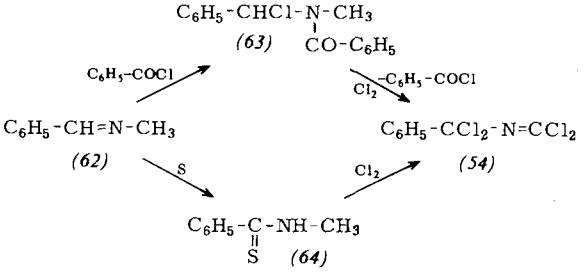
The Schiff bases from chloral and aniline derivatives are particularly suitable starting materials [29–31].

The acaricidally active pentachlorophenyltrichloroacetimidoyl chloride *(30)* can be obtained in practically quantitative yield by chlorination of *N*-(2,2,2-trichloroethylidene)pentachloroaniline *(61)* at 200 °C [32].

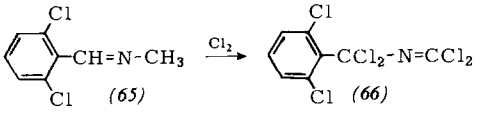


(61) *(30)*

Some Schiff bases, such as *N*-benzylidenemethylamine *(62)* cannot be chlorinated directly, since they polymerize under the chlorination conditions. However, these azomethines can be readily converted into chlorinatable intermediates either by addition of an acyl chloride [33] or by reaction with sulfur to form the thioamides [34]. The adduct *(63)* of *(62)* and benzoyl chloride, for example, can be smoothly chlorinated with deacylation to form α,α-dichlorobenzyl isocyanide dichloride *(54)*. The same product is obtained from *(62)* *via* *N*-methylthiobenzamide *(64)* by chlorolytic removal of the sulfur.



N-(2,6-Dichlorobenzylidene)methylamine *(65)*, on the other hand, does not polymerize so readily owing to steric hindrance, and can be chlorinated directly to form 2,6,α,α-tetrachlorobenzyl isocyanide dichloride *(66)* [35].



6. High-Temperature Chlorination of Alkylamino Nitrogen Heterocycles

The high-temperature chlorination of alkylamino nitrogen heterocycles leads first to substitution in the alkyl residue and sometimes also in the ring. The molecule is then stabilized by cleavage to form the imidoyl chloride or isocyanide dichloride grouping.

6.1. *N,N*-Dialkylamino Nitrogen Heterocycles

N,N-Dialkylamino nitrogen heterocycles behave in basically the same manner as the *N,N*-dialkylarylamines on high-temperature chlorination. If the dialkylamino group is in the α-position with respect to a doubly-bonded nitrogen atom, removal of the chloroheterocycle after the fashion of a deacylation can occur together with the principal dealkylation reaction.

An interesting example of this is the chlorination of 2-dimethylamino-4,6-dichloro-*s*-triazine *(67)* [36], which leads

[27] *R. Neidlein* and *W. Haussmann*, Chem. Ber. *99*, 239 (1966).

[28] *G. Beck* and *H. Heitzer*, unpublished.

[29] *G. Kresze* and *R. Albrecht*, Angew. Chem. *74*, 781 (1962); Angew. Chem. internat. Edit. *1*, 595 (1962).

[30] *R. Albrecht*, *G. Kresze*, and *B. Mlakar*, Chem. Ber. *97*, 483 (1964).

[31] *H.-G. Schmelzer*, *E. Degener*, *G. Unterstenhöfer*, *H. Tarnow*, and *I. Hammann*, German Pat. Appl. F 50561 IVb/12o (Oct. 28, 1966), Farbenfabriken Bayer AG.

[32] *H.-G. Schmelzer*, *E. Degener*, *H. Tarnow*, *H. Holtschmidt*, *G. Unterstenhöfer*, and *W. Zecher*, German Pat. Appl. F 50560 IVb/12o (Oct. 28, 1966), Farbenfabriken Bayer AG.

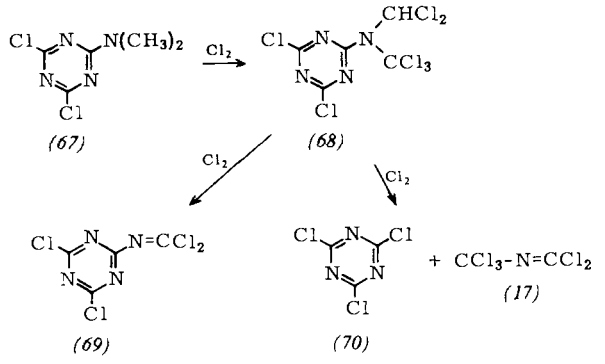
[33] *H. Böhme* and *K. Hartke*, Chem. Ber. *96*, 600 (1963).

[34] *B. Böttcher* and *F. Bauer*, Liebigs Ann. Chem. *568*, 218 (1950).

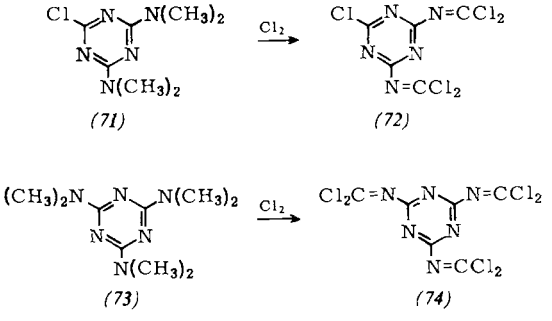
[35] *E. Roos*, unpublished.

[36] *H. Holtschmidt* and *W. Zecher*, German Pat. 1179214 (Sept. 13, 1961) = Belg. Pat. 622382 (Sept. 12, 1962), Farbenfabriken Bayer AG; Chem. Abstr. *59*, 11534f (1963).

via the isolable intermediate *(68)*[10] to a 72% yield of "tetrameric cyanogen chloride" *(69)*. Small quantities of cyanuryl chloride *(70)* and trichloromethyl isocyanide dichloride *(17)* are also formed by deacylation.

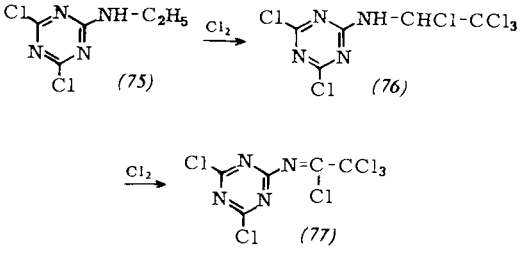


Similarly, though in much poorer yields, the bis(isocyanide dichloride) *(72)* (pentameric cyanogen chloride) is obtained from *(71)* and the tris(isocyanide dichloride) *(74)* (hexameric cyanogen chloride) from *(73)*.

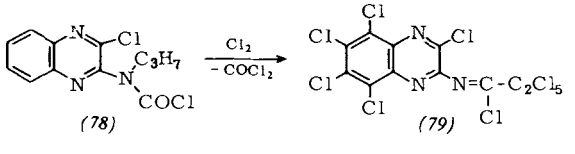


6.2. *N*-Alkylamino Nitrogen Heterocycles and their Acyl Compounds

Monoalkylamino nitrogen heterocycles lose hydrogen chloride in the same way as the secondary amines. The chlorination of 2-ethylamino-4,6-dichloro-*s*-triazine *(75)* leads *via* the isolable tetrachloroethylamine *(76)*[10] to a 90% yield of the imidoyl chloride *(77)*[17].

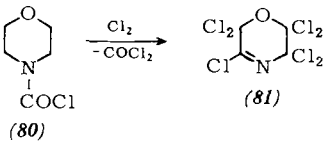


N-Acyl-*N*-alkylamino nitrogen heterocycles are deacylated on high-temperature chlorination; for example, the quinoxaline derivative *(78)* gives the perchlorinated imidoyl chloride *(79)* in 73% yield.



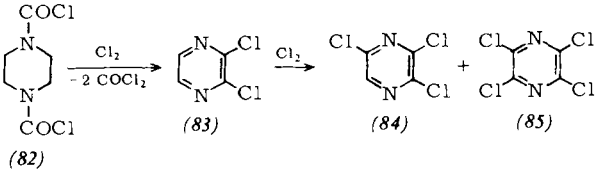
7. High-Temperature Chlorination of Cyclic Aliphatic Amines and their Acyl Compounds

The high-temperature chlorination of cyclic aliphatic amines and their acyl compounds proceeds similarly to the chlorination of open-chain amines, usually with formation of a cyclic imidoyl chloride grouping. Thus the chlorination of *N*-chlorocarbonylmorpholine *(80)* leads in good yield to the cyclic imidoyl chloride *(81)*[12].

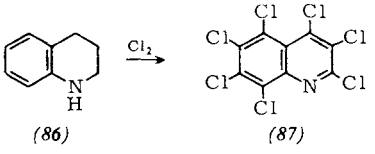


7.1. Aromatization

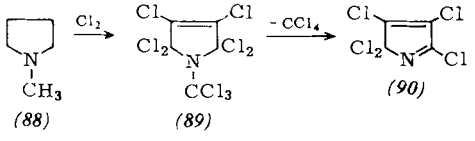
Five- and six-membered rings can be aromatized during the high-temperature chlorination[7]. Thus *N,N'*-bis(chlorocarbonyl)piperazine *(82)* is first doubly deacylated with formation of 2,3-dichloropyrazine *(83)*[12], which can be further chlorinated to tri- and tetrachloropyrazine *(84)* and *(85)*[37,38].



An example of a secondary cyclic amine is 1,2,3,4-tetrahydroquinoline *(86)* which gives perchloroquinoline *(87)* in moderate yield on high-temperature chlorination[39].



N-Methylpyrrolidine *(88)* first gives the chlorinated pyrroline *(89)*. On prolonged heating, *(89)* loses carbon tetrachloride to form pentachloro-2*H*-pyrrole *(90)*. This product can also be synthesized from dichloromaleimide and phosphorus pentachloride[41].



[37] *G. Palamidessi, L. Bernardi,* and *A. Leone,* Farmaco (Pavia), Ediz. sci. *21,* 805 (1966).

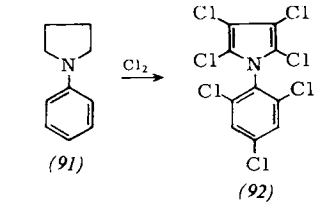
[38] *G. Palamidessi* and *P. Luini,* Farmaco (Pavia), Ediz. sci. *21,* 811 (1966).

[39] *W. Zecher, H. Tarnow,* and *H. Holtschmidt,* German Pat. 1222918 (Dec. 21, 1964), Farbenfabriken Bayer AG.

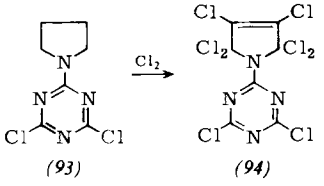
[40] *H. Holtschmidt,* Angew. Chem. *74,* 848 (1962); Angew. Chem. internat. Edit. *1,* 632 (1962).

[41] *R. Anschütz* and *G. Schroeder,* Liebigs Ann. Chem. *295,* 67 (1897).

If the nitrogen atom of the pyrrolidine carries an aryl or heterocyclic residue as in *(91)* and *(93)*, the substituent is not removed. Thus *(91)* aromatizes to give the pyrrole derivative *(92)* [40], while *(93)* gives the pyrroline derivative *(94)*.



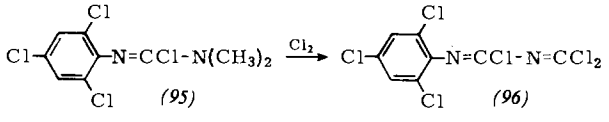
(91) *(92)*



(93) *(94)*

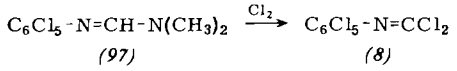
8. High-Temperature Chlorination of *N,N*-Dialkylamidines

The high-temperature chlorination of *N,N*-dialkylamidines leads either to dealkylation or, corresponding to the deacylation of *N,N*-dialkylcarbonamides, to cleavage of the amidine grouping. *N,N*-Dimethyl-*N'*-(2,4,6-trichlorophenyl)chloroformamidine *(95)* is converted in 58 % yield into the isocyanide dichloride *(96)*, *i.e.* the chloroformamidine grouping is retained [7].

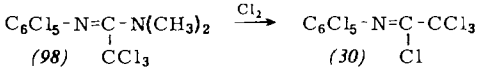


(95) *(96)*

On chlorination of *N,N*-dimethyl-*N'*-(pentachlorophenyl)formamidine *(97)* and of the corresponding trichloroacetimidine *(98)*, on the other hand, the amidine grouping is cleaved to give pentachlorophenyl isocyanide dichloride *(8)* or *N*-pentachlorophenyltrichloroacetimidoyl chloride *(30)* and chlorinated methyl isocyanide dichlorides.



(97) *(8)*

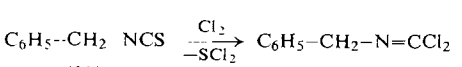


(98) *(30)*

9. High-Temperature Chlorination of Thioamides

9.1. Isothiocyanates

The chlorination of alkyl and aryl isothiocyanates leads even at low temperatures, and generally in an exothermic reaction, to removal of sulfur chlorides and formation of alkyl and aryl isocyanide dichlorides [42, 43]. Benzyl isothiocyanate *(99)*, for example, gives benzyl isocyanide dichloride *(52)* in almost quantitative yield [25].



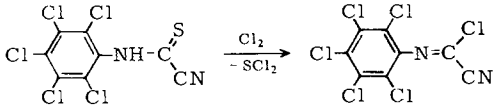
(99) *(52)*

The high-temperature chlorination of isocyanide dichlorides has already been described in detail in Section 5.4.1. If these reactions are carried out as a one-reactor process starting with the isothiocyanates, it is often advantageous to remove the sulfur after the first chlorination stage to avoid side reactions.

9.2. *N*-Monosubstituted Thioamides

The chlorination of *N*-alkylthioamides, which are readily obtainable by sulfurization of Schiff bases [34], has already been described in Section 5.4.4.

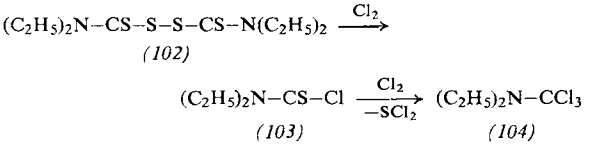
The adducts of hydrocyanic acid and isothiocyanates, *e.g.* *(100)*, are thioamides of cyanoformic acid [44]. They give cyanoformimidoyl chlorides *(101)* on chlorination [45].



(100) *(101)*

9.3. *N,N*-Disubstituted Thioamides

The behavior of the *N,N*-disubstituted thioamides on high-temperature chlorination differs from that of the corresponding carbonamides. *N,N*-Disubstituted thiocarbamoyl chlorides such as *(103)*, which can be prepared *e.g.* by chlorolysis of thiouram disulfides *(102)* [46], give tertiary amines *(104)* containing a trichloromethyl group on chlorination under mild conditions [47, 48].



(102) *(103)* *(104)*

The high-temperature chlorination of *(103)*, on the other hand, leads to a mixture of the isocyanide dichloride *(19)* and the imidoyl chloride *(28)*.

[42] *E. Sell* and *G. Zierold*, Ber. dtsch. chem. Ges. 7, 1228 (1874).

[43] *R. S. Bly*, *G. A. Perkins*, and *W. L. Lewis*, J. Amer. chem. Soc. *44*, 2896 (1922).

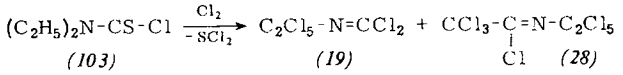
[44] *A. Reissert* and *K. Brüggemann*, Ber. dtsch. chem. Ges. *57*, 981 (1924).

[45] *E. Degener* and *H. Holtschmidt*, German Pat. 1224305 (April 14, 1965), Farbenfabriken Bayer AG.

[46] *E. J. Ritter*, US-Pat. 2466276 (Feb. 2, 1946), Sharples Chemicals Inc.; Chem. Abstr. *43*, 5038c (1949).

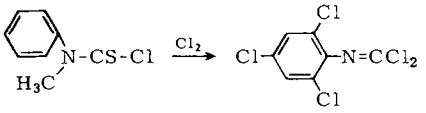
[47] *N. N. Yarovenko* and *A. S. Vasileva*, Ž. obšč. Chim. *29*, 3786 (1959); J. gen. Chem. USSR (Eng. Transl.) *29*, 3747 (1959).

[48] *A. Senning*, Chem. Reviews *65*, 385 (1965).



(103) (19) (28)

2,4,6-Trichlorophenyl isocyanide dichloride *(7)* is formed from *N*-methyl-*N*-phenylthiocarbamoyl chloride *(105)*.

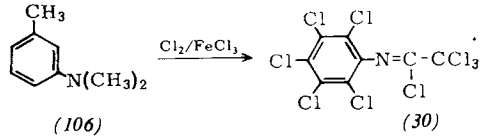


(105) (7)

10. Peculiarities of High-Temperature Chlorination

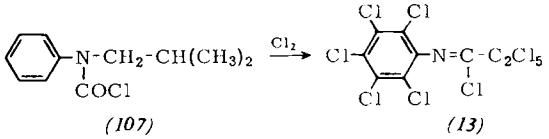
10.1. Cleavage and Formation of C–C Bonds

Under the vigorous conditions of high-temperature chlorination, the normal reaction products are frequently accompanied by substances which are formed by cleavage or formation of C–C bonds. In the chlorination of *N*,*N*-dimethylaniline *(5)* (see Section 2.1.), 3–5 % of *N*-pentachlorophenyltrichloroacetimidoyl chloride *(30)* are formed as a by-product. This compound surprisingly becomes the principal product in the chlorination of *N*,*N*-dimethyl-*m*-toluidine *(106)* in the presence of iron(III) chloride. Both reactions could involve a free-radical mechanism, in which a trichloromethyl radical is responsible for the formation of the C–C bond.



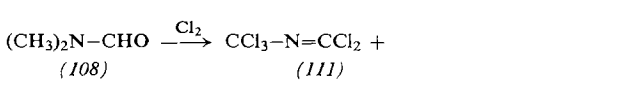
(106) (30)

In the high-temperature chlorination of *N*-isobutylanilinium hydrochloride or of *N*-isobutyl-*N*-phenylcarbamoyl chloride *(107)*, a methyl group is removed, and the product formed is *N*-pentachlorophenylpentachloropropionimidoyl chloride *(13)*.



(107) (13)

Dimethylamino compounds in particular tend to dimerize with formation of C–C bonds on high-temperature chlorination. Thus dimethylformamide *(108)* in suitable solvents gives, not only trichloromethyl isocyanide dichloride *(111)*, but also (formally by dimerization of the fragment $-CCl_2-N=CCl_2$) tetrachloroethylene-1,2-bis(isocyanide dichloride) *(21)*. Attempted chlorination of *(108)* in the absence of solvent generally resulted in explosive decomposition.



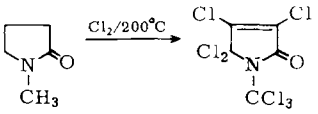
(108) (111)

$Cl_2C=N-CCl_2-CCl_2-N=CCl_2$

(21)

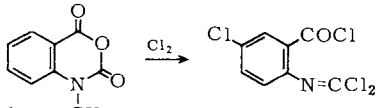
10.2. Cleavage of Cyclic Amides with Chlorination

Peculiarities are found in the chlorination of cyclic *N*-substituted amides[7], since deacylation in this case leads to ring opening. However, the cyclic structure has a certain stabilizing effect, so that the tendency toward cleavage is expected to be lower. Accordingly, the cyclic substitution product *(110)* is obtained as main product on high-temperature chlorination of *N*-methylpyrrolidone *(109)*.



(109) (110)

The chlorination of the less stable *N*-methylisatoic anhydride *(112)* on the other hand, leads to ring cleavage and formation of 2-chlorocarbonyl-4-chlorophenyl isocyanide dichloride *(113)*.



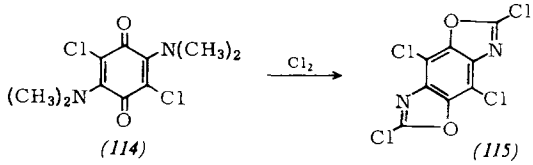
(112) (113)

10.3. Ring Closure Reactions

With favorable steric arrangements, ring closures with formation of C–O, C–N, and C–C bonds are possible under the conditions of high-temperature chlorination.

10.3.1. Oxazole Ring Closure in *N*,*N*-Dialkylaminoquinones

Double ring closure with formation of C–O bonds to give the oxazolobenzoxazole *(115)* occurs on chlorination of 2,5-bis(dimethylamino)-3,6-dichloro-*p*-benzoquinone *(114)*[7].

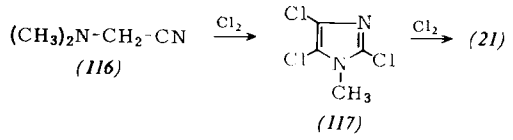


(114) (115)

10.3.2. Ring Closure Reactions of Dialkylaminonitriles

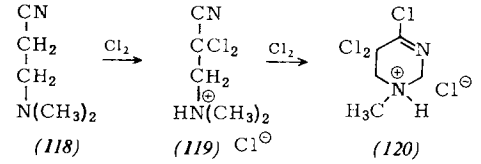
If the amino and nitrile groups in alkylaminonitriles are separated by one or two carbon atoms, the high-temperature chlorination is accompanied by cyclization to form five- or six-membered heterocycles.

The chlorination of dimethylaminoacetonitrile *(116)* leads first, at low temperatures, to cyclization and formation of 2,4,5-trichloro-1-methylimidazole *(117)* which undergoes practically quantitative ring opening on further chlorination at 180–200 °C to give tetrachloroethylene-1,2-bis(isocyanide dichloride) *(21)*[18].

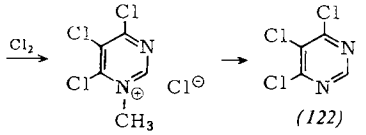


(116) (117) (21)

The chlorination of 3-dimethylaminopropionitrile (118) leads *via* the isolable intermediates (119)–(121) to 4,5,6-trichloropyrimidine (122)[49].

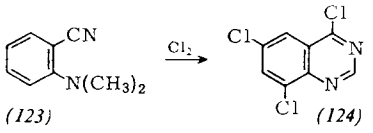


(118) (119) (120)



(121) (122)

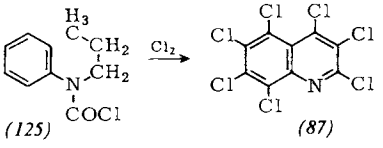
In a similar ring closure reaction, 2-dimethylaminobenzonitrile (123) gives 4,6,8-trichloroquinazoline (124)[18].



(123) (124)

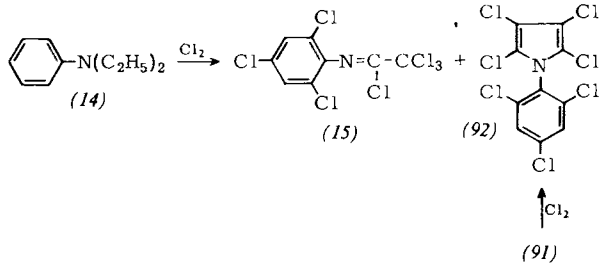
10.3.3. Ring Closure with Formation of C–C Bonds

Ring closure with formation of C–C bonds is observed in the high-temperature chlorination of *N*-chlorocarbonyl-*N*-propylaniline (125), which gives heptachloroquinoline (87) in a yield of approximately 50 %[50].



(125) (87)

In the high-temperature chlorination of *N,N*-diethylaniline (14), cyclization to form the pyrrole derivative (92) competes with the normal dealkylation to form (15); (92) is also formed from *N*-phenylpyrrolidine (91)[51].



(14) (15) (92) (91)

[49] *G. Beck* and *H. Holtschmidt*, German Pat. Appl. F 51475 IVd/12p (Feb. 9, 1967), Farbenfabriken Bayer AG.

[50] *H. Tarnow, H. Holtschmidt*, and *O. Bayer*, German Pat. 1186859 (Oct. 20, 1962), Farbenfabriken Bayer AG; Chem. Zbl. *1965*, 39–2688.

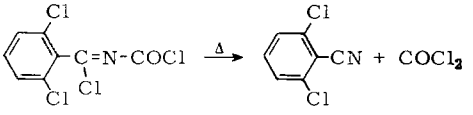
[51] *H. Tarnow, H. Holtschmidt*, and *I. Ugi*, German Pat. Appl. F 37066 IVd/12p (June 14, 1962), Farbenfabriken Bayer AG.

11. Thermal Cleavage of the Polychloroamine Derivatives

As can be seen from the conditions of their preparation, the polychloroamine derivatives obtained by high-temperature chlorination generally have a very high thermal stability. Repeated reference has already been made to the stability of the imidoyl chloride grouping. Imidoyl chlorides and isocyanide dichlorides can, however, undergo thermal cleavage under more forcing conditions.

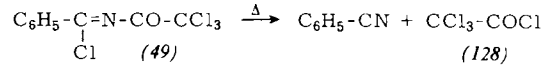
11.1. *N*-(1-Chloroalkylidene)amides

N-(1-Chloroalkylidene)carbamoyl chlorides and *N*-(1-chloroalkylidene)amides (acylimidoyl chlorides), which may be formally regarded as adducts of acyl chlorides with nitriles, decompose into these components even below 200 °C. The cleavage is catalyzed by Lewis acids. Thus 2,6-α-trichlorobenzylidenecarbamoyl chloride (126) gives 2,6-dichlorobenzonitrile



(126) (127)

(127) and phosgene, while *N*-(α-chlorobenzylidene)-trichloroacetamide (49) decomposes into benzonitrile and trichloroacetyl chloride (128).

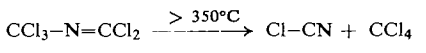


(49) (128)

11.2. Perchloroalkyl Isocyanide Dichlorides and *N*-Perchloroalkylimidoyl Chlorides

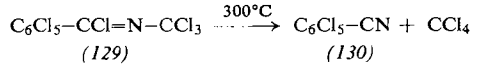
Perchloroalkyl isocyanide dichlorides and *N*-perchloroalkylimidoyl chlorides are much more stable than the unchlorinated compounds, the decomposition of which into alkyl halide and nitrile is well known[52]. The perchloro compounds generally decompose only above 300 °C into perchloroalkane and nitrile.

Trichloromethyl isocyanide dichloride (17) decomposes in the gas phase above 350 °C into cyanogen chloride and carbon tetrachloride; similarly, pentachloroethyl isocyanide dichloride gives cyanogen chloride and hexachloroethane.



(17)

Pentachlorobenzonitrile (130) and carbon tetrachloride are formed in quantitative yield from *N*-trichloromethylpentachlorobenzimidoyl chloride (129) at about 300 °C[18].



(129) (130)

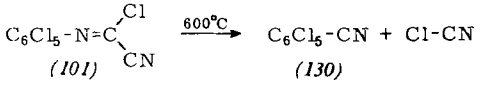
[52] *J. v. Braun*, Angew. Chem. *47*, 611 (1934).

11.3. Perchloroaryl Isocyanide Dichlorides and *N*-Perchloroarylimidoyl Chlorides

Pentachlorophenyl isocyanide dichloride *(8)* is thermally extremely stable. It is broken down into hexachlorobenzene and cyanogen chloride only on prolonged heating at 400 °C, or more rapidly on passage through a quartz tube heated to 700 °C. Pentachlorobenzonitrile *(130)* and chlorine are formed in rather smaller quantities [18].

$$\underset{(8)}{C_6Cl_5\text{-}N{=}CCl_2} \xrightarrow{400\text{–}700^\circ C} C_6Cl_6 + Cl\text{-}CN + \underset{(130)}{C_6Cl_5\text{–}CN} + Cl_2$$

The *N*-arylcyanoformimidoyl chlorides give the nitriles in very good yields on passage over quartz at 600 °C [53]. *N*-Pentachlorophenylcyanoformimidoyl chloride *(101)* gives pentachlorobenzonitrile *(130)* and cyanogen chloride in 91 % yield.



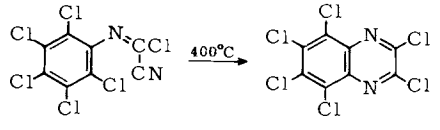
(101) *(130)*

12. Thermal Ring Closure of Polychloroamine Derivatives

Degradation to nitriles is not the only manner in which polychloroamine derivatives can change on pyrolysis. Another possibility is stabilization by ring closure.

12.1. Ring Closure with *N*-Arylation of the Nitrile Group

With suitable steric arrangements, cyclization with *N*-arylation of the nitrile group is possible under extreme thermal conditions. *N*-Pentachlorophenylcyanoformimidoyl chloride *(101)*, which gives pentachlorobenzonitrile at 600 °C in the gas phase (see Section 11.3), cyclizes at 400 °C in the absence of diluents to give hexachloroquinoxaline *(131)* [54].



(101) *(131)*

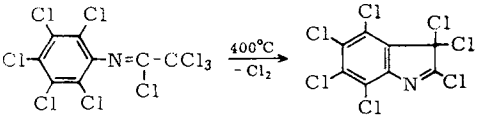
The reaction is confined to the perchlorinated compound.

[53] *G. Beck, E. Degener,* and *H. Holtschmidt*, German Pat. Appl. F 50630 IVb/12o (Nov. 9, 1966), Farbenfabriken Bayer AG.

[54] *H. Holtschmidt* and *E. Degener*, German Pat. Appl. F 49914 IVd/12n (Aug. 10, 1966), Farbenfabriken Bayer AG.

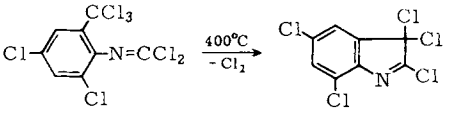
12.2. Ring Closure with Formation of C–C Bonds

Some polychlorinated *N*-arylimidoyl chlorides or aryl isocyanide dichlorides having a steric arrangement such that the formation of five- or six-membered rings is possible react at 300–400 °C with elimination of chlorine and formation of new C–C bonds to give condensed aromatic ring systems [55]. Thus *N*-pentachlorophenyltrichloroacetimidoyl chloride *(30)* loses chlorine at 400 °C to give heptachloro-3*H*-indole *(132)*.



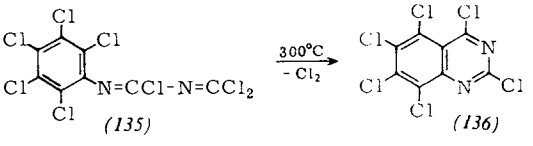
(30) *(132)*

2,3,3,5,7-Pentachloro-3*H*-indole *(134)* is formed under the same conditions from 2,4-dichloro-6-trichloromethylphenyl isocyanide dichloride *(133)* by cyclization of the *o*-trichloromethyl group with the isocyanide dichloride group.



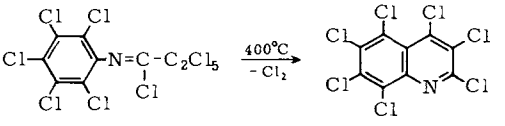
(133) *(134)*

Hexachloroquinazoline *(136)* is obtained in a yield of about 40 % when the isocyanide dichloride *(135)* is heated at 300 °C.



(135) *(136)*

N-Pentachlorophenylpentachloropropionimidoyl chloride *(13)* cyclizes at 400 °C with loss of chlorine to give heptachloroquinoline *(87)* in 81 %.



(13) *(87)*

We are grateful to Dr. Beck, Dr. Dankert, Dr. Grohe, and Dr. Roos for their cooperation. We also thank Dr. Pestemer, Dr. Lauerer, and Dr. Heitzer for carrying out numerous spectroscopic examinations.

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Translated by Express Translation Service, London

[55] Belg. Pat. 673779 (Dec. 16, 1964), Farbenfabriken Bayer AG.

Chalcogenocarbonic Acids and Their Anions

BY M. DRÄGER AND G. GATTOW [*]

Carbonic acids in which the oxygen has been wholly or partly replaced by sulfur, selenium, and/or tellurium are known as "chalcogenocarbonic acids". The aim of the present article is to review existing knowledge of these acids and so establish a basis for further systematic syntheses. The anions required for the synthesis of chalcogenocarbonic acids will also be briefly characterized.

1. Introduction

The known derivatives of "free carbonic acid $OC(OH)_2$" and its sulfur, selenium, and tellurium analogs are numerous, and have been widely studied[1]. Information on derivatives with acidic hydrogen bound to O, S, Se, or Te, with few exceptions, is unsatisfactory, and these compounds have often been dismissed as unstable without further discussion.

2. Possible Syntheses

There are theoretically four simple possibilities for the synthesis of chalcogenocarbonic acids.

1. Addition of two molecules to form the desired chalcogenocarbonic acid, *e.g.*:

$$H_2S + CS_2 \rightarrow SC(SH)_2 \qquad (1)$$

2. Addition of protons to the appropriate anion, *e.g.*:

$$CS_3^{2-} + 2\,H^+ \rightarrow SC(SH)_2 \qquad (2)$$

3. Cleavage of ester linkages in an ester of a chalcogenocarbonic acid, *e.g.*:

$$SC(SR)_2 + 2\,H_2O \rightarrow SC(OH)_2 + 2\,HSR \qquad (3)$$

4. Transchalcogenation of an existing chalcogenocarbonic acid, *e.g.*:

$$S{=}C(SH)_2 + H_2O \rightarrow S{=}C\begin{matrix}\diagup\,OH\\ \diagdown\,SH\end{matrix} + H_2S \qquad (4)$$

Reaction (1) is thermodynamically possible in some cases, but is sufficiently fast only in alkaline media. Similarly, reactions (3) and (4) can only be carried out as direct substitutions in alkaline media; a primary addition to form an orthocarbonic acid derivative followed by elimination has for some time been regarded as conceivable, but no conclusive proof of this course has yet been found[2,3]. In acidic media, on the other hand, the primary step is generally cleavage to form the starting materials of reaction (1).

Reactions (1), (3), and possibly (4) thus yield the anion of the acid, so that the only reaction that might be truly acid-forming is (2). This is the route that has been taken in all definite preparations of chalcogenocarbonic acids so far. The main problem in further syntheses of this type is to use a temperature and a medium such that reaction (2) is sufficiently fast and the resulting acid thermodynamically stable, or if this is impossible, to provide a device that rapidly converts the acid into a thermodynamically stable, or at least metastable, state. Another problem is the purification of a "crude acid" obtained in this way.

The anions required for the preparation of the acid are generally obtained by reaction (1) in alkaline media, *e.g.*:

$$CS_2 + HS^- \rightarrow HCS_3^- \xrightarrow{-H^+} CS_3^{2-} \qquad (1a)$$

3. Unsubstituted Trichalcogenocarbonic Acids

3.1. Simple Anions

The only trichalcogenocarbonate ions that have been definitely detected are those listed in Table 1, dashes indicate other possible combinations. Salts of the ions CO_3^{2-}, CS_3^{2-}, CSe_3^{2-}, and CS_2Se^{2-} can be obtained in the pure state; CO_2S^{2-} has been detected polarographically in aqueous solution, COS_2^{2-} by UV spectroscopy in aqueous solution, and $CSSe_2^{2-}$ by IR spectroscopy in solid solutions with CSe_3^{2-}.

Table 1. Trichalcogenocarbonate ions CX_3^{2-}.

	X_3	X_2			X_1					
	—	S	Se	Te	S_2	SSe	STe	Se_2	SeTe	Te_2
O	CO_3^{2-}	CO_2S^{2-}	—	—	COS_2^{2-}	—	—	—	—	—
S	CS_3^{2-}		CS_2Se^{2-}	—				$CSSe_2^{2-}$	—	—
Se	CSe_3^{2-}			—						
Te	—									—

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[1] For reviews see: *R. Howe* in *E. H. Rodd*: Chemistry of Carbon Compounds. 2nd Edit. Elsevier, Amsterdam 1965, Vol. I/C, p. 268ff.; *S. Petersen* and *H.-F. Piepenbrink* in *Houben-Weyl-Müller*: Methoden der organischen Chemie, Thieme-Verlag, Stuttgart 1952, Vol. VIII, p. 75ff.; *M. Bögemann, S. Petersen, O.-E. Schultz*, and *H. Söll, ibid.* Vol. IX, 1955, p. 773ff.; *H. Rheinboldt, ibid.*, p. 1180ff.

[2] *G. Ingram* and *B. A. Toms*, J. chem. Soc. (London) *1957*, 4328; *1961*, 117.

[3] *B. Philipp* and *C. Fichte*, Faserforsch. u. Textiltechn. *11*, 118, 172 (1960).

All these ions are formed in accordance with eq. (1a) from CO_2, COS, CS_2, or CSe_2 and OH^-, SH^-, or SeH^-[14]; corresponding reactions with COSe, CSSe, CSTe, and HTe^- have evidently not yet been attempted.

Carbonates and trithiocarbonates[7–14] have been known for a long time. The barium[15–17] and potassium[15] salts of the CSe_3^{2-} ion and the barium[15,16,18], potassium[15], and sodium[15] salts of the CS_2Se^{2-} ion have been prepared. Barium salts can be prepared in aqueous media, while alkali metal salts are obtainable only in alcoholic solution, with subsequent precipitation by ether. CS_3^{2-} occurs, not only in simple salts with a metal cation, but also frequently as a ligand in complex transition metal anions[19,20]. The only crystal structure determination of a trithiocarbonate that has been reported so far is that of bis(tetraphenylarsonium) bis(trithiocarbonato)niccolate(II)[21]; like CO_3^{2-} and CSe_3^{2-}, CS_3^{2-} is planar.

Apart from the thermal degradation of some trithiocarbonates[8–10,22] and of $BaCSe_3$[23], from which the stability limits of phases having various degrees of hydration and some enthalpies of formation have been obtained, and the behavior of the chalcogenocarbonate ions in aqueous solution (cf. Section 3.3), the main sources of structural information have been the vibration[24–26] and electronic excitation spectra[27] of the ions CO_3^{2-}, CS_3^{2-}, and CSe_3^{2-}. In the free state these ions have D_{3h} symmetry, but their symmetry is decreased in the crystal because of the "site effect". Spectra of complex salts[20,28] and lattice vibrations[29] have also been studied. The fundamental vibrations of the ions are given in Table 2.

Table 2. Fundamental vibrations (cm^{-1}), valence force constants f_r (mdyne/Å), bond numbers N of the C-chalcogen bonds, according to *Siebert* [33], bond lengths $r_{spectr.}$ (Å) according to *Badger* [35], and bond lengths $r_{X\text{-ray}}$ (Å) [21, 36, 37] of CO_3^{2-}, CS_3^{2-}, and CSe_3^{2-} [38].

	ν_S	γ	ν_{as}	δ
CO_3^{2-}	1063	880	1415	680
CS_3^{2-}	520	505	905	320
CSe_3^{2-}	316	420	802	185

	f_r	N	$r_{spectr.}$	$r_{X\text{-ray}}$
CO_3^{2-}	7.66	1.42	1.30	1.294
CS_3^{2-}	3.72	1.16	1.68	1.68–1.70
CSe_3^{2-}	3.36	1.17	1.78	1.82

Complete sets of force constants and mean vibration amplitudes[32] have been calculated from the spectra for a general valence force system[26,30] and for a Urey-Bradley potential[26,31]. Values for the valence force constant f_r, which is linearly related to the Pauling electronegativities of the atoms O, S, and Se, are also shown in Table 2. The table also contains the bond numbers N found from f_r for the C-chalcogen

[4] Contrary to earlier views, *Hovenkamp* [5] has now been able, on the basis of a recalculated value of about 10^{-20} for the second dissociation constant of H_2S, definitely to assign the role of the acting ion to HS^-. For H_2Se ($K_2 \approx 10^{-15}$ [6]), on the other hand, reaction *via* the more active Se^{2-} ion cannot be ruled out.

[5] *S. G. Hovenkamp*, Dissertation, Delft University 1965.

[6] *R. H. Wood*, J. Amer. chem. Soc. *80*, 1559 (1958).

[7] Fundamental work directed to the preparation of trithiocarbonates and perthiocarbonates is described by *E. W. Yeoman*, J. chem. Soc. (London) *119*, 38 (1921).

[8] Na_2CS_3 and hydrates: *P. Silber* and *M. Maurin*, C. R. hebd. Séances Acad. Sci. *247*, 602 (1958); *M. Maurin*, Ann. Chimie *6*, 1221 (1961); *M. Maurin*, Dissertation, Montpellier University, 1962.

[9] K_2CS_3 and hydrates: *M. Maurin*, C. R. hebd. Séances Acad. Sci. *254*, 4470 (1962); *M. Maurin* and *P. Silber*, Rev. Chim. minérale *1*, 99 (1964).

[10] Rb_2CS_3 and Cs_2CS_3: *P. Silber*, *E. Philippot*, and *M. Maurin*, C. R. hebd. Séances Acad. Sci. *261*, 4126 (1965).

[11] Ammoniate adducts of alkali metal trithiocarbonates: *M. Maurin*, *E. Philippot*, and *P. Silber*, C. R. hebd. Séances Acad. Sci. *262*, 110 (1966); *E. Philippot*, Rev. Chim. minérale *4*, 643 (1967); *E. Philippot*, Dissertation, Montpellier University, 1967.

[12] Tl_2CS_3: *M. Picon* and *H. Le Chatelier*, C. R. hebd. Séances Acad. Sci. *195*, 1274 (1932); *M. Picon*, Bull. Soc. chim. France (4) *53*, 248 (1933).

[13] $In_2(CS_3)_3$: *G. J. Sutton*, Roy. Austral. chem. Inst. J. Proc. *1950*, 249.

[14] $PbCS_3$: *U. Gerwarth*, Diploma Thesis, Göttingen University, 1965; cf. also [25].

15] *H. Seidel*, Naturwissenschaften *52*, 539 (1965).

[16] *N. Hofmann-Bang* and *B. Rasmussen*, Naturwissenschaften *52*, 660 (1965).

[17] *G. Gattow* and *M. Dräger*, Z. anorg. allg. Chem. *348*, 229 (1966).

[18] *G. Gattow* and *M. Dräger*, Z. anorg. allg. Chem., in press.

[19] *J. P. Fackler, jr.* and *D. Coucouvanis*, Chem. Commun. *1965*, 556; J. Amer. chem. Soc. *88*, 3913 (1966); Proc. 9. int. Conf. Coordinat. Chem., St. Moritz-Bad 1966, 300; *K. N. Johri* and *K. Singh*, Indian J. appl. Chem. *30*, 1 (1967).

[20] *D. Coucouvanis* and *J. P. Fackler, jr.*, J. Amer. chem. Soc. *89*, 1346 (1967).

[21] *J. S. McKechnie*, *S. L. Miesel*, and *I. C. Paul*, Chem. Commun. *1967*, 152; *E. Philippot* and *M. Maurin*, C. R. hebd. Séances Acad. Sci. *266*, 1290 (1968).

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[23] *G. Gattow* and *M. Dräger*, unpublished.

[24] CO_3^{2-}: *S. D. Ross* and *J. A. Goldsmith*, Spectrochim. Acta *20*, 781 (1964), review of earlier literature given therein; *J. A. Goldsmith* and *S. D. Ross*, *ibid.* *22*, 1069 (1966); concerning the γ-vibrations in ^{13}C- and ^{14}C-labeled carbonates, cf. *W. Sterzel* and *E. Chorinsky*, *ibid.* Part A, *24*, 353 (1968).

[25] CS_3^{2-}: *H. Seidel*, Naturwissenschaften *52*, 257 (1965); *B. Krebs*, *G. Gattow*, and *A. Müller*, Z. anorg. allg. Chem. *337*, 279 (1965); *B. Krebs*, *A. Müller*, and *G. Gattow*, Z. Naturforsch. *20b*, 1017 (1965); *A. Müller* and *M. Stockburger*, *ibid.* *20a*, 1242 (1965); *A. Müller* and *B. Krebs*, Spectrochim. Acta *22*, 1535 (1966).

[26] CSe_3^{2-}: *H. Seidel*, Naturwissenschaften *52*, 539 (1965); *A. Müller*, *G. Gattow*, and *H. Seidel*, Z. anorg. allg. Chem. *347*, 24 (1966).

[27] *A. Müller*, *H. Seidel*, and *W. Rittner*, Spectrochim. Acta *23A*, 1619 (1967); *A. Müller* and *B. Krebs*, Mh. Chem. *98*, 1540 (1967).

[28] *B. Krebs* and *A. Müller*, Z. Naturforsch. *20a*, 1664 (1965); *A. Müller* and *B. Krebs*, Z. anorg. allg. Chem. *345*, 165 (1965).

[29] *E. E. Angino*, Amer. Mineralogist *52*, 137 (1967).

[30] *C. W. F. T. Pistorius*, J. chem. Physics *29*, 1174 (1958); *J. A. Ladd*, *W. J. Orville-Thomas*, and *B. C. Cox*, Spectrochim. Acta *20*, 1771 (1964); *L. Beckmann*, *L. Gutjahr*, and *R. Mecke*, *ibid.* *21*, 141 (1965); *B. Krebs* and *A. Müller*, Z. Naturforsch. *20a*, 1124 (1965); *A. Fadini*, *A. Müller*, and *B. Krebs*, *ibid.* *20a*, 1241 (1965); *A. Müller* and *A. Fadini*, Z. physik. Chem. N.F. *54*, 129 (1967); *A. Fadini* and *A. Müller*, Z. physik. Chem. (Leipzig) *236*, 309 (1967).

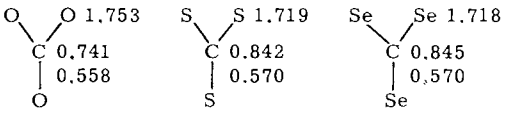
[31] *G. J. Janz* and *Y. Mikawa*, J. molecular Spectroscopy *5*, 92 (1960); *E. C. Curtis*, *ibid.* *17*, 108 (1965); *B. Krebs* and *A. Müller*, Spectrochim. Acta *22*, 1532 (1966).

[32] *G. Nagarajan* and *A. Müller*, Z. Naturforsch. *21b*, 393 (1966).

bonds[33,34], as well as the bond lengths $r_{spectr.}$[35] found from f_r, which can be compared with $r_{X\text{-ray}}$ for C–O in calcite[36], C–S in the bis(trithiocarbonato)niccolate(II) ion[21], and C–Se in *N*-benzoyl-*N'*-phenylselenourea[37].

The bands in the electronic excitation spectra of the ions CO_3^{2-}, CS_3^{2-}, and CSe_3^{2-} in aqueous solution have been assigned on the basis of an MO scheme and a simple HMO calculation[27]. The π-electron densities and π-bond orders obtained from the HMO calculation are shown in Scheme 1.

The π-bond orders vary in the opposite direction from *Siebert*'s bond number *N*.



Scheme 1.

Attempts to prepare $BaCSSe_2$[18] always lead to a substance whose IR spectrum points to a mixture of $BaCSe_3$ and $BaCSSe_2$[39], since the bands remaining on elimination of the CSe_3^{2-} spectrum show a logical relationship to the corresponding bands of the CS_2Se^{2-} ion, and all the bands for both ions can be assigned without difficulty to the six fundamental vibrations expected for an ion CX_2Y having C_{2v} symmetry[18]; these are shown in Table 3.

Table 3. Fundamental vibrations of the ions CS_2Se^{2-} and CSe_2S^{2-} (cm^{-1}).

CX_2Y	CS_2Se^{2-}	CSe_2S^{2-}
ν(CY)	842	930
ν_s(CX)	478	455
δ_s	299	193
γ	443	421
ν_{as}(CX)	930	898
δ_{as}	335	315

The ions CO_2S^{2-} and COS_2^{2-} are the primary products of the reactions of COS and CS_2 with OH^- ions in aqueous solution[40,41]; COS_2^{2-} is also formed on decomposition of simple xanthates in strongly alkaline media[3]. COS_2^{2-} can be detected by its characteristic UV absorption at 272 nm, and CO_2S^{2-} by its polarographic behavior. Dilute (10^{-4} M) solutions of COS_2^{2-} in 5 N sodium hydroxide solution have an average lifetime of about 50 hours (at room temperature). More concentrated solutions cannot be prepared, since COS_2^{2-} reacts rapidly with an excess of CS_2 to form CS_3^{2-}. Dilute solutions of CO_2S^{2-} in 5 N sodium hydroxide solution, on the other hand, have a half-life of only about 5 min at room temperature, but can be stabilized for a few hours by cooling to −30 °C (the freezing point of the aqueous solution being lowered by addition of $NaClO_4$). Both ions decompose rapidly in more weakly alkaline solution. COS_2^{2-} first forms COS, which reacts with OH^- to form CO_2S^{2-}; CO_2S^{2-} decomposes to form SH^- and CO_3^{2-}. CS_2 is not regenerated[40,41].

3.2. Hydrogen Anions HCX_3^-

Aqueous solutions of the anions listed in Table 1 or the corresponding acids always contain the monoprotonated anion in the dissociation equilibrium (cf. Section 3.3). However, since the decomposition of CO_2S^{2-}[40] and CS_3^{2-}[42], and probably also of CS_2Se^{2-}[18], proceeds *via* the hydrogen anions HCX_3^-, it is not surprising that no salts of any of these ions have been obtained.

Hydrogen carbonates have been known for a very long time. However, these do not contain free HCO_3^- groups, but infinite chains[43] or dimers[44] held together by hydrogen bonds. The stability of these salts is therefore primarily due to the strong O–H···O bond. HCO_3^- groups that are no longer held together by hydrogen bonds occur in the crystalline state when samples of hydrogen carbonate in alkali metal halide disks are heated to 480 °C[45]; these groups are retained when the disks are quenched to room temperature, and can be detected by their IR spectrum, which contains all nine fundamental vibrations of the HCO_3^- ion. A force constant determination gave values of 9.12 mdyne/Å for the valence force constant f_r[45], 1.53 for the Siebert bond number *N*[33], and 1.27 Å for the length $r_{spectr.}$ of the two free C–O bonds[38].

3.3. Acids

The anions of Table 1 are all fairly stable in strongly alkaline aqueous solution and in an atmosphere of nitrogen, whereas they rapidly decompose in acidic

[33] *H. Siebert*, Z. anorg. allg. Chem. *273*, 170 (1953).

[34] The required valence force constant of the corresponding single bond was also calculated as described by *Siebert* [33].

[35] *R. M. Badger*, J. chem. Physics *3*, 710 (1935).

[36] *R. L. Sass*, *R. Vidale*, and *J. Donohue*, Acta crystallogr. *10*, 567 (1967).

[37] *H. Hope*, Acta crystallogr. *18*, 259 (1965).

[38] The values given for *N* and $r_{spectr.}$ have been recalculated.

[39] A mixture of $BaCSe_3$ and $BaCS_3$, according to [15]; however, the IR spectra in [18] clearly show that the product does not contain $BaCS_3$.

[40] Reaction of COS with OH^-: *B. Philipp*, Faserforsch. u. Textiltechn. *6*, 433 (1955); *B. Philipp* and *H. Dautzenberg*, Z. physik. Chem. (Leipzig) *229*, 210 (1965).

[41] Reaction of CS_2 with OH^-: *E. Treiber*, *W. Lang*, and *E. Mader*, Holzforschung *8*, 97 (1954), and review of earlier literature given therein; *B. Philipp*, Faserforsch. u. Textiltechn. *6*, 433, 509 (1965); *M. Wronski*, Zeszyty naukowe Uniw. Łódzkiego, Ser. II *2*, 107 (1956); Faserforsch. u. Textiltechn. *7*, 175 (1956); *8*, 32 (1957); Roczniki Chem. (Ann. Soc. chim. Polonorum) *32*, 849 (1958); Z. physik. Chem. (Leipzig) *211*, 118 (1959); *H. Schmiedeknecht* and *W. Claus*, Faserforsch. u. Textiltechn. *14*, 386 (1963); *S. G. Hovenkamp*, J. Polymer Sci., Part C *2*, 341 (1963); Faserforsch. u. Textiltechn. *17*, 100, 139 (1966); cf. also [5]; *B. Philipp* and *H. Dautzenberg*, Mber. dtsch. Akad. Wiss. Berlin *6*, 148 (1964); Faserforsch. u. Textiltechn. *17*, 1 (1966).

[42] *G. Gattow* and *B. Krebs*, Z. anorg. allg. Chem. *323*, 13 (1963); *S. G. Hovenkamp*, Faserforsch. u. Textiltechn. *17*, 305, 370, 400 (1966); *J. R. Mickelsen* and *T. H. Norris*, Inorg. Chem. *5*, 917 (1966); cf. also [5].

[43] *R. L. Sass* and *R. F. Scheuermann*, Acta crystallogr. *15*, 77 (1962); *R. Brooks* and *T. C. Alcock*, Nature (London) *166*, 435 (1950).

[44] *C. J. Brown*, *H. S. Peiser*, and *A. Turner-Jones*, Acta crystallogr. *2*, 167 (1949); *G. E. Bacon* and *N. A. Curry*, *ibid. 9*, 82 (1956); *I. Nitta*, *Y. Tomiie*, and *C. H. Koo*, *ibid. 5*, 292 (1952); *P. Herpin* and *P. Meriel*, J. Physique *25*, 484 (1964); *B. Pedersen*, Acta crystallogr. B *24*, 478 (1968).

[45] *D. L. Bernitt*, *K. O. Hartman*, and *I. C. Hisatsune*, J. chem. Physics *42*, 3553 (1965).

solution *via* the undissociated acid or the hydrogen anion. *e.g.*:

$$H_2CO_3 \rightarrow H_2O + CO_2 \quad (5)$$

$$HCO_2S^- \rightarrow HS^- + CO_2 \quad (6)$$

$$H_2COS_2 \rightarrow H_2S + COS \quad (7)$$

$$HCS_3^- \rightarrow HS^- + CS_2 \quad (8)$$

$$HCS_2Se^- \rightarrow HSe^- + CS_2 \quad (9)$$

$$H_2CSe_3 \rightarrow H_2Se + \text{polymeric C–Se products} \quad (10)$$

(5) is a very fast reaction, which, like the slow reverse reaction of the hydration of CO_2, has been very extensively studied because of its practical importance[46]. Reactions (6) and (7), which are also very fast, have not yet been followed in acidic solution[40,41]. The rapidity of reactions (5) to (7) makes it impossible to obtain these acids from the aqueous phase.

The same is true of H_2CSe_3, which has a half-life of 15 sec in 10^{-3} M solution at 0 °C and so permits conductivity measurements, but decomposes very rapidly in more concentrated solutions to form C-Se polymers that have not yet been studied in detail [reaction (10)][17,47]. Thus H_2CSe_3 also cannot be obtained from aqueous solution. H_2CS_3[42] and H_2CS_2Se[18], on the other hand, decompose *via* their hydrogen anions, and are therefore so stable in fairly concentrated strongly acidic solution that the free acids can be precipitated from aqueous solutions of their salts owing to their low solubility in water.

Extensive measurements on aqueous solutions of the salts and the free acids have led to the values given in Table 4 for the electrolytic dissociation constants; the constants for perthiocarbonic acid H_2CS_4[49] are also given for comparison.

Table 4. Dissociation constants K_1 at 0 °C and K_2 at 25 °C.

	H_2CO_3 [48]	H_2CS_3 [42]	H_2CSe_3 [47]	H_2CS_2Se [18]	H_2CS_4 [49]
K_1	1.55×10^{-4}	1.2 [a]	6.9×10^{-2}	1.2×10^{-5}	2.8×10^{-4} [b]
K_2	4.69×10^{-11}	1.2×10^{-7} [a]	6.9×10^{-8}	1.0×10^{-11}	5.75×10^{-8}

[a] Value for 20 °C. [b] Value for 2 °C.

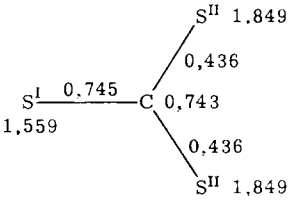
Free H_2CS_3 is formed on reaction of an aqueous suspension of $BaCS_3$ with hydrochloric acid at 0 °C. It occurs as a red oil, which can be separated from the aqueous phase without appreciable decomposition, dried, and stored at −78 °C[50]. Many physical and thermodynamic constants of the substance, which solidifies at −26.9 °C, have been determined[50,51].

An X-ray structural analysis at −100 °C showed that solid H_2CS_3 exists in the form of isolated molecules, which are joined by hydrogen bonds to form double spirals with alternating left-hand and right-hand twists. The CS_3 group is planar, and the various C–S distances are given in Table 5.

Table 5. C–S distances in solid H_2CS_3 at −100 °C [52].

C=S	S as H-bond acceptor	1.69–1.70 Å
C–S–H	S as H-bond donor	1.75–1.77 Å
C–S–H	S not bound by H bond	1.71–1.73 Å

The hydrogen bonds in solid and liquid H_2CS_3 are indicated in the IR system[50,53] by an S–H stretching band at about 2500 cm^{-1}, which is replaced by a sharp split band at 2550 cm^{-1} in dilute solutions of H_2CS_3 in CCl_4, in which the H bonds are broken. The other IR bands have been assigned to the fundamental vibrations of the $SC(SH)_2$ molecule[54]. HMO calculations[54,55] for the CS_3 skeleton of the acid give the π-electron densities and π-bond orders shown in Scheme 2.



Scheme 2.

H_2CS_3 is of little importance as a reagent in preparative chemistry. The only known reactions in which the CS_3 grouping is retained are the reaction with oxalyl chloride to form 4,5-dioxo-2-thioxo-1,3-dithiolane[56], the reaction with chlorosulfanes S_xCl_2 to form $(CS_{3+x})_n$ (n about 10, x = 1 to 6)[57], and the oxidation by bromine at −30 °C to give $(CS_3)_n$[58] (n about 9). The products obtained in all other cases are also obtainable by similar reactions with H_2S[62]. However, H_2CS_3 is frequently more reactive[59]. Heavy metal

[46] *D. M. Kern*, J. chem. Educat. *37*, 14 (1960): comprehensive summary of the reactions occurring between CO_2, H_2O, H_2CO_3, HCO_3^- und CO_3^{2-}; cf. also [66].

[47] *G. Gattow* and *M. Dräger*, Z. anorg. allg. Chem. *349*, 202 (1967).

[48] *K. F. Wissbrun*, *D. M. French*, and *A. Patterson*, J. physic. Chem. *58*, 693 (1954); *H. S. Harned* and *S. R. Scholes*, J. Amer. chem. Soc. *63*, 1706 (1941).

[49] *G. Gattow* and *J. Wortmann*, Z. anorg. allg. Chem. *345*, 137, 172 (1966).

[50] *G. Gattow* and *B. Krebs*, Z. anorg. allg. Chem. *321*, 143 (1963).

[51] *G. Gattow* and *B. Krebs*, Z. anorg. allg. Chem. *322*, 113 (1963).

[52] *B. Krebs* and *G. Gattow*, Naturwissenschaften *51*, 554 (1964); Z. anorg. allg. Chem. *340*, 294 (1965).

[53] *P. A. Tice* and *D. B. Powell*, Spectrochim. Acta *21*, 835 (1965).

[54] *A. Müller*, *B. Krebs*, and *G. Gattow*, Z. anorg. allg. Chem. *349*, 74 (1967).

[55] *J. Fabian*, *A. Mehlborn*, *A. Bormann*, and *R. Mayer*, Wiss. Z. Techn. Univ. Dresden *14*, 285 (1965).

[56] *B. Krebs* and *G. Gattow*, Angew. Chem. *75*, 978 (1963); Angew. Chem. internat. Edit. *2*, 618 (1963); *A. Müller*, *B. Krebs*, and *R. Ahlrichs*, Z. Naturforsch. *21b*, 389 (1966).

[57] *M. Schmidt*, Angew. Chem. *73*, 394 (1961).

[58] *B. Krebs* and *G. Gattow*, Z. anorg. allg. Chem. *338*, 225 (1965). Polymeric $(CS_{2.5})_n$ with $n \approx 8$–9 was also obtained by reaction of Na_2CS_3 or Na_2S with thiophosgene.

[59] Compare the formation of dimeric and polymeric thiomalonic anhydride on reaction with malonyl chloride [60] and the reaction with dimeric thiophosgene to form 4,4-dichloro-1,3-dithia-2-cyclobutanethione [61], which affords derivatives of ditrithiocarbonic acid with Na_2S, thiols, or amines [61].

[60] *B. Krebs* and *G. Gattow*, Angew. Chem. *78*, 210 (1966); Angew.Chem. internat. Edit. *5*, 250 (1966).

[61] *J. Wortmann*, *G. Kiel*, and *G. Gattow*, Z. Naturforsch., in press.

[62] Thiosuccinic anhydride [63], very pure Al_2S_3 [63], thiophthalic anhydride [61], chlorothiolacetic acid [61], thioltere-phthalic acid [61], thiolisophthalic acid [61].

[63] *B. Krebs* and *G. Gattow*, Angew. Chem. *77*, 1086 (1965); Angew. Chem. internat. Edit. *4*, 1090 (1965).

trithiocarbonates can be readily obtained in the pure state by reaction of the acetates with H_2CS_3 in dimethyl sulfoxide [14].

Like H_2CS_3, free H_2CS_2Se can be obtained by reaction of an aqueous suspension of the barium salt with hydrochloric acid [18]. It is a bluish-red oil, which cannot be obtained in the pure state owing to rapid decomposition, but can only be separated by dissolution in a stabilizing organic phase. It is stable at low temperatures in this phase after drying. H_2CS_2Se probably exists in the asymmetric form *(1)*, since only H_2Se and CS_2 can be detected when it decomposes, and methylation of CS_2Se^{2-} yields the asymmetric dimethyl ester *(2)* [64].

(1) *(2)*

The other trichalcogenocarbonic acids, on the other hand, can be prepared only in nonaqueous solution, *i.e.* from the anhydrous salts, so that H_2CO_2S and H_2COS_2, whose anions are known only in aqueous solution, have not yet been obtained.

Free carbonic acid is formed as the dimethyl ether monoadduct $H_2CO_3 \cdot O(CH_3)_2$ on reaction of dry Na_2CO_3 with HCl in dimethyl ether at −35 °C; the excess of dimethyl ether is evaporated off under vacuum at −80 °C [65, 66]. The white crystalline adduct melts at −47 °C with polymerization, and decomposes at temperatures >−26 °C to give H_2O, CO_2, and $O(CH_3)_2$. ^{1}H-NMR studies have shown the presence of C−O−H protons [66]. A number of thermodynamic constants have been determined from vapor pressure measurements [65–67]. A monoadduct with diethyl ether reported earlier [68] could not be definitely confirmed by other investigators [66]. The description of the experiment [68] suggests the presence of an addition compound having a variable composition [69].

Similar experiments on a suspension of $BaCSe_3$ in diethyl ether with HCl at −30 °C lead to the formation of a dark red, highly viscous oil, which decomposes very rapidly above −10 °C [17]. Owing to low solubility in organic solvents, it has not yet been possible to separate H_2CSe_3 from $BaCl_2$ formed at the same time.

4. Monoalkylated Trichalcogenocarbonic Acids

The various types of monoalkyl trichalcogenocarbonic acids and trichalcogenocarbonates are listed in Table 6. The alkyl group may be bound to different chalcogen atoms. The most extensively studied of these compounds are the ethyl derivatives.

Table 6. Monoalkyl trichalcogenocarbonic acids and trichalcogenocarbonates; existence of compounds in brackets still doubtful (examples of R : C_2H_5, CH_3).

Anions	Acids
CO_2−OR$^-$	[CO(OH)−OR]
COS−OR$^-$	–
[CO_2−SR$^-$]	[CO(OH)−SR]
CS_2−OR$^-$	CS(SH)−OR
COS−SR$^-$	–
CS_2−SR$^-$	CS(SH)−SR
–	[CO(SeH)−OR]
CSSe−OR$^-$	[CS(SeH)−OR]
CSe_2−OR$^-$	

4.1. Anions

Monoalkyl trichalcogenocarbonates are generally prepared by reaction of CO_2, COS, CS_2, CSSe, and CSe_2 with alkoxides or thiolates [1]; reactions with selenolates or tellurolates have not yet been examined. Transesterifications and partial hydrolyses of dialkyl compounds can also be used.

Alkyl carbonates in aqueous solution exist in the equilibrium

$$R{-}O{-}CO_2^- + H_2O \rightleftharpoons HCO_3^- + R{-}OH$$

The equilibrium constant at 0 °C is $K = 12$ for the methyl compound and $K = 23$ for the ethyl compound [70]. Salts can therefore only be obtained in alcoholic solutions. In acidic and in alkaline media, the equilibrium is strongly displaced toward the decomposition products; equilibrium is reached very rapidly in acidic solution, but slowly in alkaline solution [70]. Whereas alkaline earth metal alkyl carbonates have high CO_2 partial pressures, dry alkali metal salts are very stable [70]. Alkyl carbonates are used as carboxylating agents [71, 72].

O-Alkyl monothiocarbonates are formed when COS is passed into alcoholic alkoxide solutions [1]; the best known of these compounds is potassium *O*-ethyl monothiocarbonate (Bender's salt) [73]. These compounds decompose rapidly in aqueous solution *via*

[64] *M. Dräger* and *G. Gattow*, unpublished.

[65] *G. Gattow* and *U. Gerwarth*, Angew. Chem. *77*, 132 (1965); Angew. Chem. internat. Edit. *4*, 149 (1965).

[66] *G. Gattow* and *U. Gerwarth*, Z. anorg. allg. Chem. *357*, 78 (1968).

[67] Calculation of thermodynamic functions for the ideal gas state from assumed molecular parameters: *A. A. Antonov* and *P. G. Maslov*, Russ. J. inorg. Chem. (Engl. transl. of Ž. neorg. Chim.) *38*, 318 (1964).

[68] *A. G. Galinos* and *A. A. Carotti*, J. Amer. chem. Soc. *83*, 752 (1961).

[69] *W. Hempel* and *J. Seidel*, Ber. dtsch. chem. Ges. *31*, 2997 (1898).

[70] *C. Faurholt*, Z. physik. Chem. *126*, 72, 85, 211, 227 (1927); *C. Faurholt* and *I. C. Jespersen*, *ibid. 165*, 79 (1933); *C. Faurholt*, *K. Noiesen*, and *F. Rath*, Dansk. Tidskr. Farmaci *11*, 267 (1937); *C. Faurholt* and *K. P. Hansen*, *ibid. 16*, 73 (1942); *C. Faurholt* and *J. C. Gjaldbaek*, *ibid. 17*, 213 (1943); *19*, 255 (1945); *V. Lund*, *J. C. Gjaldbaek*, and *C. Faurholt*, *ibid. 21*, 243 (1947); *H. Soling* and *C. Faurholt*, *ibid. 25*, 89 (1951).

[71] *J. I. Jones*, Chem. and Ind. *1958*, 228.

[72] *M. Stiles*, Ann. New York Acad. Sci. *88*, 332 (1960); *K. Winterfeld* and *H. Buschbeck*, Arch. Pharmaz. *294*, 468 (1961); *R. F. Ruthruff*, U.S. Pat. 3038006 (June 5, 1962); U.S. Pat. 3102906 (Sept. 3, 1963); *G. D. Buckley*, British Pat. 940371 (Oct. 30, 1963) ICI; *H. L. Finkbeiner* and *G. W. Wagner*, J. org. Chemistry *28*, 216 (1963); *H. L. Finkbeiner*, J. Amer. chem. Soc. *87*, 4588 (1965). For the formation of high polymers from unsaturated monoalkyl carbonates, cf. *F. Pochetti*, Rass. chim. *11*, 232 (1965).

[73] *C. Bender*, Liebigs Ann. Chem. *148*, 137 (1868) regarding the rate of the reaction COS-ethanol, cf. *B. Philipp* and *H. Dautzenberg*, Z. physik. Chem. (Leipzig) *231*, 270 (1966).

the free *O*-ethyl monothiocarbonic acid. The rate of decomposition consequently decreases steadily above pH ~ 9, while it rapidly increases below this pH value [3, 74]. IR spectroscopic data for the alkyl monothiocarbonates are given in Table 7 [75]. *S*-Alkyl monothiocarbonates are much less stable, and have so far been obtained only in solution. They are formed from alkyl carbonates on transesterification with thiolates [71].

O-Alkyl dithiocarbonates, which are generally known as xanthates, are the most extensively studied and the (technically) most important group of alkyl chalcogenocarbonates. They are formed by reaction of CS_2 with alkoxides [11, 76]. Xanthates are relatively stable in aqueous solution between pH 7 and pH 14 [3], but decompose rapidly outside this range [77, 78]. The decomposition in acidic solution [77] proceeds *via* the free xanthic acid with formation of alcohol and CS_2 (cf. Section 4.2), while that in alkaline solution [78], proceeds *via* a dithiocarbonate to give sulfide and carbonate.

Crystal structure determinations [79] have shown that the ionic alkali metal xanthates consist of isolated cations and xanthate groups, while the xanthates of arsenic and antimony, as well as of the transition metals, have complex molecules in which the xanthate sulfur has a square-planar arrangement around M^{II} or a distorted octahedral arrangement around M^{III} [80]. The two C–S bonds in the ionic xanthates are equivalent (C–S = 1.68 Å), whereas the complex xanthates contain one short (1.56–1.65 Å) and one long (1.70–1.79 Å) C–S bond. The CS_2O portion is planar in all the xanthates. On examination of the IR spectrum [80, 81] (see Table 7), no definite distinction could be made between C=S and C–O–C vibrations, which couple strongly with one another. The electronic excitation spectrum contains strong absorption maxima at 301 and 226 nm [82].

Table 7. IR bands of alkyl chalcogenocarbonates.

ν (cm⁻¹)	COS–OR [75]	CS_2–OR [80, 81]	COS–SR [84]	CS_2–SR [81]	CSe_2–OR [88]
νCO	1570–1580		1560		
νCS	1025–1040	1020–1070	950–960	1000–1050	
νCSe					940–950
νCOC	1090–1120	1100–1280			

The *S*-alkyl dithiocarbonates are also much less stable than the *O*-alkyl compounds. They are formed on careful hydrolysis of *O*,*S*-dialkyl dithiocarbonates with tertiary amines in organic solvents below room temperature [83], and decompose in aqueous solution into COS and alkanethiols.

The alkyl trithiocarbonates, which are obtained by reaction of alkanethiolates with CS_2 [1], form salts that are relatively stable even in aqueous solution [81, 82].

Alkyl selenocarbonates corresponding to the xanthates, *i.e.* *O*-alkyl thioselenocarbonates [85] and *O*-alkyl diselenocarbonates [86] have been obtained in the form of their alkali metal salts by reaction of alkoxides with CSSe or CSe_2. These salts form yellow crystals, and are stable only under nitrogen, in the absence of light, and at low temperatures. CSe_2 reacts vigorously with cellulose to give cellulose selenoxanthate, the rapid formation of which is followed by equally rapid decomposition [87].

4.2. Acids

The xanthic acids [89] and the trithiocarbonic acids [90] can be precipitated from aqueous solutions of salts

[74] *M. Wronski*, Faserforsch. u. Textiltechn. *10*, 46 (1959).

[75] *F. G. Pearson* and *R. B. Stasiak*, Appl. Spectroscopy *12*, 116 (1958).

[76] Concerning reaction of formation, cf. *M. Wronski*, Roczniki Chem. (Ann. Soc. chim. Polonorum) *33*, 1061 (1959); Z. physik. Chem. (Leipzig) *211*, 113 (1959) as well as [5].

[77] Decomposition of xanthate in acid medium: *H. v. Halban* and *W. Hecht*, Z. Elektrochem. angew. physik. Chem. *24*, 65 (1918); *C. V. King* and *E. Dublon*, J. Amer. chem. Soc. *54*, 2177 (1932); *A. Chatenever* and *C. V. King*, *ibid. 71*, 3587 (1949); *A. C. Cranendonc*, Recueil Trav. chim. Pays-Bas *70*, 431 (1951); *I. Iwasaki* and *S. R. B. Cooke*, Mining Engng. *9*, 1267 (1957); J. Amer. chem. Soc. *80*, 285 (1958); J. physic. Chem. *63*, 1321 (1959); *68*, 2031 (1964); *E. Klein*, *J. K. Bosarge*, and *I. Normann*, *ibid. 64*, 1666 (1960); *R. Zahradnik*, Z. physik. Chem. (Leipzig) *213*, 318 (1960); *B. Toernell*, Svensk Papperstidn. *69*, 658, 695 (1966); *V. Hejl* and *F. Pechar*, Chem. Zvesti *21*, 261 (1967), as well as [3].

[78] Decomposition of xanthate in alkaline medium: *M. Wronski*, Zeszyty naukowe Uniw. Łódzkiego, Ser. II *3*, 177 (1957); Z. physik. Chem. (Leipzig) *211*, 113 (1959); *H. J. Bär*, *H. Dautzenberg*, and *B. Philipp*, Z. physik. Chem. (Leipzig) *237*, 145 (1968), as well as [3].

[79] Crystal-structure determination of xanthates: K ethyl: *F. Mazzi* and *C. Tadini*, Z. Kristallogr. Kristallgeometr., Kristallphysik, Kristallchem. *118*, 378 (1963); As ethyl: *G. Carrai* and *G. Gottardi*, *ibid. 113*, 373 (1960); Sb ethyl: *G. Gottardi*, *ibid. 115*, 451 (1961); Ni ethyl: *M. Franzini*, *ibid. 118*, 393 (1963); Mo ethyl (binuclear): *A. B. Blake*, *F. A. Cotton*, and *J. S. Wood*, J. Amer. chem. Soc. *86*, 3024 (1964); Cd *n*-butyl: *H. M. Rietveld* and *E. N. Maslen*, Acta crystallogr. *18*, 429 (1965); Zn ethyl: *T. Ikeda* and *H. Hagihara*, *ibid. 21*, 919 (1966); Pb ethyl: *H. Hagihara* and *S. Yamashita*, *ibid. 21*, 350 (1966); Pb *n*-butyl: *H. Hagihara* and *Y. Watanabe*, *ibid.* B *24*, 960 (1968); Te ethyl: *S. Husebye*, Acta chem. scand. *21*, 42 (1967).

[80] Preparation and IR spectrum of complex transition metal xanthates: *G. W. Watt* and *B. J. McCormick*, J. inorg. nuclear Chem. *27*, 898 (1965); Spectrochim. Acta *21*, 753 (1965); *U. Agarwala*, *Lakshmi*, and *P. B. Rao*, Inorg. chim. Acta *2*, 337 (1968). For the strength of the ligand field, cf. the NMR measurements on ^{59}Co complexes: *C. R. Kanekar*, *M. M. Dhingra*, *V. R. Marathe*, and *R. Nagarajan*, J. chem. Physics *46*, 2009 (1967).

[81] Review of the IR spectra of xanthates, alkyl trithiocarbonates, and dithiocarbamates: *M. L. Shankaranarayana* and *C. C. Patel*, Spectrochim. Acta *21*, 95 (1965); *D. Coucouvanis* and *J. P. Fackler*, *jr.*, Inorg. Chem. *6*, 2047 (1967).

[82] Review of the UV spectra of xanthates, alkyl trithiocarbonates, and dithiocarbamates: *M. L. Shankaranarayana* and *C. C. Patel*, Acta chem. scand. *19*, 1113 (1965).

[83] *H. Yoshida* and *S. Inokawa*, J. chem. Soc. Japan, pure Chem. Sect. (Nippon Kagaku Zasshi) *86*, 950 (1965); *H. Yoshida*, *S. Inokawa*, and *T. Ogata*, *ibid. 86*, 1179 (1965); *87*, 1209, 1212 (1966); Bull. chem. Soc. Japan *39*, 411 (1966).

[84] Recorded for tetramethylammonium *S*-methyl dithiocarbonate. We are grateful to *H. Yoshida*, Hamamatsu, for supplying the substance.

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[86] *A. Rosenbaum*, *H. Kirchberg*, and *E. Leibnitz*, J. prakt. Chem. (4) *19*, 1 (1963); *A. Rosenbaum*, *ibid. 37*, 200 (1968); Bergakademie, Freiberger Forschungsh. Ausg. A *328*, 59 (1964).

[87] *E. Treiber* and *J. Rehnström*, Papier *12*, 274 (1958).

[88] *K. A. Jensen*, *J. B. Carlsen*, *A. Holm*, and *P. H. Nielsen*, Acta chem. scand. *17*, 550 (1963).

[89] Xanthic acids: methyl: [53]; ethyl: *H. v. Halban* and *A. Kirsch*, Ber. dtsch. chem. Ges. *45*, 2418 (1912); Z. physik. Chem. *82*, 325 (1913); *n*-propyl: *S. Scala*, Gazz. chim. ital. *17*, 79 (1887); isoamyl: *O. L. Erdmann*, J. prakt. Chem. (1) *31*, 4 (1844); allyl: *B. Oddo* and *G. del Rosso*, Gazz. chim. ital. *39*, 15 (1909); benzyl: [77].

[90] Alkyltrithiocarbonic acids: methyl: [53]; ethyl: *B. Holmberg*, J. prakt. Chem. (2) *73*, 239 (1906); *p*-chlorobenzyl and *p*-bromobenzyl: *H. v. Halban*, *A. Mackert*, and *W. Ott*, Z. Elektrochem. angew. physik. Chem. *29*, 445 (1923).

of alkyl trichalcogenocarbonic acids by dilute hydrochloric acid or sulfuric acid. They separate out as oily liquids or even in the crystalline form, and can be isolated without difficulty. The rate of decomposition of the other alkyl chalcogenocarbonates in acidic media is so high, on the other hand, that the free acids cannot be obtained from aqueous solution.

Distillation of liquid CO_2 into alcohols at −50 °C under pressure yields compounds having the empirical formulas of alkyl esters of carbonic acid[69] (the methyl, ethyl, propyl, *tert*-butyl, and amyl compounds have been prepared). However, these are probably addition compounds rather than free alkyl carbonic acids, since a reaction between CO_2 and alcohol under these conditions is very unlikely. Equally improbable is the formation of a stable solid *S*-ethyl thiocarbonic acid by oxidation of ethylthioacetylene with 30% H_2O_2 in glacial acetic acid on heating[91]. *O*-Ethyl selenocarbonic acid is reported to be formed on reaction of ethyl chloroformate and magnesium hydrogen selenide bromide as colorless needles having m.p. 122–123 °C[92].

Free selenoxanthic acid is formed on acidification of aqueous monoselenoxanthate solution as an oil that decomposes rapidly with formation of selenium[85].

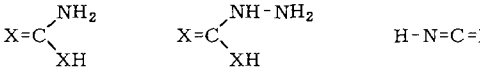
Xanthic acids are very stable in the perfectly pure state or in apolar solvents even at 50 °C[89, 93]. Even traces of polar substances, however, cause decomposition into CS_2 and alcohol, which further accelerates the decomposition autocatalytically. Extensive measurements on the decomposition kinetics[77] have shown that the first step in the decomposition of the acid is the formation of an active zwitterionic complex. The rate of decomposition of the xanthic acids decreases again in strongly acidic solution, since they are then present in the protonated form. The dissociation constant of ethylxanthic acid is 0.023 at 0 °C and 0.027 at 25 °C[77].

Pure xanthic acids and alkyl trithiocarbonic acids contain intermolecular hydrogen bonds[53], which are broken in solutions of the acids.

High molecular weight cellulosexanthic acid is formed as the initial product in the reaction of cellulose xanthate with acids in aqueous solution[94]. The decomposition can be followed by measurement of the UV absorption at 270 nm; the dissociation constant is about 0.05.

5. Chalcogenocarbonic Acids Containing Nitrogen

Known chalcogenocarbonic acids containing nitrogen are carbamic acids, carbazic acids, and isocyanic acids.



[91] *R. Adams* and *A. Ferretti*, J. Amer. chem. Soc. *81*, 4927 (1959).

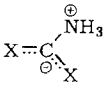
[92] *Q. Mingoia*, Gazz. chim. ital. *58*, 670 (1928).

[93] *G. M. Lewis*, Dissertation, New York University, 1947.

[94] *H. Jost* and *J. Ludwig*, Faserforsch. u. Textiltechn. *17*, 29, 194 (1966); *18*, 274 (1967).

Chalcogenocarbamic acids in general are prepared by reaction of their salts, the chalcogenocarbamates[95], with acids. Ammonium or alkylammonium salts are readily obtained by reaction of CO_2, COS, CS_2, or CSe_2 with ammonia or amines[1, 86, 96–99]. In addition to a number of IR[81, 100] and UV[82, 101] spectroscopic studies, special mention should be made of the numerous crystal structure determinations of a wide range of dithiocarbamate complexes[102]. In these complexes, in contrast to the xanthate complexes, the two C–S bonds generally appear, to a close approximation, to be equivalent (C–S ≈ 1.68–1.71 Å).

This tendency to form equivalent C-chalcogen bonds in the form of a zwitterion is also found in the free acids. However, extensive decomposition measure-



ments in aqueous dithiocarbamate solutions have shown[103] that their decomposition begins with a zwitterionic form of this type, so that the rate of decomposition of the chalcogenocarbamic acids increases rapidly with increasing *N*-alkylation (and

[95] Cf. *W. Haas* and *K. Irgolič*, Z. analyt. Chem. *193*, 248 (1963).

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[100] *R. A. Nyquist* and *W. J. Potts*, Spectrochim. Acta *17*, 679 (1961); *D. L. Frasco*, J. chem. Physics *41*, 2134 (1964); *K. Nakamoto*, *J. Fujita*, *R. Condrate*, and *Y. Morimoto*, *ibid. 39*, 423 (1963) as well as [88].

[101] *E. Svatek*, *R. Zahradnik*, and *A. Kjaer*, Acta chem. scand. *13*, 442 (1959); *M. J. Janssen*, Recueil Trav. chim. Pays-Bas *79*, 454, 1066 (1960).

[102] Recent determinations of the crystal structures of dithiocarbamates: *K. A. Fraser* and *M. M. Harding*, Acta crystallogr. *22*, 75 (1967); *R. Bally*, *ibid. 23*, 295 (1967); *G. F. Gasparri*, *M. Nardelli*, and *A. Villa*, *ibid. 23*, 384 (1967); *G. Peyronel* and *A. Pignedoli*, *ibid. 23*, 398 (1967); *M. Colapietro*, *A. Domenicano*, *L. Scaramuzza*, *A. Vaciago*, and *L. Zambonelli*, Chem. Commun. *1967*, 583; *M. Colapietro*, *A. Domenicano*, *L. Scaramuzza*, and *A. Vaciago*, *ibid. 1968*, 302; *K. Bowman* and *Z. Dori*, *ibid. 1968*, 636; *A. Domenicano*, *L. Torelli*, *A. Vaciago*, and *L. Zambonelli*, J. chem. Soc. (London) A *1968*, 1351; *P. T. Beurskens*, *H. J. A. Blaauw*, *J. A. Cras*, and *J. J. Steggerda*, Inorg. Chem. *7*, 805 (1968); *P. T. Beurskens*, *J. A. Cras*, and *J. J. Steggerda*, *ibid. 7*, 810 (1968).

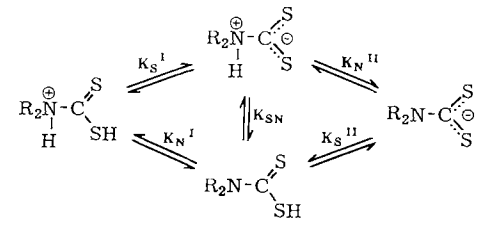
[103] *P. Zuman* and *R. Zahradnik*, Z. physik. Chem. (Leipzig) *208*, 135 (1957); *R. Zahradnik* and *P. Zuman*, Chem. Listy *52*, 231 (1958); Collect. czechoslov. chem. Commun. *24*, 1132 (1959); *B. Philipp*, *H. Dautzenberg*, and *H. Lang*, Faserforsch. u. Textiltechn. *19*, 325 (1968).

hence increasing basicity of the amide group), while carboxyl or phenyl groups on the amide nitrogen stabilize the free acids. Apart from unsubstituted dithiocarbamic acid[104], therefore, all the known[109] chalcogenocarbamic acids are stabilized in this way, *i.e.* *N*-(2-acetyl-2-ethoxycarbonylthioacetyl)-, *N*-[2,2-bis(ethoxycarbonyl)thioacetyl]-, *N*-(2,2-diacetylthioacetyl)-, and *N*-(2-ethoxycarbonyl-2-cyanothioacetyl)-carbamic acids[105] and *N*,*N*-diphenyl-[106], *N*-cyano-[107], and *N*-thiocarbamoyldithiocarbamic acid[108].

Dithiocarbamic acid itself is formed as colorless needles when concentrated hydrochloric acid is added dropwise to an aqueous solution of its ammonium salt at 0 °C[104]. It is stable below 0 °C, but decomposes rapidly at higher temperatures to give CS_2 and ammonium dithiocarbamate[110]. The crystals melt at about 35 °C. According to its IR spectrum[104], unsubstituted dithiocarbamic acid in the crystalline state also consists of unionized acid molecules, which are joined in pairs by strong S–H···N bonds. The resulting double molecules are linked to one another by weaker S–H···S bonds. The decomposition of the acid in the double molecule begins with the transfer of the bridge proton from the sulfur to the nitrogen, the acceptor molecule then breaking down into CS_2 and NH_4^+.

The recently described preparation of the liquid compounds[111] *N*-β-hydroxyethylcarbamic acid (perfectly stable up to 120 °C) and *N*,*N*-dimethylcarbamic acid (distils at 60 to 61 °C without decomposing), both of which appear to exist as zwitterions, is contrary to all other experience with carbamic and dithiocarbamic acids. Spectroscopic methods were not used in the elucidation of the structures of these compounds.

Depending on the pH range, aqueous dithiocarbamate solutions contain *S*-anions, free acids in the neutral and zwitterionic forms, or *N*-protonated cations. The situation is shown in Scheme 3[103].



Scheme 3.

An equilibrium constant K_2 of 1.13×10^{-3}[104] has been found for dithiocarbamic acid at 20 °C; for *N*,*N*-diethyldithiocarbamate, $K_1 = 1.6 \times 10^{-8}$ and $K_2 = 1.0 \times 10^{-8}$ (both at 20 °C)[112]. These constants have not yet been assigned to S- or N-dissociation.

A carbamic acid containing selenium, *i.e.* *N*,*N*-dimethyldiselenocarbamic acid[98], has also been prepared. The above stability considerations based on the tendency to form a zwitterion with equivalent carbon-chalcogen bonds do not apply to this acid. A similar conclusion is indicated by the results of a crystal structure determination on nickel bis(*N*,*N*-diethyldiselenocarbamate)[113], according to which there are two different C–Se distances in *N*,*N*-diselenocarbamate (C–Se = 1.84 and 1.97 Å[114]). The C–S distances in the corresponding dithio compound are approximately equal (1.68 and 1.70 Å)[115].

5.2. Chalcogenocarbazic Acids

Hydrazinium salts of the chalcogenocarbazic acids are formed on reaction of hydrazine with CO_2[116], COS[117], CS_2[118], CSSe[119], or CSe_2[118,120]. In addition to the hydrazinium salts, a number of transition metal complexes are also known[118,121].

The free carbazic acids are found only as β-protonated zwitterions, owing to the strong basicity of their β nitrogen. This strongly hinders the α-protonation required to initiate the decomposition. At the same time there is a substantial gain in lattice energy

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[107] *A. Hantzsch* and *M. Wolvekamp*, Liebigs Ann. Chem. *331*, 265 (1904); *F. B. Johnson*, *A. J. Hill*, and *B. H. Bailey*, J. Amer. chem. Soc. *37*, 2406 (1915). For the complexing tendency and preparative use of the anion of *N*-cyanodithiocarbamic acid, cf. [19]; *F. A. Cotton* and *J. A. McCleverty*, Inorg. Chem. *6*, 229 (1967); *R. J. Timmons* and *L. S. Wittenbrook*, J. org. Chemistry *32*, 1566 (1967); *J. J. D'Amico* and *R. H. Campbell*, *ibid. 32*, 2567 (1967); *K. A. Jensen* and *L. Henriksen*, Acta chem. scand. *22*, 1107 (1968); *F. A. Cotton* and *C. B. Harris*, Inorg. Chem. *7*, 2140 (1968). S-addition leads to dimercapto-1,2,4-thiadiazole: *E. Söderbäck*, Acta chem. scand. *17*, 362 (1963).

[108] Trithioallophanic acid: [107]; *A. Rosenheim*, *R. Levy*, and *H. Grünbaum*, Ber. dtsch. chem. Ges. *42*, 2923 (1909).

[109] LCAO-MO calculation for a free carbamic acid: *E. L. Wagner*, J. physic. Chem. *63*, 1404 (1959).

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[111] *P. F. Pascoe*, Liebigs Ann. Chem. *705*, 109 (1967); *708*, 72 (1967).

[112] *K. P. Soni* and *A. M. Trivedi*, J. Indian chem. Soc. *37*, 349 (1960); *K. P. Soni*, *A. M. Trivedi*, and *I. M. Bhatt*, *ibid. 43*, 85 (1966).

[113] *M. Bonamico* and *G. Dessy*, Chem. Commun. *1967*, 1114.

[114] C–Se = 1.82 Å in *N*-benzoyl-*N'*-phenylselenourea [37].

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[116] *R. Stollé* and *K. Hofmann*, Ber. dtsch. chem. Ges. *37*, 4523 (1904); *F. Ephraim* and *E. Lasocki*, *ibid. 44*, 395 (1911).

[117] *K. A. Jensen*, Z. anorg. allg. Chem. *221*, 15 (1934); *E. Nachbaur* and *W. Gottardi*, Mh. Chem. *95*, 779 (1964).

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[118b] *U. Anthoni*, *C. Larsen*, and *P. Nielsen*, Acta chem. scand. *21*, 2571, 2580 (1967).

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in the crystalline state. The carbazic acids are consequently much more stable than corresponding carbamic acids. The zwitterionic character has been conclusively demonstrated by IR spectroscopy [118].

Carbazic acid is formed as a white powder by way of a hydrazinium salt [122] when CO_2 is passed into hydrazine for several days [116]. Dithiocarbazic acids (*N,N*-dimethyl-, *N,N*-diethyl-, *N,N*-diisopropyl-, *N,N*-pentamethylene- [*], and *N*-phenyldithiocarbazic acids) and diselenocarbazic acids (*N,N*-dimethyl- and *N*-phenyldiselenocarbazic acids) are formed as white or orange-red crystals on dropwise addition of aqueous solutions of their salts to an equimolar quantity of 6 N hydrochloric acid [118a]. *N,N*-Diisopropylthioselenocarbazic acid is formed by reaction of *N*-isothiocyanatodiisopropylamine with H_2Se; an analogous reaction with H_2Te yielded only ditelluride [118b]

5.3. Chalcogenoisocyanic Acids

Anions of chalcogenoisocyanic acids are formed by addition of O, S, Se, or Te to cyanide [1]. Salts of OCN^-, SCN^-, and $SeCN^-$ [123] have been known for a long time; $TeCN^-$, on the other hand, has only been detected in small concentrations in aqueous solution by its UV spectrum [124], whereas all attempts to prepare it as such have so far been unsuccessful [125].

The simple linear shape of the chalcogenocyanates, their interesting formation conditions, and their pronounced tendency to form complexes have led to numerous investigations on their vibration [126] and electronic excitation spectra [124] as well as to crystal structure determinations [126] and theoretical calculations [127, 128]. The metal complexes can contain X-metal or N-metal bonds, or even metal-XCN-metal bonds with an XCN bridge. The fundamental vibration frequencies of the anions accordingly differ widely [126].

Of the free acids, isocyanic acid can be obtained by pyrolysis of its trimer, cyanuric acid, at red heat [129] or by passage of HCl gas through dry NaNCO [130] and collection of the escaping gas at −78 °C; the acid obtained by the second of these methods contains less impurity [130]. In the pure state it is a colorless liquid that polymerizes readily (m.p. −86 °C, b.p. 23.5 °C, formation of macromolecular cyamelide below 150 °C and of trimeric cyanuric acid above 150 °C [129]), which is stable only at −78 °C and occurs in the solid state in a high-temperature and a low-temperature modification (transition point about −100 °C) [131]. In all aggregation states and in apolar solvents it exists only as isocyanic acid molecules H−N=C=O [131, 132]. In the crystal lattice of the solid acid, the molecules of the high-temperature modification are held together by N−H···N bonds, and those of the low-temperature modification by N−H···O bonds [131]. Isocyanic acid is a medium-strong acid in aqueous solution ($K_a = 3.4 \times 10^{-4}$ at 25 °C) [134].

Isothiocyanic acid is formed as a colorless gas on careful reaction of KSCN with $KHSO_4$ [135]; it can be condensed at −190 °C to form a white solid, which melts at −110 °C and trimerizes above −90 °C; extensive polymerization takes place above 0 °C [135]. The gas phase and solutions in apolar solvents again contain only isothiocyanic acid molecules H−N=C=S [136]; in polar solvents, on the other hand, an equilibrium probably occurs with the thiocyanic

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[*] Correct name: *N*-piperidinodithiocarbamic acid.

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acid form $N\equiv C-S-H$[136]. Isothiocyanic acid is a strong acid in aqueous solution (K = 69 at 25 °C)[137].

Dilute aqueous solutions of selenocyanic acid, which rapidly decompose with separation of selenium, are formed by the action of H_2S on lead selenocyanate[138]. No attempt has yet been made to prepare this acid again in nonaqueous media.

6. Chalcogenocarbonic Acids Containing Phosphorus

The phosphinochalcogenoformic acids $H_2P-CXXH$, which would correspond to the chalcogenocarbamic acids, have not yet been prepared. Metal complexes of *P,P*-diphenylphosphinomonothioformic and -dithioformic acids are formed on reaction of phenyldiphenylphosphinozinc[139], triphenyldiphenylphosphinotin[140], and tetrakis(diphenylphosphino)tin[140] with CS_2 or COS. According to their IR spectrum these last complexes contain covalent Sn–S and Sn–O bonds[140].

When CS_2 or CSe_2 is brought into contact with tertiary phosphines, zwitterions of the phosphinoformic acids are formed[141]. Corresponding carbamic acids are unknown.

The betaines are much more stable than the rapidly decomposing zwitterions of the *N,N*-dialkylcarbamic acids, but react as a mixture of tertiary phosphine and CS_2[141,142]. Their structure has been confirmed by IR spectroscopic studies[141,143] and a crystal structure determination[144] on the triethylphosphine–CS_2 compound ("triethylscarphan").

CS_2 reacts with Pt(0)- or Pd(0)-triphenylphosphines to give addition compounds having the formulas $Pt[P(C_6H_5)_3]\cdot CS_2$ and $Pd[P(C_6H_5)_3]\cdot CS_2$. These compounds do not contain C–P bonds; on the contrary, an angular CS_2 molecule (136 and 139.7 °) is bound to Pt or Pd by C and an S atom[145]. Similar complexes with CS_2 and COS are known for other transition metals[145].

7. Chalcogenocarbonic Acids Containing Halogen and Pseudohalogen

Halogen derivatives of the chalcogenocarbonic acids YCXXH (where X = chalcogen, Y = halogen) are named as halogenoformic acids. Only the esters are known so far as stable solid compounds. Free chloroformic acid[67] is formed in the photochemical reaction of Cl_2-formic acid mixtures as a short-lived intermediate having a half-life of 50 to 70 μsec[146]; it has been detected by means of its C–Cl absorption at 768 cm^{-1} with a fast-recording instrument in a mixture ignited by flash photolysis. Chloroformic acid decomposes into CO_2 and HCl. Chlorothioformic acid is reported to be formed on careful hydrolysis of thiophosgene[147]. Halogenoformic acids are also postulated as active substances in the corrosion of metals by halogens[148].

On the other hand, cyanodithioformic acid, which contains the pseudohalogen CN, and which precipitates out as a colorless solid on dropwise addition of hydrochloric acid to a nonaqueous solution of one of its salts, is surprisingly stable[149]. Its salts are formed on reaction of CS_2 with cyanides in dimethylformamide[149–151]. The sodium salt changes readily into the disodium salt of dimercaptomaleonitrile[149,150].

Salts of cyanodiselenoformic acid are formed in a vigorous reaction of CSe_2 with cyanide, again in dimethylformamide[149].

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8. Chalcogenocarbonic Acids in the Ortho Form

Very stable tetraalkyl esters of chalcogenocarbonic acids with four chalcogen atoms directly bonded to the C atom can be prepared [1]. On the other hand, neither the free acids nor any of their salts can be obtained as such, or even detected indirectly, though ortho compounds of this type are frequently postulated as intermediates in the hydration of carbon dioxide [152] and in the formation and decomposition of trithiocarbonate [2, 153], xanthate [2, 3, 154], and carbamate [155]. Though plausibility considerations are very convincing, particularly in the xanthate reactions [3], there is still absolutely no proof of the occurrence of such intermediates.

The same is true of the silver salts that are reported to be formed from xanthate and $AgNO_3$ [2] and of a nickel orthocarbonate [156] whose occurrence has been postulated in the thermogravimetric degradation of basic nickel carbonates.

9. Perchalcogenocarbonic Acids

In this context the term "perchalcogenocarbonic acids" will be taken to mean compounds that contain the grouping X–X instead of a single chalcogen atom X.

9.1. Peroxocarbonic Acid and Peroxocarbonates [157]

Peroxocarbonates can be obtained by three methods:

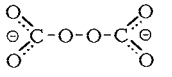
1. Anodic oxidation of concentrated carbonate solutions [158];

2. Action of CO_2 on peroxides or hydrogen peroxides [159];

3. Reaction of carbonate or ethyl carbonate with H_2O_2 [160].

Only the products obtained by methods 1 and 2 are true peroxocarbonates with C–O–O bonds. The third reaction yields carbonates containing H_2O_2 of crystallization [161].

The composition of the peroxocarbonates varies widely with the preparation conditions, and whereas extensive studies have provided considerable information on the kinetics of their anodic formation [158], nothing definite is yet known about the structure of individual peroxocarbonates. Suggestions [157] include the formulas of a simple peroxocarbonate CO_4^{2-}, a dimer [162],



and a hydrogen peroxocarbonate HCO_4^-.

Free peroxocarbonic acid is reported to be formed on reaction of peroxocarbonates with phosphoric acid as a substance that can be extracted with ether [163], as well as from CO_2 and H_2O_2 in aqueous solution [164] and on irradiation of water containing CO_2 with X rays [165]. These data are based more on assumptions than on accurate identification of the acid formed, and have in some cases been definitely refuted [163, 164]. On the other hand, polarographic studies have shown that the hydrolytic decomposition of peroxocarbonates in aqueous solution proceeds *via* a free acid [166].

9.2. Perthiocarbonic Acid and Perthiocarbonates

Solutions of the supposed trithioperoxocarbonate ion CS_3O^{2-} are formed when dilute aqueous trithiocarbonate solutions are left in air for several days [2, 167]. The solutions give UV absorptions at 308 and 378 nm, whereas the absorption bands of the CS_3^{2-} ion have completely disappeared. Solutions exhibiting the same UV absorption are also formed on saturation of dilute hydrogen sulfide solutions with COS and O_2 [2].

The tetrathiocarbonate ion CS_4^{2-} (referred to as perthiocarbonate in the following discussion) is formed on reaction of disulfides with CS_2 in alcohol; crystalline or initially oily salts can be precipitated with ether [7, 49]. Solutions of CS_4^{2-} are also formed on treatment of trithiocarbonate solutions with sulfur [2, 168]. The known salts include alkali metal salts,

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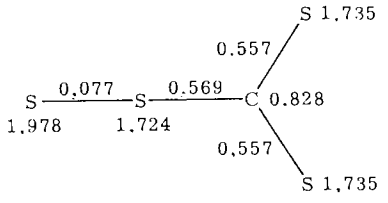
in some cases with widely differing contents of water of crystallization[169], calcium salts having widely varying compositions[170], and a few transition metal complexes[120,171].

Analysis of the vibration spectrum of the CS_4^{2-} ion shows that it has a true perthiocarbonate structure[172]. An elementary HMO calculation gave the π-electron densities and π-bond orders shown in Scheme 4[172].



Scheme 4.

Free perthiocarbonic acid H_2CS_4 is formed on reaction of equimolar quantities of ammonium perthiocarbonate and HCl gas in dimethyl ether at −78 °C[49]; filtration of the solution and evaporation of the dimethyl ether at −78 °C under vacuum yields H_2CS_4 as a yellow crystalline substance melting at −36.5 °C to give a red oil, which rapidly becomes cloudy owing to the separation of sulfur. The acid is stable at −190 °C; at −78 °C, it decomposes slowly into H_2S, CS_2, and sulfur. The IR spectrum of H_2CS_4 in CCl_4 contains two S–H stretching bands at 2575 and 2395 cm^{-1}; H_2CS_4 thus has the unsymmetrical structure HS–C(S)–S–S–H. This structure explains why H_2CS_4 cannot be obtained from H_2CS_3 and sulfur[168], whereas its anion can be obtained by reactions of this type. The thermodynamic data obtained by vapor pressure measurements over the decomposing acid[49], in conjunction with the corresponding data for trithiocarbonic acid[51], show that the formation of the perthio acid from H_2CS_3 and S would be thermodynamically possible above 57 °C. However, neither H_2CS_4 nor H_2CS_3 is stable at this temperature. Dissociation constants of perthiocarbonic acid in aqueous solution are given in Table 4.

9.3. Peroxocarbonates Containing Selenium

CSe_3^{2-} solutions do not react with selenium[117]. Concentrated aqueous Na_2CS_3 solutions take up 0.6 g-atom of selenium per mole of CS_3^{2-}, but there is no evidence of compound formation corresponding to the formation of CS_4^{2-} from CS_3^{2-} and sulfur; Na_2CS_3 and selenium are precipitated separately on addition of alcohol and ether[173].

On the other hand, when a suspension of sulfur in an aqueous $BaCS_2Se$ solution is vigorously stirred, the UV bands of the CS_2Se^{2-} ion (325, 365, and 535 nm) disappear, to be replaced by a spectrum containing absorption bands at 319 and 397 nm, which (apart from a small shift toward longer wavelengths) is of the same form as the spectrum of the CS_4^{2-} ion[23]. It may therefore be assumed that an ion $^{\ominus}Se-C(S)-S-S^{\ominus}$ is formed.

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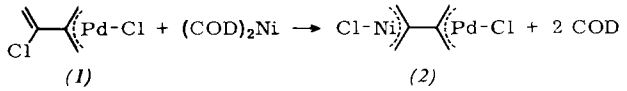
COMMUNICATIONS

Bimetallic π-Allyl Complexes of Nickel and Palladium

By *W. Keim*[*]

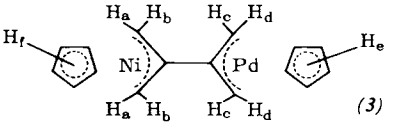
Dedicated to Professor K. Ziegler on the occasion of his 70th birthday

If, in accord with the method of *G. Wilke et al.*[1] for the preparation of π-allylnickel halides, bis(1,5-cyclooctadiene)-nickel is treated with *(1)*[2] in toluene for 24 h at 0 °C, the complex 2,2'-bis(π-allyl)dichloronickelpalladium *(2)* is formed in 70–80% yield. The precipitation of metallic nickel during the reaction suppresses the formation of *(2)*.



(1) *(2)*

The brown insoluble compound *(2)* reacts with cyclopentadienylsodium, forming 2,2'-bis(π-allyl)dicyclopentadienylnickelpalladium *(3)*, which is readily soluble in organic solvents, sublimes at 90 °C/10^{-4} torr, and forms red needles that decompose at 150–160 °C. Hydrogenation of *(3)* affords metallic nickel and palladium, 2,3-dimethylbutane, and cyclopentane. Its mass spectrum[3] is in accord with structure *(3)*. The ^1H–NMR spectrum shows six sharp signals (see Table 1).



(3)

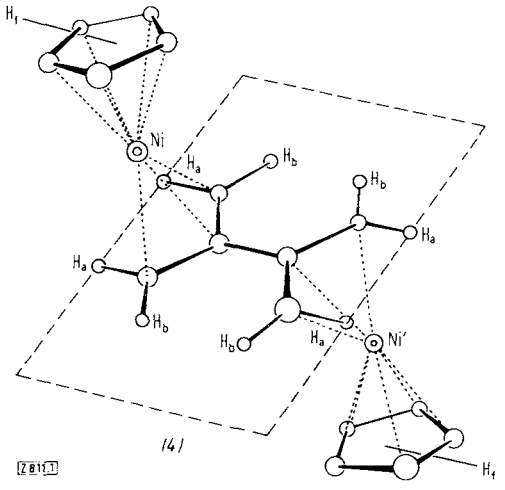
Table 1. ^1H–NMR spectral bands of *(3)* and *(4)* in C_6D_6 at ~ 30 °C (internal reference tetramethylsilane; Varian A 60).

Proton	*(3)* (ppm)	*(3)* relative intensity	*(4)* (ppm)	*(4)* relative intensity
H_a	1.15	2	1.3	2
H_b	2.75	2	3.05	2
H_c	3.65	2	—	—
H_d	2.15	2	—	—
H_e	5.75	5	—	—
H_f	5.15	5	5.30	5

If a tetrahydrofuran/hexane solution of *(3)* is kept for three months at 25 °C, deep red crystals of composition $C_{16}H_{18}Ni_2$ separate, apparently owing to the transmetalation:

$$2\ C_{16}H_{18}NiPd \rightarrow C_{16}H_{18}Ni_2 + C_{16}H_{18}Pd_2$$
(3) *(4)* *(5)*

The mass spectrum [3] of the complex *(4)* shows the expected signals. The ^1H–NMR spectrum shows three sharp signals (see Table 1).



(4)

An X-ray structure analysis confirms the π-allyl structure assigned to *(4)*, the nickel atoms and the cyclopentadienyl rings being in *trans*-positions to one another [4]. The complex *(5)* has not yet been isolated with complete spectral and analytical purity.

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[1] *G. Wilke et al.*, Angew. Chem. *78*, 157 (1966); Angew. Chem. internat. Edit. *5*, 151 (1966).

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Hydrogenation of Polyenes by Tricarbonylcyclopentadienylhydrido-molybdenum and -tungsten

By *A. Miyake* and *H. Kondo* [*]

Dedicated to Professor K. Ziegler on the occasion of his 70th birthday

Tricarbonylcyclopentadienylhydridochromium *(1)* hydrogenates polyenes [1]. We have now found that the corresponding complexes of Mo [*(2)*] and W [*(3)*] react analogously.

If a solution of isoprene *(4)* (0.23 g, 3.4 mmoles) and tricarbonylcyclopentadienylhydridomolybdenum *(2)* [2] (1.54 g, 6.3 mmoles) in *n*-heptane (10 ml) is warmed to 59 °C, the solution at once becomes red and bis(tricarbonylcyclopentadienylmolybdenum) *(5)* soon separates as red crystals. After 4.7 h the reaction mixture was analyzed by gas chromatography; it contained 2-methyl-2-butene, 2-methyl-1-butene,

$$2\ C_5H_5(CO)_3MoH + CH_2{=}CH{-}C(CH_3){=}CH_2 \rightarrow$$
(2) *(4)*

$$[C_5H_5(CO)_3Mo]_2 + CH_3{-}CH{=}C(CH_3)_2$$
(5)

$$2\ C_5H_5(CO)_3WH + CH_2{=}CH{-}(CH{=}CH)_2{-}CH{=}CH_2 \rightarrow$$
(3) *(6)*

$$[C_5H_5(CO)_3W]_2 + CH_3{-}(CH{=}CH)_3{-}CH_3$$
(7) *(8)*

$C_5H_5(CO)_3CrH$ *(1)* $[C_5H_5(CO)_3Cr]_2$ *(9)*

3-methyl-1-butene, and unchanged *(4)* in the molar ratio 82:6:3:9.

1,3,5,7-Octatetraene *(6)* [3] (0.5 g, 4.1 mmoles) in *n*-pentane (20 ml) was treated with tricarbonylcyclopentadienylhydridotungsten *(3)* [3] (3.2 g, 9.6 mmoles); red crystals of bis(tricarbonylcyclopentadienyltungsten) *(7)* separated at once. After 4.7 h the reaction mixture was analyzed by gas chromatography. It contained 2,4,6-octatriene *(8)* and unidentified products (three components) in the ratio 89:11. The tetraene *(6)* was completely consumed. The triene *(8)* was gas-chromatographically identical with a sample obtained by another route [4].

Table 1. Half-reaction time for hydrogenation of polyenes by hydrido complexes.

Hydrido-complex	Polyene	Temp. (°C)	$t_{1/2}$ [a] (hr)	Products
(1)	2,4-Hexadiene	20	6	[b]
(2)	2,4-Hexadiene	59	20	[c]
(2)	4-Methyl-1,3-pentadiene	20	10	[d]
(2)	4-Methyl-1,3-pentadiene	59	0.2	[d]
(2)	2,4,6-Octatriene	20	0.1	[e]
(2)	1,3,5-Hexatriene	20	0.03	[f]
(3)	4-Methyl-1,3-pentadiene	60	70	[g]
(3)	1,3,5-Hexatriene	20	9	[h]
(3)	1,3,5,7-Octatetraene	20	0.2	[i]

[a] Half-reaction time for the polyene in a mixture with initial concentrations: polyene 0.5 mole/l; hydrido complex 1 mole/l. Hydrogenation products:

[b] *trans*-2- and -3-Hexene 89%, *cis*-2- and -3-hexene 11%.

[c] *trans*-2- and -3-Hexene 79%, *cis*-2- and -3-hexene 21%.

[d] 2-Methyl-2-pentene 76%, 4-methyl-2-pentene 24%.

[e] Two products (probably 3,5-octadiene and 2,4-octadiene) in the ratio 83:17.

[f] 2,4-Hexadiene, *trans,trans* 66%, *trans,cis* 31%, *cis,cis* 3%.

[g] 2-Methyl-2-pentene 72%, 4-methyl-2-pentene 28%.

[h] 2,4-Hexadiene, *trans,trans* 67%, *trans,cis* 30%, *cis,cis* 4%.

[i] See text.

As shown in Table 1, the reactivity of the hydrido complexes decreases in the series *(1)* > *(2)* > *(3)*. *(1)* reacts 10^2 to 10^3 times faster than *(2)*, and *(2)* reacts 10^2 to 10^3 times faster than *(3)*. The reactivity of the polyenes increases with increasing number of conjugated double bonds.

The Mo–Mo and W–W bonds in *(5)* and *(7)* are much more stable than the readily fissile Cr–Cr bond in bis(tricarbonylcyclopentadienylchromium) *(9)* [5]. Whereas hydrogenation of *(9)* to *(1)* proceeds smoothly [1,2], reduction of *(5)* or *(7)* by hydrogen to *(2)* or *(3)*, respectively, is not to be expected; and our attempts to reduce polyenes catalytically by means of *(5)* or *(7)* were unsuccessful. When compared with hydro-

genation catalyzed by *(9)*, the stoichiometric hydrogenation by the readily accessible complexes *(2)* and *(3)* has the advantage that conjugated polyenes can be reduced stepwise.

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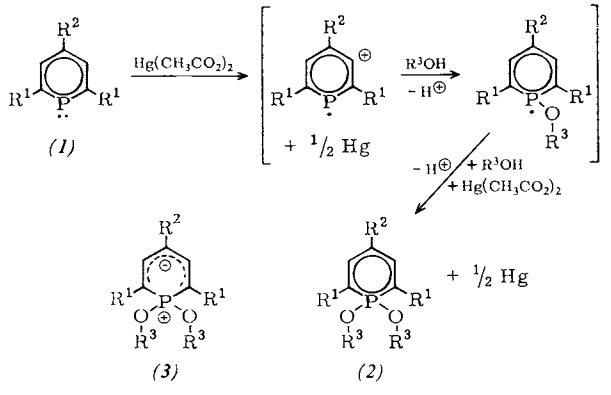
1,1-Dialkoxy- and 1,1-Diaryloxy-phosphorins, a New Class of Organophosphorus Compounds

By *K. Dimroth* and *W. Städel*[*]

Dedicated to Professor K. Ziegler on the occasion of his 70th birthday

2,4,6-Trisubstituted phosphorins *(1a)–(1f)* are oxidized to stable radical cations by, *inter alia*, mercury(II) acetate[1,2]; in the presence of alcohols or phenols the reaction proceeds with separation of mercury to form the novel, strongly fluorescent 1,1-dialkoxy- or 1,1-diaryloxyphosphorins *(2a)* to *(2f)* as highly stable crystalline compounds. The reaction probably proceeds *via* the cation radical stage, which can be detected by ESR spectroscopy.

The new compounds *(2)* (for examples, see Table) are only weakly basic. We were not able to alkylate them with oxonium salts, nor acylate them with acyl chlorides. They are insoluble in dilute acids and are protonated only by strong acids such as trifluoroacetic acid, whereupon their fluorescence disappears; compounds *(2)* are regenerated on treatment with bases. ^{1}H–NMR-spectroscopic observations on *(2b)* and deuteriotrifluoroacetic acid showed that C-2 and C-4 are protonated in the ratio of 3:1. The low basicity of compounds *(2)* and comparison of the dipole moments [*(1a)*: μ = 1.54 D; *(2a)*: μ = 1.28 D (both in benzene)] indicate structure *(2)* rather than *(3)*.



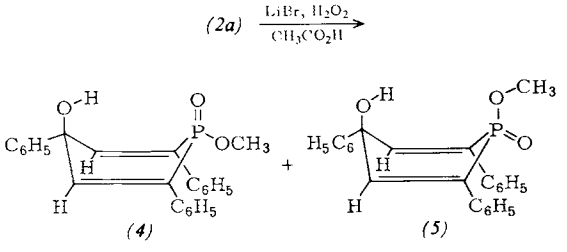
(1) *(3)* *(2)*

The symmetrical structure of compounds *(2)* is proved by ^{1}H–NMR measurements on *(2b)* in $CDCl_3$. The protons attached to C-3 and C-5 give rise to a doublet at $\delta = -7.93$ ppm ($J_{P-C-C-H} = 36.5$ Hz); the signal of the methoxy protons ($\delta = -3.40$ ppm) is split to a doublet by coupling with the phosphorus ($J_{P-O-C-H} = 13.5$ Hz). TMS as internal reference.)

The ^{31}P–NMR signals of *(2a)–(2d)* in benzene lie between −58 to −65 ppm and show only a slight shift in trifluoroacetic acid [*(2a)* in benzene: $\delta = -65.2$ ppm, in trifluoroacetic acid: $\delta = -62.2$ ppm; *(1a)* in benzene: $\delta = -178.2$ ppm; measured with respect to 85% H_3PO_4 as external reference].

Compounds *(2)* can be both oxidized to novel stable phosphorus radical cations [coupling constant for *(2a)* $a_P = 20.1$ gauss] and reduced to radical anions that are likewise new. During the latter process, a doublet having $a_P = 31.6$ gauss is first observed, which changes to a broad singlet, having a suggestion of a fine structure, on further reduction[3].

Treatment of *(2a)* in dimethoxyethane with LiBr, acetic anhydride, and H_2O_2 affords the isomers *(4)* and *(5)* of 1-methoxy-2,4,6-triphenyl-4-hydroxy-1-phospha-2,5-cyclohexadienone (m.p. 198 °–200 °C and 194–198 °C). Their OH groups can be acetylated without isomerization with acetic anhydride in pyridine. However, with trifluoroacetic acid, *(4)* and *(5)* give the same deep blue salt *(6)* [λ_{max} in trifluoroacetic acid = 335 nm ($\varepsilon = 0.46 \times 10^4$), 394 ($0.49 \times 10^4$), 560 ($3.54 \times 10^4$), and 695 ($2.53 \times 10^4$)] (cf. reference[4]). *(6)* affords *(7)* and *(8)* when treated with alcohols, and regenerates *(4)* and *(5)* with aqueous acetic acid.



(4) *(5)*

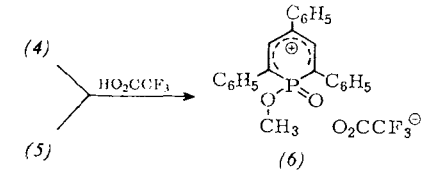
The NMR data recorded for compounds *(2)* show a marked similarity to those of 1-alkyl-1-phenyl-2,4,6-triphenylphosphorins, which were obtained by *Märkl et al.*[5] and for which an "aromatic" bonding state with contributions from d_π-p_π bonds comes into consideration – as is the case with our compounds *(2)*.

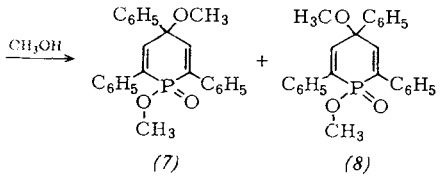
	R^1	R^2	R^3	*(2)* M.p. (°C)	λ_{max} (nm) [c] 1.	2.	$\varepsilon \times 10^{-4}$ 1.	2.
(a)	C_6H_5	C_6H_5	CH_3	112	307	420	1.34	1.84
(b)	C_6D_5	C_6D_5	CH_3	112	305	419	1.43	1.81
(c)	C_6H_5	C_6H_5	C_2H_5	107	283	423	1.76	2.00
(d)	*p*-$CH_3OC_6H_4$	C_6H_5	C_2H_5 [a]	127	286	419	1.85	2.28
(e)	C_6H_5	C_6H_5	C_6H_5	152–154	290	413	1.75	1.80
(f)	*p*-$CH_3OC_6H_4$	C_6H_5	*p*-$NO_2C_6H_4$	192	288[b]	406	3.17	1.67

[a] Fluorescence maximum at 490 nm (in methanol).

[b] No fluorescence (in dichloromethane).

[c] In cyclohexane.





1,1-Dimethoxy-2,4,6-triphenylphosphorin (2a):

2,4,6-Triphenylphosphorin *(1a)* (0.84 g, 2,6 mmole) and mercury(II) acetate (0.83 g, 2.6 mmole) are stirred for 15 h at 20 °C in a mixture of dry benzene/methanol (1:1) (100 ml). Column chromatography on silica gel in benzene affords analytically pure *(2a)* (0.78 g, 77% yield) having m.p. 112 °C.

Stereoisomeric 4-hydroxy-1-methoxy-2,4,6-triphenyl-1-phospha-2,5-cyclohexadien-1-one (4) and (5):

30% hydrogen peroxide (2.5 g) and acetic anhydride (2.5 g) are added to *(2a)* (2.5 g, 6.5 mmole) and LiBr (3.0 g, 34 mmole) in dimethoxyethane (50 ml) with ice-cooling and stirring; the mixture is then stirred for 15 h at 20 °C. Column chromatography in benzene/acetic ester (4:1) on silica gel yields *(4)* [0.3 g, m.p. 198–200 °C (decomp.)] and *(5)* [0.08 g, m.p. 194–198 °C (decomp.)] (yields 12% and 2%, respectively), alongside other unidentified substances. ^{1}H–NMR spectra (in [D_6]-dimethyl sulfoxide): *(4)* and *(5)*, respectively: δ = −6.8 to −7.4 and −6.8 to −7.3 ppm, resp. (15 phenyl protons), m; δ = −6.35 and −6.31 ppm, resp. (H attached to C-3 and C-5), d, J_{P-H} = 32 and 33 Hz, resp.; δ = −6.37 and −6.40 ppm, resp. (hydroxyl proton), s; δ = −3.16 and −3.24 ppm, resp. (methoxy protons), d, J_{P-H} = 12 and 11 Hz, resp.; TMS as internal reference.

Stereoisomeric 1,4-dimethoxy-2,4,6-triphenyl-1-phospha-2,5-cyclohexadien-1-one (7) and (8):

(4) (0.30 g, 0.77 mmole) is dissolved in trifluoroacetic acid (5 ml) and stirred for 1 h. Methanol (100 ml) is then added dropwise to the deep blue solution. Column chromatography over silica gel in benzene/acetic ester (5:1) affords a mixture (0.15 g, 50% yield) of the isomers *(7)* and *(8)* in the approximate ratio of 1:1 and having m.p. 98–101 °C. ^{1}H–NMR spectra (in $CDCl_3$): δ = −6.8 to −7.3 ppm (2 × 15 phenyl protons), m; δ = −6.16 ppm (H attached to C-3 and C-5), d, J_{P-H} = 33 Hz; δ = −6.11 ppm (H attached to C-3 and C-5), d, J_{P-H} = 33 Hz; δ = −3.30 ppm (2 × methoxy protons), s; δ = −3.26 ppm ($POCH_3$ protons), d, J_{P-H} = 12 Hz; δ = −3.24 ppm ($POCH_3$ protons), d, J_{P-H} = 12 Hz; TMS as internal reference.

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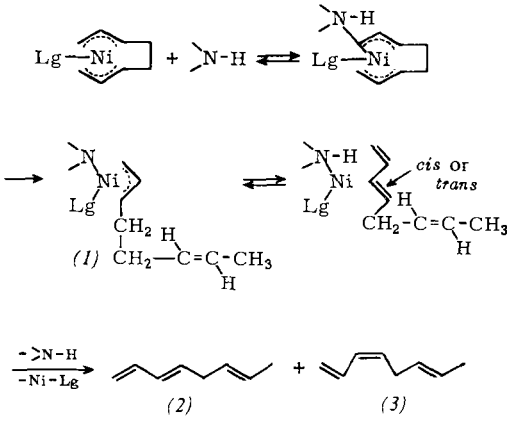
cis,trans- and *trans,trans*-1,3,6-Octatriene from Butadiene

By *P. Heimbach*[*]

Dedicated to Professor K. Ziegler on the occasion of his 70th birthday

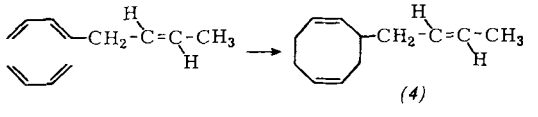
In the presence of morpholine (or another dialkylamine) butadiene is dimerized almost exclusively to *cis,trans-* and *trans,trans*-1,3,6-octatriene *(3)* and *(2)*, respectively, at a nickel-triethyl phosphite catalyst[1–3]; the yield is 90% at 50% conversion. (Molar proportions at the beginning of the reaction Ni: $P(OC_2H_5)_3$: morpholine: butadiene = 1:1:50:800.)



Scheme 1. Lg = phosphite or phosphine.

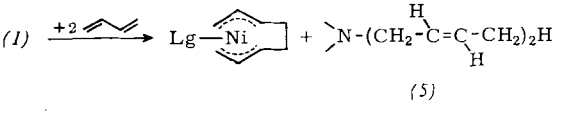
Evidence for the reaction's proceeding according to Scheme 1 is provided by the following observations:

1. When *o*-substituted triaryl phosphites are present as ligands (Lg), which screen the higher coordination positions of the Ni[4], they lead to formation mainly of eight-membered rings that otherwise arise only in the absence of amines. In addition, codimerization of butadiene with 1,3,6-octatriene occurs [up to 25% of the reaction product consists of *(4)*].

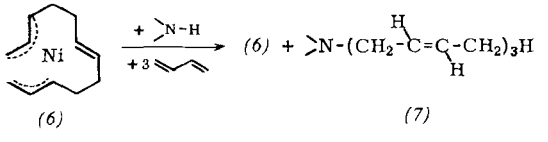


2. If *cis*-1,2-divinylcyclobutane, which rearranges to the bis-(π-allyl) chain at the nickel[5], is used in place of butadiene, then compounds *(2)* and *(3)*, as well as C_{16} olefins, are formed alongside *cis,cis*-cyclooctadiene at almost quantitative conversion. Under the same conditions, butadiene affords C_{12} and C_{16} olefins (see below).

3. The formation of trialkylamines in a side reaction is in accord with the proposed course of the reaction. This aminoalkylation, which yields *(5)*, becomes the main reaction at 20 °C (>75% yield calculated with respect to reacted amine).



In the absence of additional phosphorus-containing ligands, three butadiene molecules are joined to one amine molecule in the presence of nickel to form *(7)*. *(5)* and *(7)* can be hydrogenated to the saturated tertiary amines[6].



4. The reaction course proposed in Scheme 1 corresponds to the dimerization of butadiene to methylheptatriene in the presence of cobalt catalysts[7,8]; "Co–H" and "N–Ni–H" would be comparable with each other as "active principle". If the conversion of butadiene is too high, compounds *(2)* and *(3)* react further as 1,3-dienes with butadiene to form mainly the butenyloctatrienes 4(2-*trans*-butenyl)-1,3,6-*trans*-octatriene, 5-(2-*trans*-butenyl)-1,3-*trans*, 6-*trans*-octatriene, 5-(2-*trans*-butenyl)-1,3-*cis*, 6-*trans*-octatriene.

Similarly to butadiene, substituted butadienes can also be dimerized. A 1:1 mixture of *(2)* and *(3)* yields 61% of 5,6-dipropyldecane, 38% of 5-propyltridecane, and 1% of hexadecane (after hydrogenation).

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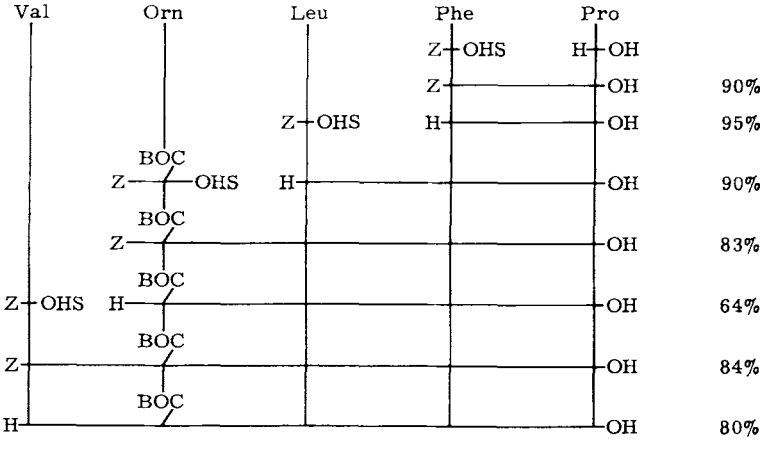
Synthesis of all-L-Gramicidin S[1][**]

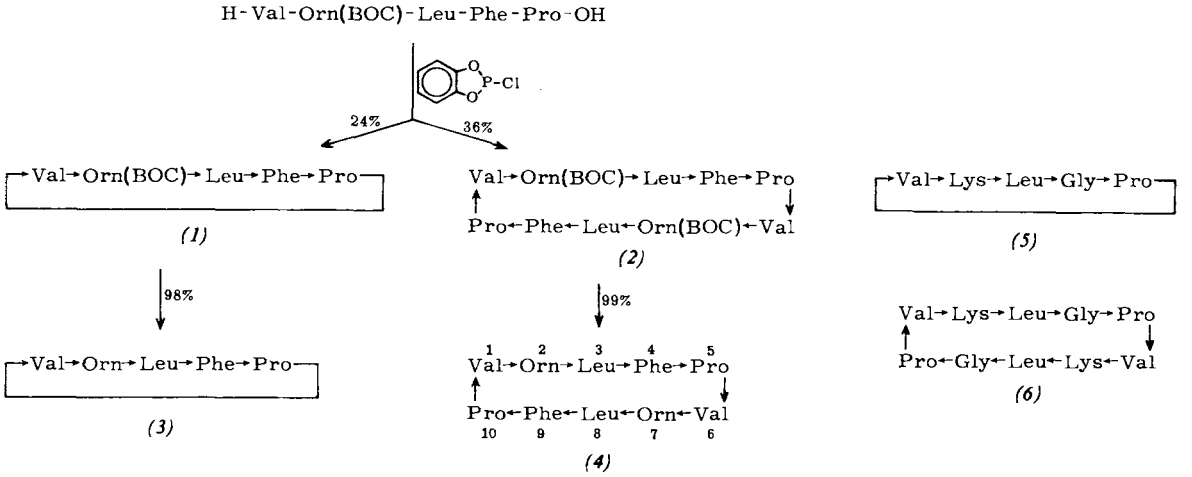
By *M. Rothe* and *F. Eisenbeiss*[*]

We have synthesized the long sought[3] cyclodecapeptide all-L-gramicidin S *(4)*, in which the two D-phenylalanine groups of gramicidin S (from *Bacillus brevis*) are replaced by the L-isomer[2].

We first prepared the linear pentapeptide Val-Orn(BOC)-Leu-Phe-Pro by stepwise synthesis from the carboxyl end by the hydroxysuccinimide ester method[4]. The path of the synthesis is shown in Schemes 1 and 2. The ring closure proceeded in 60% yield by the phosphite method[5] with *o*-phenylene chlorophosphite[6] in 5×10^{-3} M solution in diethyl phosphite at 100 °C. The reaction led, not only to the 15-membered cyclopentapeptide *(1)*, but also by dimerization to the desired 30-membered cyclodecapeptide *(2)* (ratio about 2:3); the products were separated on Sephadex LH 20 in methanol solution. The ring sizes were established by



Scheme 1. Synthesis of Val-Orn(BOC)-Leu-Phe-Pro. The values on the right are the yields of recrystallized TLC-pure products. BOC = *tert*-butyloxycarbonyl, Z = benzyloxycarbonyl, OHS = hydroxysuccinimide ester.



Scheme 2. Synthesis of cyclosemi-all-L-gramicidin S *(3)* and all-L-gramicidin S *(4)*. *(5)* and *(6)* were prepared in a similar manner.

molecular weight determinations [*(1)*: calc. 670.9, found 671 by mass spectrometry; *(2)*: calc. 1341.7, found 1275 by vapor pressure osmometry]. The δ-BOC protective group of the ornithine was removed with N HCl/glacial acetic acid at room temperature.

The dihydrochloride of *(4)* crystallizes as rods from ethanol/2 N HCl; the analytical data point to a tetrahydrate. The quantitative amino-acid analysis[7] after total hydrolysis (6 N HCl, 110 °C) gave the following values: Val 0.92, Orn 1.14, Leu 1.01, Phe 1.05, Pro 1.00 (reference value).

Lys^2, Gly^4-cyclosemigramicidin S *(5)* and Lys^2, Gly^4, Lys^7, Gly^9-gramicidin S *(6)* could be obtained in a similar manner as the hydrochloride and the dihydrochloride respectively. Some physical data for compounds *(1)–(6)* are given in Table 1.

Table 1. Physical data for *(1)–(6)*.

Cpd.	M.p. (°C)	$[\alpha]_D^t$ (°)	*t* (°C)	*c*	Solvent
(1)	136	−111.8	26	0.8	Methanol
(2)	185–190 decomp.	−82.1	26	1.54	Methanol
(3) [b]	184	−91.4	25	0.33	Methanol
(4) [a]	246–247	−76.8	24	0.66	60%Ethanol
(5) [b]	204–206	−156.1	25	0.92	Ethanol
(6) [a]	275 decomp.	−191.9	23	0.6	Methanol

[a] Dihydrochloride; [b] Hydrochloride.

All-L-gramicidin S and the cyclopeptides *(5)* and *(6)* have no antibiotic activity toward gram-negative bacteria (*E.coli*); *(6)* shows growth inhibition > 40 μg/ml [10^6 organisms], glucose broth, against gram-positive bacteria (*Staph. aureus*); gramicidin S (synthesized according to *Merrifield* and cyclized as described above) gives a value of < 1 μg/ml[8]. This shows that in addition to the known factors (basic amino acids, hydrophobic side chains, minimum ring size), the D-amino acids are also essential to the activity of cyclopeptide antibiotics (specific conformation, resistance to enzymatic cleavage).

The ring closure to form *(1)* and *(2)* is a new example of the concentration- and solvent-dependent formation of homologous rings in the cyclization of oligopeptides[2,9].

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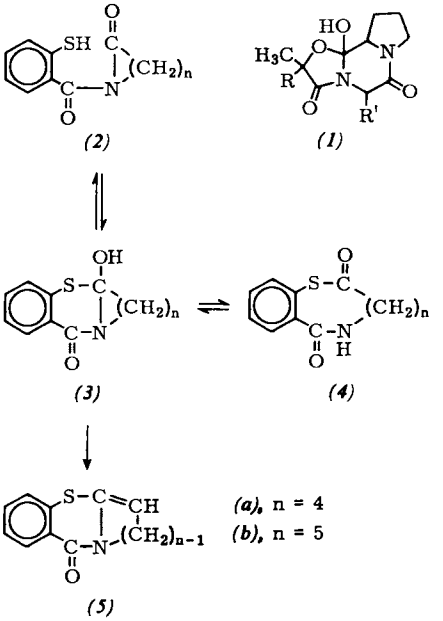
Thiacyclols and Cyclothiodepsipeptides[1][**]

By *M. Rothe* and *R. Steinberger*[*]

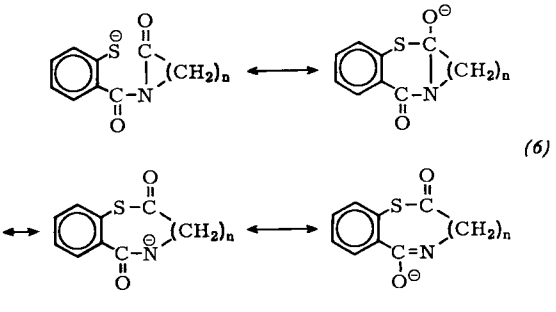
Orthocarboxylic acid derivatives containing a free OH group are stable only in exceptional cases, *e.g.* in the form of the cyclol grouping[2], which occurs in the peptide part of the ergot alkaloids *(1)*.

We have synthesized the first thiacyclols *(3)*[***], *N*-acylated orthoacid monothioester monoamides, from *N*-(ω-mercaptoacyl)lactams *(2)* which can be obtained from *S*-protected mercaptoacyl chlorides and *N*-trimethylsilyllactams by elimination of trimethylchlorosilane followed by removal of the protective group[3]. Aromatic *o*-mercaptoacyllactams, *e.g.* *N*-(*o*-mercaptobenzoyl)-δ-valerolactam *(2a)* and -ε-caprolactam *(2b)*, are unstable, and react spontaneously to form the thiacyclols *(3a)* and *(3b)* or to give the cyclothiodepsipeptides *(4a)* and *(4b)*, which have also been unknown until now.



The structures of *(3)* and *(4)* are clearly shown by their IR spectra (Table 1). Cyclothiodepsipeptides give the characteristic thioester and amide-II bands, which do not appear in the spectra of the thiacyclols. As expected, the thiacyclols give only one a carbonyl band and the OH band, while the mass spectrum contains a weak molecular peak, together with a strong peak at M − 18 corresponding to dehydrothiacyclol *(5a)*, m.p. 60.5–61.5 °C, whose double bond can be detected by NMR spectroscopy (one vinyl proton at τ = 4.92 in CCl_4, TMS as internal reference). This dehydration can also be detected in the mass spectrum of the cyclothiodepsipeptides, and shows the ease of cyclol formation with transannular amide-thioester interaction in ten- and eleven-membered rings. *(5a)* was synthesized from *(3a)* by dehydration with acidic Al_2O_3 (activity I).

The existence of the equilibrium *(2)* ⇌ *(3)* ⇌ *(4)* is shown by the conversion of *(3b)* into *(4b)* in acetone/water, which can



(6)

be accelerated by the addition of catalytic quantities of $OH^{\ominus}$, and by the methylation of *(3b)* with CH_3I under S_N2 conditions, the ambident anion *(6)* giving the *S*-methyl ether of *(2b)*, m.p. 88–89 °C. All the compounds were pure on thin layer chromatography and on analysis.

Table 1. Melting points and IR spectra of thiacyclols and cyclothiodepsipeptides.

	M.p. (°C)	ν (cm⁻¹) OH	NH	Amide I	Amide II	C=O (thioester)	C=O (thiazinone)
(3a)	129–130	3236	–	–	–	–	1613
(4a)	195–196	–	3268	1645	1550	1712	–
(3b)	122–123	3236	–	–	–	–	1605
(4b)	222–224	–	3289	1642	1553	1686	–

5a-Hydroxy-6,7,8,9-tetrahydro-5aH,11H-pyrido[2,1-b]benzo-[e]-[1,3]thiazin-11-one (3a)

Ag acetate (955 mg, 5% excess) is added under nitrogen to a solution of (*S*-acetyl-*o*-mercaptobenzoyl)valerolactam (1.50 g, 5.40 mmole) [m.p. 99–100 °C, synthesized according to ref. [3]] in methanol (30 ml) and pyridine (2 ml). The mixture is stirred for 30 min at room temperature, poured into water, and the colloidally dissolved Ag thiolate is salted out with HNO_3. The solid thus obtained is filtered off, dissolved in acetone/water (5:1) (50 ml), and H_2S is introduced into the solution with stirring. After the AgS has been filtered off and the acetone removed under vacuum, 950 mg (75%) of the crystalline thiacyclol *(3a)* (m.p. 129–130 °C) is obtained. Compound *(3a)* rapidly turns yellow to form *(5a)*, but is stable at −15 °C. *(3a)* (10.0 g) is recrystallized from a mixture of acetone (150 ml), water (75 ml), and triethylamine (0.5 ml). 75 mg of *(4a)* (m.p. 195–196 °C, from acetic acid) in the crystalline state is obtained at room temperature.

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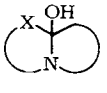
[***] It has become common practice to use the name cyclol for the grouping



where X = O, S, NH, *etc.* Representatives having X = O are usually called just cyclols and are only rarely termed oxacyclols.

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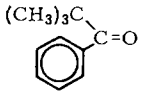
Energy Differences in the Inner Molecular Orbitals of *tert*-Butyl and Trimethylsilyl Phenyl Ketones[1]

By *H. Bock, H. Alt*, and *H. Seidl* [*]

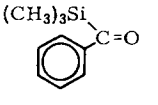
In contrast to the colorless alkyl ketones, monosilyl ketones are yellow [2,4] and disilyl ketones are violet [3]. The following interpretations are offered in the literature for the reduced excitation energy of the n → π* transition responsible for the color: (a) "Through space" interaction d_{Si}/n_0 between the free electron pair n_0 of the carbonyl oxygen, which is orthogonal to the CO π-system, and unoccupied 3d atomic orbitals of the silicon leads to a "superchromophore" Si–C=O [4]. (b) The π^*_{CO} molecular orbital is lowered by d_{Si}/π^*_{CO} splitting [5]. (c) The σ-donor and π-acceptor properties of R_3Si groups stabilize the n → π* excited state of the ketone π system relative to the ground state [6]. (d) The strong inductive effect of R_3Si groups increases in particular the level $E(n_0)$ of the free electron pair on the oxygen [7]. It should be possible to decide between these interpretations on the basis of additional energy data for alkyl and silyl ketones.

Investigations on the substituent effects of R_3C and R_3Si groups on linear and cyclic π-electron systems have shown that the following values can be used to determine the energy differences between the inner molecular orbitals π, n, and π*: According to *Koopmans'* theorem [8], vertical ionization energies IE found by mass spectroscopy correspond to the energy of the highest occupied molecular orbital $E(n)$ or $E(\pi)$ in the ground state [9]. Charge-transfer excitation energies $\tilde{\nu}_m^{CT}$ of suitable donor-acceptor complexes are proportional to the energy $E(\pi)$ of the highest occupied π molecular orbital [9,10]. Half-wave reduction potentials $E_{1/2}^{Red}$ can be correlated with the energy $E(\pi^*)$ of the lowest unoccupied π molecular orbital [11]. With the aid of the electronic excitation energies $\tilde{\nu}_m^{n\to\pi^*}$ and $\tilde{\nu}_m^{\pi\to\pi^*}$, these energy values can be used to construct approximate energy level diagrams for the inner molecular orbitals [12] by introduction of simplifying assumptions concerning the differentiation of molecular orbitals and electronic states.

The approximate energy level diagrams (Fig. 1) for *tert*-butyl *(1)* and trimethylsilyl phenyl ketone *(2)* may be deduced from the experimental values (Table 1).



(1)



(2)

Table 1. Experimental values for *tert*-butyl *(1)* and trimethylsilyl phenyl ketones *(2)*.

	IE (eV)	$\tilde{\nu}_m^{n\to\pi^*}$ (cm⁻¹)	$\tilde{\nu}_m^{\pi\to\pi^*}$ (cm⁻¹)	$E_{1/2}^{Red}$(V)	$\tilde{\nu}_m^{CT}$ (cm⁻¹) [a]
(1)	9.04	31250	42000	−1.57	19700
(2)	8.20	23650	40000	−1.30	21700
Δ	0.84	7600	2000	−0.27	−2000

[a] Measured for methyl and trimethylsilyl β-naphthyl ketone [13].

ΔIE is due to the different energies $E(n_0)$ of the free electron pair on the carbonyl oxygen, and is also reflected in the different p*K* values [14] of the two compounds. The lowering of the π* level in the silyl ketone *(2)* deduced from the large difference in the n → π* excitation energies $\Delta\tilde{\nu}_m^{n\to\pi^*}$ is confirmed by the fact that the half-wave reduction potential $E_{1/2}^{Red}$ of *(2)* is more positive. A similar lowering of the π level suggested by the smaller difference in the π → π* excitation energy $\Delta\tilde{\nu}_m^{\pi\to\pi^*}$ is confirmed by the different charge-transfer excitation energies $\tilde{\nu}_m^{CT}$ of tetracyanoethylene complexes of methyl and trimethylsilyl β-naphthyl ketone [13].

The fact that the n → π* excitation energy of the yellow silyl ketone is lower than that of the colorless *tert*-butyl ketone can be explained (on the basis of a σ/π separation) as follows: The strong inductive effect of the trimethylsilyl group $+I_{SiR_3} > +I_{CR_3}$ raises all the inner molecular orbitals. However, this becomes observable only in the free electron pair of the carbonyl oxygen, which is orthogonal to the π

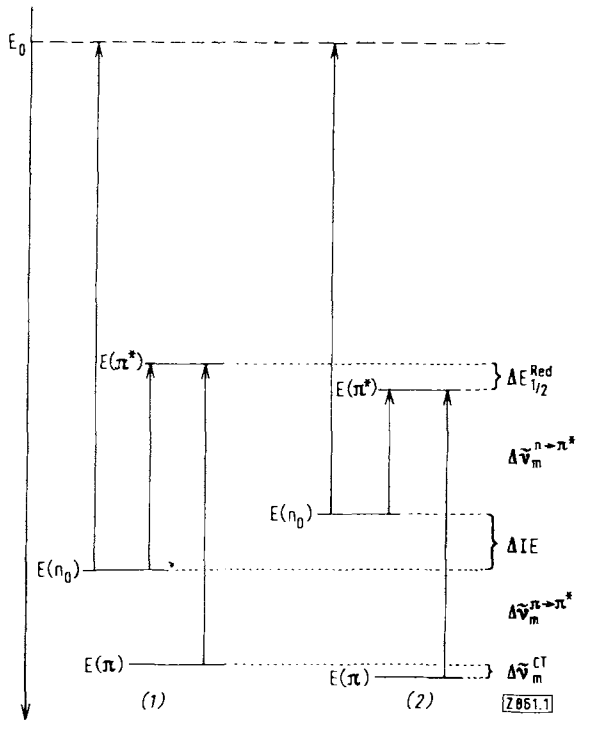


Fig. 1. Approximate energy level diagrams for *tert*-butyl *(1)* and trimethylsilyl phenyl ketone *(2)*.

system and is situated in the β position with respect to the silicon. The energies of the ground state and the excited states, on the other hand, are lowered by the possibility of back-donation Si ← C_π from the π system into empty atomic orbitals of the silicon, which is in the α-position in this case. As expected, this interaction is greater in the excited states because of the smaller energy difference in relation to the unoccupied Si acceptor orbitals. The acceptor function of trimethylsilyl groups, which must be of π symmetry, may involve unoccupied 3d atomic orbitals of the silicon.

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[1] Lecture to the 2nd International Symposium on Organosilicon Compounds in Bordeaux, July 1968. Part 13 of d-Orbital Effects in Silicon-substituted π-Electron Systems. – Part 12: *H. Bock* and *H. Seidl*, J. chem. Soc. (London) *(B) 1968*, 1158.

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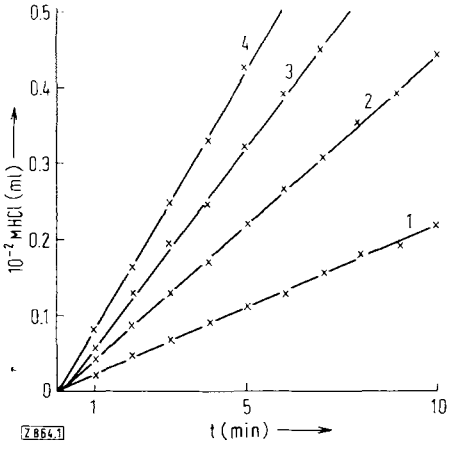
A New Test for the Determination of Pyruvate Decarboxylase Activity

By *A. Schellenberger, G. Hübner*, and *H. Lehmann* [*]

The hydroxide ions formed in the pyruvate decarboxylase reaction(PDC, 2-oxoacid carboxylase, EC 4.1.1.1) in accordance with

$$CH_3\text{–}CO\text{–}COO^\ominus \xrightarrow[+\,H_2O]{(PDC)} CH_3CHO + CO_2 + OH^\ominus$$

permit the accurate determination of the reaction rate by pH-stat titration. It can be seen from Figure 1 that the acid consumption increases linearly with time and that the slope of the curves is proportional to the enzyme concentration.



Owing to the sensitivity of the test, the pyruvate conversion is low, so that there is no inhibition of the reaction by the acetaldehyde formed. The fact that investigations can be carried out in buffer-free media, thus eliminating salt and foreign-ion effects, represents a further advantage. The enzyme activities found in the optical test described by *Holzer* [1] and in the Warburg test agree to within a good approximation with those found in the pH-stat test (Table 1).

Table 1. Comparison of enzyme activity measurements.

pH	Enzyme activity (I.U.)/0.05 ml standard (*ca.* 2 mg PDC/ml)		
	pH-stat test	optical test	Warburg test
5.2	0.29		
5.6	0.70		
6.0	0.88	0.90	0.82
6.4	0.79	0.80	
6.8	0.62	0.62	
7.5	0.16	0.16	

The pH-stat test can be used between pH = 5.2 and 7.5. The enzyme activities found at various pH values exhibit good agreement with those reported by *Singer* and *Pensky*[2].

The pH-stat test can also be used to measure the decarboxylation rate of substrate analogs such as aliphatic α-keto acids and substituted phenylglyoxylic acids, which cannot be measured by the optical test. Since no auxiliary enzyme system is required, the determination can also be carried out in the presence of product.

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Friedel-Crafts Reactions of Octachlorocyclotetra(phosphazene)

By *V. B. Desai, R. A. Shaw*, and *B. C. Smith*[*]

Friedel-Crafts reactions of octachlorocyclotetra(phosphazene) have been attempted, but no pure products have been isolated[1]. The preparation of two crystalline compounds from the reaction with benzene is reported here.

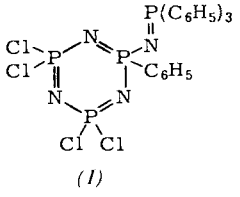
A mixture of octachlorocyclotetra(phosphazene) (14.1 g), anhydrous aluminum chloride (30.9 g), and triethylamine (9.2 g) in benzene (620 ml) was boiled under reflux (48 h). The product was divided into two portions.

1. Hydrolysis by cold dilute hydrochloric acid, extraction with benzene, and filtration through short alumina and silica columns gave 2,2,4,4-tetrachloro-6-phenyl-6-(2,2,2-triphenylphosphazenyl)cyclotri(phosphazene) *(1)* (yield 0.6%, m.p. and mixed m.p. 181 °C)[2]. The product was isolated by recrystallization from light petroleum (b.p. 40–60 °C)/methylene chloride (1:1).

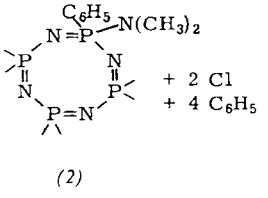
This is the first reported example of a ring contraction resulting from Friedel-Crafts reactions in the phosphazene series of compounds.

2. An excess of dimethylamine was added at 0 °C, and the mixture was boiled under reflux (1 h). Filtration through a short silica column gave dichlorodimethylaminopentaphenylcyclotetra(phosphazene) *(2)*, which was isolated by recrystallization from light petroleum (b.p. 40–60 °C)/methylene chloride (1:3) (yield 0.6%, m.p. 171 °C).

The dimethylamino ^{1}H–NMR spectrum of this product ($^3J_{P-H}$ 11.6 Hz) confirms the presence of a $P(C_6H_5)N(CH_3)_2$ group. The mass spectrum exhibits a peak at *m/e* 680 corresponding to the molecular ion $[N_4P_4(C_6H_5)_5Cl_2N(CH_3)_2]^+$, but no peak occurs at *m/e* 262 corresponding to the fragment $[P(C_6H_5)_3]^+$. The broad P=N stretching band in the infrared spectrum occurs at *ca.* 1240 cm^{-1}, *i.e.* at a higher (*ca.* 80 cm^{-1}) wave-number range than in *(1)*, thus confirming the presence of a cyclotetra(phosphazene) ring[1]. The positions of the remaining substituents are not yet known.



(1)



(2)

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Dimethyl Pentacyclo[5.2.0.0^{2,9}.0^{3,5}.0^{6,8}]nonane-1,7-dicarboxylate[1]

By *H. Prinzbach, W. Eberbach*, and *G. Philippossian*[*]

Compounds with the tetracyclo[4.2.0.0^{2,8}.0^{5,7}]octane skeleton *(3)*, the next higher homolog in the series prismane *(1)*, quadricyclane *(2)*, have often been postulated as intermediates but their existence has not yet been directly proved[2].

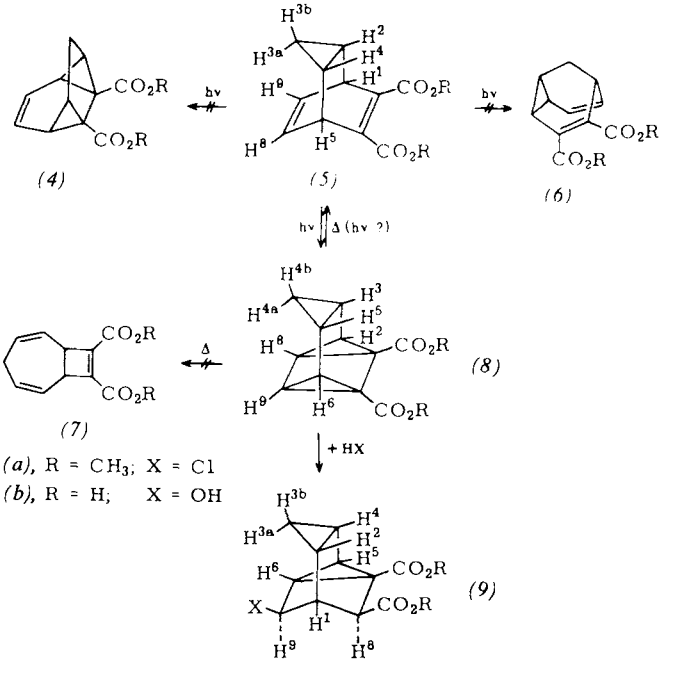
(1) *(2)* *(3)*

We have now isolated the system *(8a)* that is very closely related to the tetracycle *(3)*.

Compound *(8a)* is formed in at least 80% yield[3] on direct irradiation (Hanau Q-81 lamp, Pyrex filter, 2 h) of an ethereal solution (100 mg/300 ml) of "monohomobarrelene" *(5a)* [λ_{max} (ether) = 257 nm (ε = 2060; $\varepsilon_{280\,nm}$ = 800)] cooled to −20 °C.

Apparently this ($2\pi + 2\pi$) cycloaddition *(5)* → *(8)* is not detectably (NMR analysis) accompanied by ($2\pi + 2\sigma$) addition *(5)* → *(4)* in spite of the stereoelectronically favorable[4] *exo*-arrangement of the three-membered ring[5] to the substituted (excited) C=C double bond. Moreover, there was no indication that *(6a)* was formed, although this product would be the one most expected on triplet sensitization[6].

The photoproduct *(8a)* is very unstable thermally. When the photosolution is warmed, *(8a)* rearranges quantitatively (NMR accuracy) to *(5a)*, the half-life ($CHCl_3$) at 21.5 °C



(4) *(5)* *(6)* *(7)* *(8)* *(9)*

(a), R = CH_3; X = Cl
(b), R = H; X = OH

Table 1. Chemical shifts (τ; −10 °C) and coupling constants (J; Hz) of compounds *(5a)*, *(8a)*, and *(9a)*.

Compd.	H-1	H-2	H-3		H-4		H-5	H-6	H-8	H-9	J
			H-3a	H-3b	H-4a	H-4b					
(5a) [a]	5.95	8.62	9.28	9.40	8.62		5.95		4.00	4.00	$J_{23a} = 3.6$, $J_{23b} = 7.1$, $J_{3a3b} = 5.9$
(8a) [a]		7.90	8.3–8.9		9.77	8.9–9.5	8.3–8.9	7.90	7.90	7.90	$J_{34a} = 3.5–4$, $J_{34b} = 7–8$, $J_{4a4b} = 4–4.5$
(8a) [b]		*ca.* 8.1	8.5–9.3		10.06	9.4–9.9	8.5–9.3	*ca.* 8.1	*ca.* 8.3	*ca.* 8.3	$J_{29} = 6.7$
(9a) [a]	7.25	9.21	8.29	9.46	8.66		7.54	8.00	6.77	5.70	$J_{12} = 4.5–5$, $J_{14} < 1$, $J_{16} = 1.8$, $J_{18} = 5.1$, $J_{19} = 4.5$, $J_{23a} = 3.7$, $J_{23b} = 7.8$, $J_{24} = 8.0$, $J_{25} < 1$, $J_{3a3b} \sim 5$, $J_{3a4} = 3.7$, $J_{3b4} = 7.8$, $J_{45} = 3.5$, $J_{46} < 1$, $J_{56} = 8.0$, $J_{58} < 1$, $J_{59} < 1$, $J_{68} < 1$, $J_{69} = 3{,}0$

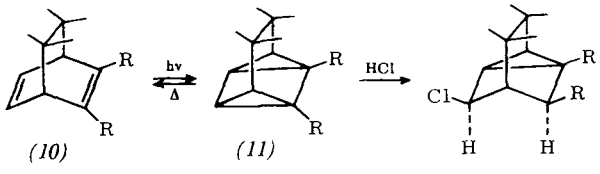
[a] In $CDCl_3$. [b] In $C_6H_6/CDCl_3$ (3:1).

being *ca.* 90 min. Compound *(8a)* is isolated by concentration of the solution at low temperature; it can be obtained in at least 95% purity [5% of *(5a)*] as colorless fine needles (m.p. 49–50 °C on rapid heating) by recrystallization from ether at −60 °C.

In this temperature range the fission *(8a)* → *(7a)*, *i.e.*, the reverse of the thermally "allowed" (2 + 2 + 2) addition *(7a)* → *(8a)*, does not compete with the thermally "forbidden" [7] isomerization *(8a)* → *(5a)*.

Whilst it was impossible [9] to effect cycloaddition to the bishomocyclobutadiene system of *(8a)* by the dienophilic reagents usually valuable [8] for polycycles of type *(2)*, the compound *(8a)* can be converted into the chloride *(9a)* (m.p. 87–89 °C) by addition of HCl (passage of gaseous HCl into a CH_2Cl_2 solution at −20 °C). This reaction is quantitative and stereospecific; the stereochemical details are proved by the NMR data (Table 1) [10]. We had previously identified the alcohol *(9b)* as the sole product of photolysis of the dicarboxylic acid *(5b)* in water and had determined the configuration at the centers C-8 and C-9 by an independent synthesis [11]. The thermal lability of *(8a)* and the ease of addition of HCl to *(8a)* raise again the question of the mechanism of the hydration *(5b)* → *(9b)* [2].

According to preliminary results, irradiation of dimethyl bicyclo[2.2.2]octadiene-2,3-dicarboxylate under the conditions used for the reaction *(5a)* → *(8a)* (Vycor filter) causes *ca.* 50% isomerization to *(11)*; NMR ($CHCl_3$), τ = 6.22 (6 H), 7.69 (2 H), 7.88 (4 H), 8.37 (2 H). Having a half-life of *ca.* 12 min. at 19 °C in $CHCl_3$, *(11)* is even less stable than *(8a)*; the reverse reaction *(11)* → *(10)* occurs quantitatively. Addition of HCl at −25 °C leads to *(12)*.



(10) *(11)* *(12)*

R = CO_2CH_3

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[9] With TCE only there are indications of adduct formation.

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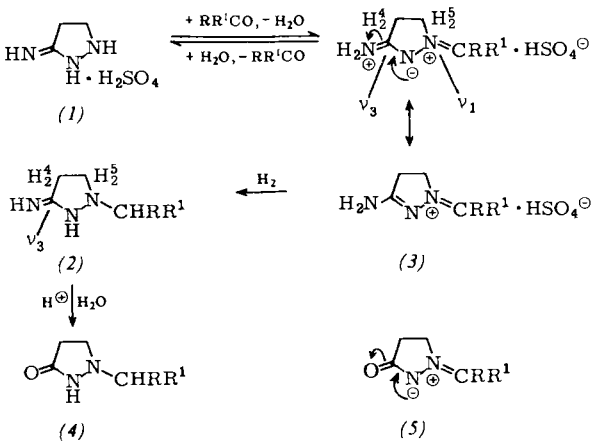
1-Alkylidene- and 1-Arylalkylidene-3-iminopyrazolidine *N,N*-Betaine Salts, a New Type of Azomethine Imine Stabilized by Mesomerism

By *H. Dorn* and *A. Otto* [*]

The reaction of 3-pyrazolidone and other cyclic acylhydrazines with carbonyl compounds provides a general route to "carbonyl-stabilized azomethine imines" *(5)* [1,2] in which the more electronegative oxygen acquires part of the charge from N-2. We have now isolated "imino-stabilized azomethine imines" as the salts *(3)*, in which the electronegativity of the imino-N atom has been raised sufficiently by salt formation.

3-Iminopyrazolidine·H_2SO_4 *(1)* [3] is readily accessible from hydrazine, acrylonitrile, and sulfuric acid; if 1 equivalent of *(1)* is heated with 1 equivalent of any desired carbonyl compound in methanol until dissolution is complete, then, on cooling, the azomethine imine salt *(3)* separates in *ca.* 100% yield; these products are mostly colorless and can be recrystallized from alcohols. When warmed, their aqueous solutions regenerate free RR^1CO quantitatively.

Catalytic hydrogenation of *(3)* (suspension in methanol, Adams Pt, 20 °C, 1 atm.) affords 100% yields of crystalline salts of 1-substituted 3-iminopyrazolines *(2)* from which the bases *(2)* are generated by methanolic NaOH [yield 92–96%; identical with authentic *(2)* [2,4]]. Salts of *(2)* are also obtained when equimolar mixtures of *(1)* and RR^1CO are catalytically hydrogenated in water or methanol-water. If aqueous solutions of salts of *(2)*, *e.g.*, *(2)*·H_2SO_4 are heated for a further 3–4 h, best after addition of a further equivalent of H_2SO_4, then 1-substituted 3-pyrazolidones *(4)* (identical with authentic specimens) are obtained in yields of 80–90%. The last mentioned reactions not only prove the position of CRR^1 in *(3)* but also afford new, very simple, and general syntheses of compounds of types *(2)* and *(4)*.



(a), $CRR^1 = (CH_3)_2C=$

(b), $CRR^1 =$

(c), $CRR^1 = C_6H_5CH=$

Compd.	M.p. (°C)	^{1}H–NMR [b]	τH-5[a]	τH-4[a]	IR (cm^{-1}) ν_3 (C=N)	ν_1 (C=N)	δ (NH_2)
(3a)	215–218	A	5.58 [c]	6.88	1600 [d]	1689 [d]	1658 [d]
(3b)	168–170	A	5.55 [c]	6.92	1602 [d]	1686 [d]	1655 [d]
(3c)	204–206	A	5.20 [c]	6.80	1588 [d]	1678 [d]	1640 [d]
(2a)	111–113	A	7.05–7.80 [e]		1657 [f]		
(2a)		B	6.82–7.58 [e]				
(2b)	104–105	B	7.00 [g]	7.42	1652 [h]		
(2c)	78–79	B [i]	7.10 [g]	7.47	1652 [k]		

[a] Referred to tetramethylsilane as internal standard. [b] A: In $(CD_3)_2SO$. B: in $CDCl_3$ (Varian A 60A). [c] A_2X_2 system, signal for CH_2–N broadened. [d] In KBr. [e] Signals for both ring-CH_2 appear together with the signals for $CH(CH_3)_2$ as a multiplet. [f] In $CHCl_3$. [g] $\tau_{H\text{-}5}$ refers to the most intense signal of the AA′ portion, $\tau_{H\text{-}4}$ to the most intense signal of the BB′ portion of the AA′BB′ system; the position of these signals is representative for τ_A and τ_B, since $\nu_A - \nu_B$ [25 Hz for *(2b)* and 22 Hz for *(2c)*] is about three times as large as J_{AB} or $J_{A'B'}$. [h] In $CHCl_3$; after H/D exchange with D_2O, 1651 cm^{-1} without change of intensity; 1665/1650 in KBr. [i] In $(CD_3)_2SO$ the corresponding signals are shifted by *ca.* 0.1 τ to higher field. [k] In $CHCl_3$; 1665 cm^{-1} in KBr.

The NMR spectra of the azomethine imine salts *(3)* contain an A_2X_2 system for the protons at C-4 and C-5; the NMR spectra of the iminopyrazolidines *(2)* contain an AA′BB′ system for these protons. $\tau_{H\text{-}5}$ for *(3)* is shifted to lower field from its position for *(2)* as a result of the lesser shielding by N^+ (see Table). The same is true for *(5)* in comparison with *(4)*. For *(3a)* $\tau_{NH_2} = 2.05$ and $\tau_{HSO_4} = 1.40$, and for *(3b)* these values are 2.07 and 1.75, respectively.

Stabilization of the charge on N-2 can be recognized in the IR spectra of the azomethine imine salts *(3)*. These spectra include three intense bands between 1580 and 1690 cm^{-1}, of which one, namely $\delta(NH_2)$, disappears on H/D exchange with D_2O; of the other two (see Table), ν_3(C=N) is shifted by *ca.* 50 cm^{-1} towards the red in comparison with ν_3(C=N) of the iminopyrazolidines *(2)* as a result of the decrease in the C···N bond order.

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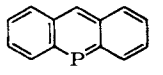
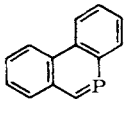
10-Phenyldibenzo[*b*,*e*]phosphorin

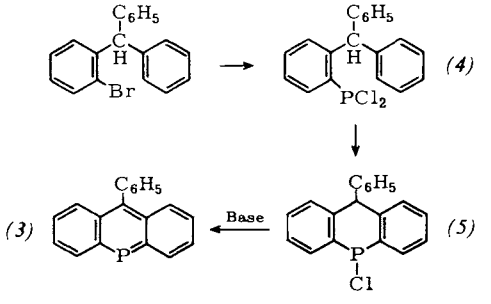
By *P. de Koe* and *F. Bickelhaupt* [*]

The tricyclic heteroaromatic phosphorus compounds *(1)* [1] and *(2)* [2] are unstable, so that their occurrence in solution has been only indirectly proved, mainly by spectroscopy. On the contrary, the monocyclic phosphorin derivatives are quite stable, isolable compounds [3–5].

One of the possible causes of this difference might be the stabilizing action of substituents, which are in the 2-, 4-, and 6-position for all the monocyclic phosphorins described so far.

(1)   *(2)*

For investigation of this problem we have prepared 10-phenyldibenzo[*b*,*e*]phosphorin *(3)*. In contrast to unsubstituted dibenzo[*b*,*e*]phosphorin *(1)*, this derivative *(3)* is a stable compound and can be sublimed at 160 °C/10^{-3} torr, but it reacts with oxygen faster than do the monocyclic phosphorins [6].



Synthesis of *(3)* was carried out by a method analogous to that used for *(1)* [1] (all reactions under nitrogen): The Grignard compound from 2-bromotriphenylmethane (30 g) in tetrahydrofuran was added to a solution of chlorobis(diethylamino)phosphine (17.6 g) in tetrahydrofuran cooled to −80 °C. The mixture was then heated at the b.p. for 16 h and the solvent was removed. The residue was extracted with cyclohexane and the extract was saturated with gaseous HCl. Finally, distillation under vacuum gave dichloro[*o*-(diphenylmethyl)phenyl]phosphine *(4)* [7], b.p. 161 °C/10^{-3} torr, m.p. 76.5–79 °C. When boiled for 10 h with a small excess of

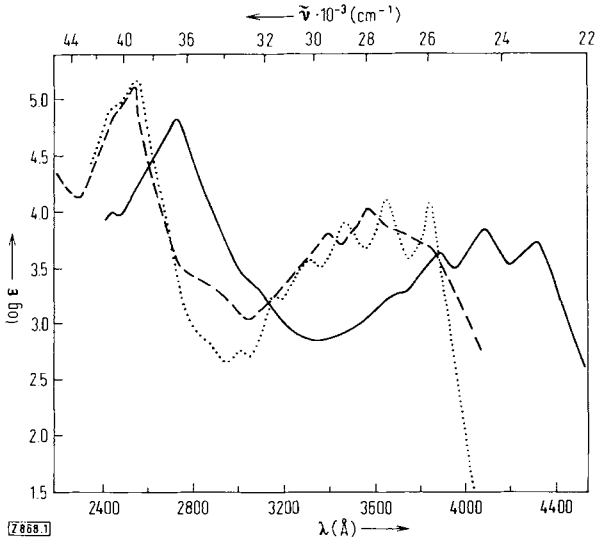


Figure 1. UV spectra of 9-phenylanthracene (in ethanol) (·····) [9], 9-phenylacridine (in ethanol/water, 20:8 v/v) (— — — —) [10] and *(3)* (in diethyl ether) (————).

aluminum chloride in carbon disulfide, this product *(4)* afforded a 41% yield of 5-chloro-5,10-dihydro-10-phenyldibenzo[*b,e*]phosphorin *(5)*[7], b.p. 131 °C/10^{-3} torr, m.p. 94–101 °C.

For removal of HCl, compound *(5)* (592 mg) in 40 ml of dimethylformamide was treated with 1,5-diazabicyclo[5.4.0]-undec-5-ene (357 mg) in a high-vacuum system. After about 12 h the solution was evaporated and the residue was purified by dissolution in cyclohexane, crystallization from toluene, and sunlimation in a vacuum. Yellow crystals of *(3)*, m.p. 173–176 °C, were obtained.

The structure of *(3)* follows from the elemental analysis, the mass spectrum[8] (molecular ion at m/e = 272, 100%), the ^{1}H–NMR spectrum [in CS_2 with tetramethylsilane as external standard: multiplets at δ = 7.7–8.5 (11 H) and 8.72 to 9.25 ppm [2 H, presumably those on C-4 and C-6], and the UV spectrum Fig. 1). The UV curve is largely similar to that of the unsubstituted parent *(1)* and in comparison with this shows a bathochromic shift of 6 nm for the longest-wavelength absorption [λ_{max} = 432 nm (ε = 7970) in diethyl ether], as is to be expected in analogy to the carbon and nitrogen analogs.

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[7] The structures of *(4)* and *(5)* were confirmed by elemental analysis and NMR spectra.

[8] We thank Prof. *Th. J. de Boer* and Drs. *N. M. M. Nibbering*, Institute of Organic Chemistry of the University of Amsterdam, for measuring the mass spectra and helping with their interpretation.

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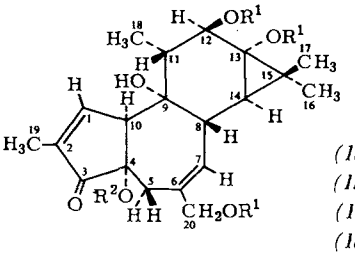
Lumiphorbol Triacetate, a Cage-like Derivative of the Diterpene 4α-Phorbol

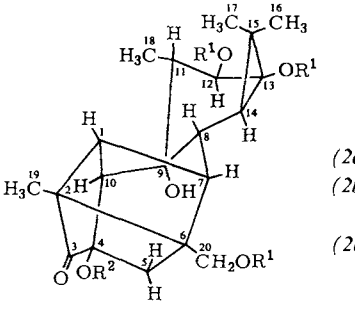
By *E. Hecker*, *E. Härle*, *H. U. Schairer*, and *P. Jacobi*
also *W. Hoppe*, *J. Gassmann*, *M. Röhrl*, and *H. Abel*[*]

During the isolation of the tetracyclic diterpene phorbol[1,2] [***] by alcoholysis of its esters that occur in croton oil[3] a mother-liquor was obtained[4] which, on acetylation by acetic anhydride and pyridine, afforded not only phorbol 12,13,20-triacetate[4] but also a triacetate *(1a)* with somewhat lower R_F value (0.55 and 0.30, respectively, ether/petroleum ether 10:1). The new triacetate has m.p. 165 to 166 °C, λ_{max} = 195, 238, 339 nm (ε_{max} = 11800, 6700, 65; in methanol), and it was also obtained when phorbol 12,13,20-triacetate was treated with sodium methoxide in methanol and then with acetic anhydride/pyridine. Isomerization is hindered by methylation of the ketol hydroxyl[5] at C-4 of phorbol. The analytical and physical data for the new compound show that it must be an isomer of phorbol 12,13,20-triacetate [*(1a)*, tentatively designated isophorbol triacetate].

In contrast to isophorbol triacetate *(1a)*, the free isophorbol *(1b)* could not be induced to crystallize. With acetic anhydride/pyridine the alcohol *(1b)* also gave a 4,12,13,20-tetraacetate *(1c)*, m.p. 164–167 °C, in contrast to phorbol[4], and with benzoyl chloride/pyridine it gave a 4,12,13,20-tetrabenzoate *(1d)*, m.p. 150–154 °C. With acetic anhydride/pyridine *(1a)* can be further acetylated to *(1c)*.



(1a), R^1 = $COCH_3$, R^2 = H
(1b), R^1 = R^2 = H
(1c), R^1 = R^2 = $COCH_3$
(1d), R^1 = R^2 = COC_6H_5



(2a), R^1 = $COCH_3$, R^2 = H
(2b), R^1 = $COCH_3$, R^2 = *p*-Br-C_6H_4-CO
(2c), R^1 = R^2 = H

Irradiation of *(1a)* by UV light (254 nm) affords almost quantitatively a new substance *(2a)*, m.p. 130–137 °C, λ_{max} = 194, 297 nm (ε = 2300, 50; in methanol), which we designate lumiphorbol triacetate. Analysis and mass, UV, IR, and particularly ^{1}H–NMR spectra show that it is a 12,13,20-triacetate and they accord with the cage-like structure *(2a)* in which the five- and the seven-membered ring must be *cis*-linked (4α,10α), *i.e.*, differently from the linkage in phorbol. Isophorbol *(1b)* is thus a 4-epimer of phorbol. Like *(1a)*, the triacetate *(2a)* can also be acylated on C-4. A 4-(*p*-bromobenzoate) *(2b)*, m.p. 182 °C, λ_{max} = 198, 246 nm (ε_{max} = 3800, 19600; in methanol), can be obtained by reaction of *(2a)* with *p*-bromobenzoyl chloride in pyridine.

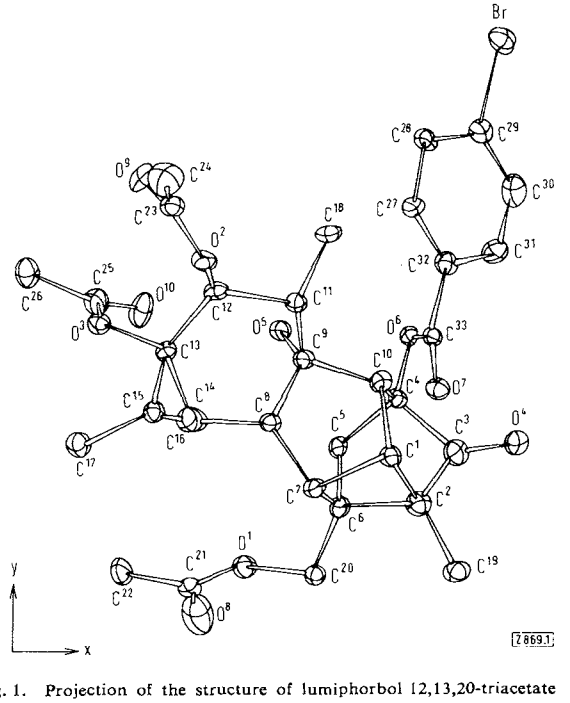


Fig. 1. Projection of the structure of lumiphorbol 12,13,20-triacetate 4-(*p*-bromobenzoate) *(2b)* [****].

X-ray analysis of the 4-(*p*-bromobenzoate) *(2b)* leads to the relative configuration of the molecule (Fig. 1) (space group $P\,2_1$, $Z = 2$, $a = 10.20$ Å, $b = 20.29$ Å, $c = 7.93$ Å, $\beta = 90.52°$). The structure was determined, fully automatically, by finding the position of the bromine atom from Patterson synthesis and subsequent treatment by phase-improvement methods. The pseudoasymmetry due to the position of the bromine could be overcome in that work [****].

This proves the structure *(2a)* of lumiphorbol triacetate, and shows isophorbol *(1b)* to be the 4α-phorbol (4α,9,12β,13,20-pentahydroxy-1,6-tigliadien-3-one). Accordingly, lumiphorbol *(2c)* is a 4α,9,12β,13,20-pentahydroxy-1,7:2,6-dicyclo-4α-tiglian-3-one or a 7,8β,10,12α-tetrahydroxy-14-(hydroxymethyl)-1,6,6,9-tetramethylhexacyclo[10.2.1.$0^{2,11}$.$0^{3,14}$.$0^{4,10}$.$0^{5,7}$]pentadecan-15-one [6].

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[**] We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Badische Anilin- & Sodafabrik for financial support.

[***] Phorbol has the formula *(1b)* but with *trans*-linked five- and seven-membered rings (4β,10α).

[****] Note added in proof: The absolute configuration determined by means of anomalous scattering corresponds to the mirror image of the structure shown in Fig. 1 [cf. *(2b)*], and is identical with the absolute configuration of neophorbol 13,20-diacetate 3-[*p*-bromobenzoate] [2].

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Preparation of Titanyl and Vanadyl Mesoporphyrin IX Dimethyl Esters

By *M. Tsutsui, R. A. Velapoldi, K. Suzuki*, and *T. Koyano* [*]

The presence of titanium porphyrins in petroleum has been suggested but not proved, yet vanadyl porphyrins have been identified as constituents [1]. Moreover, titanium porphyrins have hitherto not been prepared whereas vanadyl porphyrins have been synthesized under severe reaction conditions [2]. General methods of metal insertion and reaction with metal carbonyls have not been successful or applicable for the preparation of titanium porphyrins [3].

We wish to report the synthesis of titanyl mesopophyrin IX dimethyl ester: Mesoporphyrin IX dimethyl ester (0.300 g) and diphenyltitanium (1.527 g) [4] *molar ratio (1:15)* were ground together in the solid state and then allowed to react for 1.5 h at 210 °C in either degassed, purified mesitylene (100 ml) (bath temperature 240 °C) or triethylbenzene (100 ml) (bath temperature 210 °C) under argon. The reaction mixture was cooled and filtered in the atmosphere. A chloroform extract of the precipitate was passed through a chromatographic column of basic alumina for purification. A deep purple solid (0.083 g) was isolated from the eluent by addition of *n*-hexane followed by centrifugation and drying under vacuum.

The absorption spectrum was similar to that of the corresponding vanadyl compound [2]; with chloroform, pyridine, or *n*-hexane as a solvent, the following visible spectrum was recorded: 407 nm (log ε = 5.60), 500 nm (shoulder), 536 nm (log ε = 2.35), 574 nm (log ε = 2.46).

The compound is diamagnetic, as shown by the Gouy and NMR methods, and thus contains Ti^{IV}. This can be attributed to oxidation of the Ti^{II} to the more stable titanyl moiety during isolation of the compound in the atmosphere.

No N–H stretching frequency was observed at 3319 cm^{-1} in the infrared spectrum, which proves metal insertion. A strong, broad absorption at 1038 cm^{-1} was assigned as the titanyl stretching frequency [5]. All other absorptions in the spectrum are similar to those of either metalloporphyrins or free porphyrins.

We further wish to report a simple method for the preparation of vanadyl mesoporphyrin IX dimethyl ester: A mixture of an excess of vanadium hexacarbonyl (0.140 g) and mesoporphyrin IX dimethyl ester (0.028 g) was heated at 170 °C for 1.5 h in *n*-decane (10 ml) under nitrogen. The product (0.011 g) was isolated and purified similarly to chromium mesoporphyrin IX dimethyl ester [3], and was identified by comparison with the previously prepared compound [2].

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[1] *W. Treibs*, Liebigs Ann. Chem. *510*, 42 (1934); *517*, 172 (1935); *H. N. Dunning* and *N. A. Rabon*, Ind. Engng. Chem. *48*, 951 (1956).

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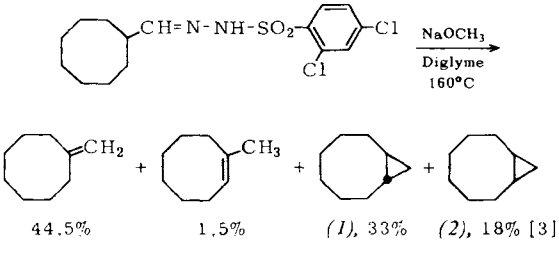
trans-Bicyclo[5.1.0]octane

By *W. Kirmse* and *Ch. Hase* [*]

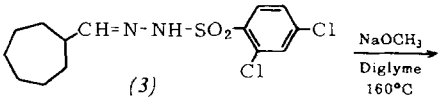
Intramolecular insertion reactions of *sec*-alkylcarbenes afford more *trans*- than *cis*-1,2-dialkylcyclopropanes [1], but because of ring strain cyclopentylcarbene and cyclohexylcarbene give only *cis*-bicyclo[*n*.1.0]alkanes ($n = 3$ or 4) [1,2]. We have



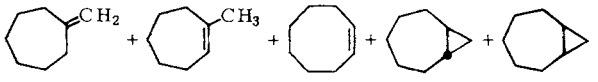
found that when $n = 6$ the *trans*-isomer *(1)* again preponderates.

The isomeric bicyclo[6.1.0]nonanes *(1)* and *(2)* can also be prepared from *cis*- and *trans*-cyclooctene[4,5] and the pairs of samples were identified by comparison.

We were able to prepare the strongly strained[6] *trans*-bicyclo-[5.1.0]octane *(7)* analogously by means of cycloheptylcarbene, although this product is not obtainable by any other route.



(3)



(4), 48% *(5)*, 2% *(6)*, 1% *(7)*, 12% *(8)*, 37%

All the products except *(7)* were identified by comparison with authentic specimens. After removal of the olefins *(4)* to *(6)* by ozonolysis, the isomers *(7)* and *(8)* were separated by gas chromatography. *(7)* was shown to be a cyclopropane derivative by its NMR spectrum (2 H at 0.08 ppm) and its IR spectrum (1013, 1037 cm^{-1}).

The increased ring strain in *(7)* is shown by catalytic hydrogenation to methylcycloheptane (glacial acetic acid-pentane 2:1, PtO_2, 1 atm of H_2, 22 h). During quantitative hydrogenation of the *trans*-compound *(7)*, 90% of the *cis*-isomer *(8)* remained unchanged. Thermal isomerization of *(7)* is only slow: under the conditions of its formation (diglyme, $NaOCH_3$, 160 °C) 11.5% of methylcycloheptene *(5)*, 9.5% of methylenecycloheptane *(4)*, and 1% of *(8)* were formed in 40 min; 78% of the *(7)* remained unchanged.

trans-Bicyclo[5.1.0]octane (7):

The sulfonylhydrazone *(3)* (decomp. 107 °C) was prepared (yield 43%) from cycloheptanecarbaldehyde[7] and 2,4-dichlorobenzenesulfonohydrazide (decomp. 108–110 °C) in methanolic hydrochloric acid. 11.2 g of the sulfonylhydrazone in 30 ml of diglyme was added during 6 min to a suspension of 8.9 g of sodium methoxide in 150 ml of boiling diglyme (85% total yield, determined by gas chromatography with cyclooctane as standard). The mixture was worked up by dilution with water, extraction with *n*-pentane, ozonolysis in methanol at −70 °C, cleavage of the ozonides with aqueous $Na_2SO_3/NaHSO_3$ solution, and extraction with *n*-pentane. On preparative gas chromatography (column 300 × 1 cm, 20% tricresyl phosphate on kieselguhr, 90 °C, 220 cc of H_2/min) we obtained *ca.* 180 mg of the bicyclooctane *(7)*.

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Synthesis, on a Preparative Scale, of Ethanol Stereospecifically Labeled on Hydrogen[***]

By *H. Simon*, *M. Kellner*, and *H. Günther*[*]

Compounds, *e.g.*, ethanol[1–3], stereospecifically labeled on hydrogen are of interest in biochemistry[1] and for the study of reaction mechanisms[2]. Such ethanol preparations, made by chemical methods, have been hitherto only of moderate optical purity[2]. Biochemical methods are not practicable on a preparative scale because of the large amounts of enzyme required[3] and furthermore need substrates or cosubstrates labeled on hydrogen.

(1*R*)-[1-D]- and (1*R*)-[1-T]-ethanol of high stereospecific purity can be obtained surprisingly easily by incubating, *e.g.*, the yeast *Torulopsis utilis*[4] in D_2O or H_2O/HOT containing 10% of ethanol for 50–90 h.

Experimental:

Starved *Torula* yeast (153 g) was suspended in D_2O (80 ml) and centrifuged off, and this process was repeated twice more. The yeast was then stirred vigorously at 30 °C under an atmosphere of oxygen for 50 h in 300 ml of D_2O and 18 ml of citrate buffer (0.3 M, pH = 5.6) in D_2O to which 34 ml of ethanol had been added. 22.7 ml of ethanol remained in the supernatant liquor.

For determination of the D content and D distribution, several samples were converted into ethyl 3,5-dinitrobenzoate, and from a part silver acetate was prepared by Kuhn-Roth oxidation. For determination of the stereospecificity the ethanol was dehydrogenated by yeast alcohol dehydrogenase to acetaldehyde[3,5] and this aldehyde was precipitated in the form of its 2,4-dinitrophenylhydrazone or dimedone derivative. All the products were measured by mass spectrometry[6]. The 2,4-dinitrophenylhydrazone was also oxidized by the Kuhn-Roth method and the acetic acid was analyzed, since under the conditions of formation of the hydrazone hydrogen exchange between the methyl group and the medium takes place[7].

Typical results for 50 h reaction are: 0.98 gram atom of D per mole of ethanol, 0.085 being in the methyl group and less than 0.07 in the (1*S*)-position; after 96 h reaction, 1.16 gram atoms of D per mole of ethanol, 0.12 being in the methyl group and 0.11 in the (1*S*)-position.

(1*S*)-[1-D]- and (1*S*)-[1-T]-Ethanol can be obtained in this way by using CH_3-CD_2OH or non-stereospecifically labeled [1-T]ethanol, respectively, in H_2O. Since yeast alcohol dehydrogenase reacts also with other alcohols, these can also be labeled, but according to our experiments more slowly.

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[***] We thank the Bundesministerium für wissenschaftliche Forschung for financial support.

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An Abnormal Ring Cleavage of 1α,2α-Epoxy-3-keto Steroids by Hydrogen Fluoride

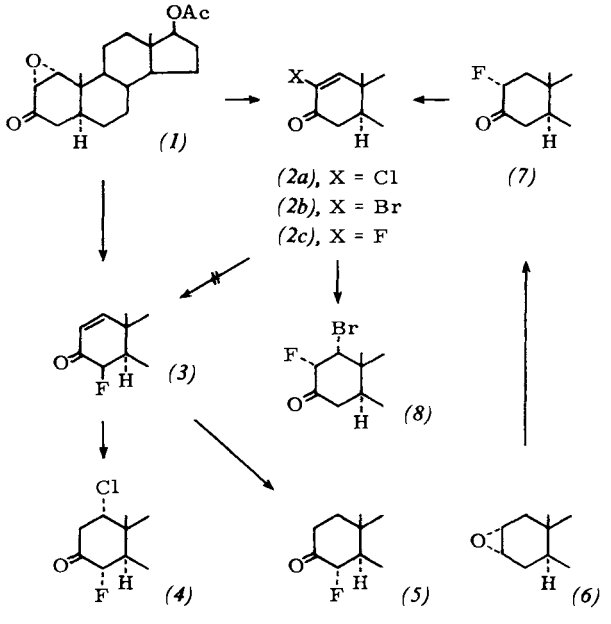
By *U. Kerb, G. Schulz,* and *R. Wiechert* [*]

2-Chloro- *(2a)* and 2-bromo-5α-androst-1-en-3-one *(2b)* have been obtained by treatment of 17β-acetoxy-1α,2α-epoxy-5α-androstan-3-one *(1)* [1] with hydrogen chloride and hydrogen bromide, respectively [2, 3].

However, hydrogen fluoride causes rearrangement, yielding, from *(1)*, 17β-acetoxy-4β-fluoro-5α-androst-1-en-3-one *(3)*, m.p. 173–174 °C (UV: $\varepsilon_{234} = 10960$) [4].

The characteristic signals in the NMR spectrum of this product *(3)* are the doublets of two olefinic protons ($\delta = 7.33$ and 6.00), the double doublet of the proton on C-4 ($\delta = 4.50$), and the signal of the 19-CH_3 group ($\delta = 1.20$) which is split to a doublet [5] by 1,3-diaxial interaction with the 4β-fluorine atom.

The 1α-chloro-4α-fluoro ketone *(4)* (m.p. 173 °C with decomp.) was obtained from *(3)* by means of hydrogen chloride in glacial acetic acid, isomerization at C-4 and addition of HCl occurring. Hydrogenation of *(3)* in presence of Pd/C in methanol and subsequent epimerization by hydrogen chloride in glacial acetic acid led to the 4α-fluoro ketone *(5)* (m.p. 187.5–188 °C). In the NMR spectra of *(4)* and *(5)* the signal of the 19-CH_3 group appears as a singlet, whence it follows that the fluorine is in the 4α position.



For further proof of the structure of *(3)*, 17β-acetoxy-2β-fluoro-5α-androstan-3α-ol (m.p. 205–206 °C) was prepared from the 2α,3α-epoxide *(6)* [6] and was oxidized to the 2β-fluoro ketone (m.p. 158–160 °C) and converted by acid isomerization into the known 2α-fluoro compound *(7)* [4] (m.p. 189–190.5 °C). The double bond was introduced into *(7)* by bromination and then removal of hydrogen bromide. The 17β-acetoxy-2-fluoro-5α-androst-1-en-3-one *(2c)* prepared in this way (m.p. 160.5–161.5 °C; UV: $\varepsilon_{238} = 10100$) gave a depression of the melting point on admixture with *(3)*. The NMR spectrum of *(2c)* contains the signal of only one olefinic proton.

We were unable to rearrange *(2c)* to *(3)* by hydrogen fluoride under the conditions of epoxide ring fission, in the way that *Djerassi* and *Scholz* [7] observed for the 17α-benzoyloxy-2-bromo-5α-androst-1-en-3-one system which was transformed into the 4-bromo isomer. Compound *(2c)* adds hydrogen bromide, yielding *(8)* (m.p. 159.5–160.5 °C).

17β-Acetoxy-4β-fluoro-5α-androst-1-en-3-one (3):

Compound *(1a)* (1 g) is added portionwise to a mixture of a) dimethylformamide (5 ml) and hydrogen fluoride (5 ml) or b) tetrahydrofuran (40 ml) and hydrogen fluoride (10 ml) and the mixture is stirred for 22 h or 48 h, respectively, at room temperature. The reaction mixture is then poured into ice-water and neutralized with K_2CO_3; the precipitate is filtered off and recrystallized from dichloromethane/isopropyl ether (yield 60%).

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Formation of Adenosine Triphosphate (ATP) from Adenosine Diphosphate (ADP) and Phosphate during Oxidation of Mercaptoacetate by Bromine [1]

By *Th. Wieland* and *E. Bäuerlein* [*]

We have converted oxidation energy into the energy of the "energy-rich" diphosphate bond, *e.g.*, that in ATP, by oxidation of *S*-alkylmonothiohydroquinones [2], *N*-acetylhomocysteine thiolactone [3], thiazolidones [4], monoacetyldurohydroquinone [5], α-tocopherol [6], and *S*-*p*-tolyl thioacetate [6] by bromine in pyridine in the presence of ADP and phosphate (P). We have now found that under these conditions mercaptoacetate also gives ATP from the tetrabutylammonium (TBA) salts of ADP and P, and that yields exceed 30%.

In several batches, 13.33 ml of 0.1 N (TBA)·OH solution in 2-propanol/methanol (Merck, Darmstadt) was treated with 0.67 ml of 1 N solution of *ca.* 90% phosphoric acid in dioxane; 0.107 g of $ADPH_3 \cdot 3\,H_2O$ (C. F. Boehringer und Soehne, Tutzing) was dissolved therein, and then 0.016 ml of freshly distilled mercaptoacetic acid was added. The solution was evaporated under vacuum, and the residue was dried over P_4O_{10} for 20 min at 0.1 torr and then dissolved with stirring in 9 ml of anhydrous pyridine, whereupon a deep yellow color developed. (A solution of the TBA salt of mercaptoacetic acid in anhydrous pyridine is colorless.) The solution was then treated, by dropwise addition within a few minutes, with $^5/_9$ mmole (0.028 ml), $^2/_9$ mmole (0.011 ml), or 0.133 mmole (= $1.2 \times {}^1/_9$ mmole) (0.007 ml) of bromine, each amount in 1 ml of anhydrous pyridine.

This caused a color change from deep yellow through deep red to pale yellow; a precipitate was formed after a few minutes. After 1 h each batch (several repeats) was worked up for determination of ATP (results in Table 1).

No more than conjectures can be made at present about the mechanism of this coupled reaction. It may be that a sulfenyl bromide is first formed by bromination of the thiol and then combines with the phosphate ion to give a mixed sulfenic phosphoric anhydride $R-S-O-PO_3H^-$, which is the actual phosphorylating agent.

Table 1. Yields of ATP (calc. on the 84% ADP used on simultaneous oxidation of equivalent amounts of $(TBA)_2HPO_4$, $(TBA)_3ADP$, and TBA mercaptoacetate by 1.2, 2.0, and 5.0 equivalents of bromine.

Br_2 (equiv)	1.2		2.0		5.0		0	
Mercaptoacetate	with	without	with	without	with	without	with	without
Yield (%) of ATP	5.8	0	12.2 10.0	0 0	36.4 37.6	3.2 1.6	0	0
			11.2	0	37.0	2.4		
Net yield (%) of ATP	5.8		11.2		34.6		0	

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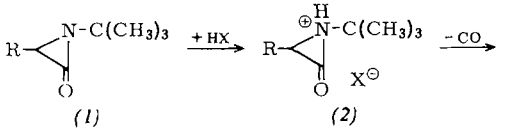
Synthesis of 1-Adamantanecarbaldehydes

By *K. Bott* [*]

According to a process described in the patent literature [1] free 1-adamantanecarbaldehydes can be prepared by reduction of 1-[1-(adamantanecarbonyl)]aziridines using $LiAlH_4$. We have now found that 1-adamantanecarbaldehydes *(4)* can be obtained in essentially higher yields (92–96%) by decomposition of the aziridinones *(1)* with aqueous mineral acids (Table 1). Compounds *(2)* and *(3)* are assumed to be intermediates because the aldimonium salts *(3)* can be isolated quantitatively on working in anhydrous ether [2].



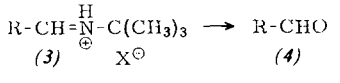


Table 1. Characterization of the aldehydes *(4)*.

Product	R	M.p. (°C)	$\tilde{\nu}$(CO) (cm^{-1})
Aldehyde [a]	1-Adamantyl	139–141 [b]	1722 [c]
Dimethyl acetal	1-Adamantyl	40–41	–
Aldehyde	3-Methyl-1-adamantyl	Colorless oil	1710
Oxime	3-Methyl-1-adamantyl	76–77	–
Aldehyde	3,5,7-Trimethyl-1-adamantyl	74–75	1710 [c]
Dimethyl acetal	3,5,7-Trimethyl-1-adamantyl	54–55	–

[a] First characterized as 2,4-dinitrophenylhydrazone [3].
[b] Described in ref. [1] as an oil; according to ref. [5], m. p. 195 to 197.3°C. [c] KBr disc.

Although 1-adamantanecarbaldehydes lose CO on heating under nitrogen, they are converted into stable dimethyl acetals when dissolved in methanol containing hydrogen chloride.

3,5,7-Trimethyl-1-adamantanecarbaldehyde:

1-*tert*-Butyl-2-(3,5,7-trimethyl-1-adamantyl)aziridinone [4] (1.50 g) is heated to 100 °C under nitrogen for a period of 15 min with a mixture of water (75 ml) and methane-sulfonic acid (7.0 g). The aldehyde formed is steam-distilled into an ice-cooled receiver, filtered off, and dried over P_2O_5 in a vacuum; yield 1.03 g (96%); m.p. 74–75 °C.

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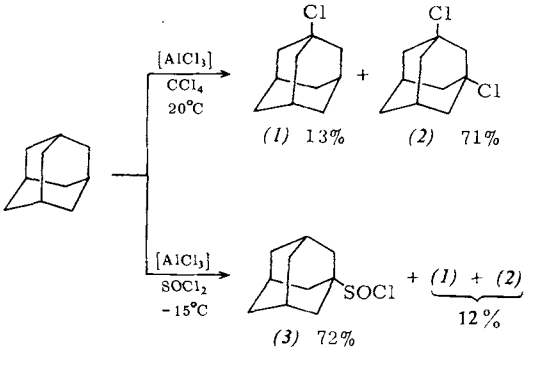
New Possibilities of Direct Substitution of Adamantane

By *H. Stetter, M. Krause*, and *W.-D. Last* [*]

An ionic mechanism has been proposed for halogenation of adamantane [1]; correspondingly, Friedel-Crafts catalysts catalyze this reaction. Adamantane can be halogenated also by halogenated hydrocarbons in the presence of such catalysts [2]. Thus treating adamantane with aluminum chloride in carbon tetrachloride at room temperature gives a mixture of 1-chloroadamantane *(1)* [1] and 1,3-dichloroadamantane *(2)* [3] in 84% yield.

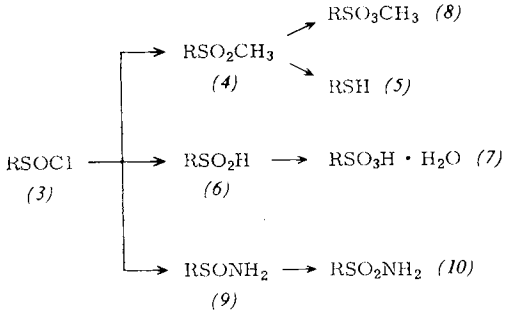


Using thionyl chloride instead of halogenated hydrocarbons also affords chlorinated adamantanes. However, surprisingly, at −15 °C 1-adamantanesulfinyl chloride *(3)* is formed in 72% yield. On increase in the temperature the proportion of *(3)* formed decreases, and 1,3,5-trichloroadamantane [3] is the main product at the boiling point. 1-Chloroadamantane *(1)* always gives a smaller proportion of the sulfinyl chloride *(3)* under comparable conditions. We assume that a chain reaction occurs in which the 1-adamantylium ion $R^{\oplus}$ participates.

$$R^{\oplus} + SOCl_2 \rightarrow RSOCl + Cl^{\oplus}$$
$$Cl^{\oplus} + RH \rightarrow R^{\oplus} + HCl$$

The chloride *(3)* can be converted into methyl 1-adamantanesulfinate *(4)* (colorless crystals, m.p. 44–46 °C) in 83% yield by means of boiling anhydrous methanol (6 h), and this ester is converted into 1-adamantanethiol *(5)* [4] in 90% yield by $LiAlH_4$ in anhydrous ether (17 h, 36 °C). Further, the acid

chloride *(3)* is converted by 5% sodium hydroxide at room temperature into 1-adamantanesulfinic acid *(6)* (yield 61%; m.p. 132–134 °C in a sealed tube), which is oxidized almost quantitatively by hydrogen peroxide to 1-adamantanesulfonic acid *(7)* [5]. The chloride *(3)* can also be used for preparation of esters and amides of 1-adamantanesulfonic acid that were not previously accessible. For this purpose *(3)* is treated with alcohols or amines, yielding 1-adamantanesulfinic acid derivatives, which can be oxidized in good yield by potassium permanganate in boiling acetone. For instance, oxidation of *(4)* gives methyl 1-adamantanesulfonate *(8)* (colorless crystals, m.p. 113–114 °C) in 85% yield. 1-Adamantanesulfonamide *(10)* (colorless needles, m.p. 197 to 198 °C) is obtained analogously in 95% yield, the 1-adamantanesulfinamide *(9)* (m.p. 141–142 °C) being prepared in 75% yield by treating *(3)* with concentrated aqueous ammonia for 2 h at 100 °C.



R = 1-adamantyl

1-Adamantanesulfinyl chloride:

$AlCl_3$ (40 g) and $SOCl_2$ (200 ml) are treated with adamantane (40.8 g) with exclusion of moisture at −15 °C over a period of 2 h; the mixture is then stirred for another 1 h at the same temperature. The clear solution is allowed to warm to room temperature, the excess of $SOCl_2$ is removed under vacuum, and the residue is taken up in CCl_4 (300 ml) and cautiously treated with water. The organic phase is separated off, dried over $CaCl_2$, and the solvent is removed. The oily residue is distilled at 130–136 °C/3–4 torr, the chloroadamantanes occurring in the first runnings. Yield 47 g (72%, m.p. 42 to 44 °C).

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Single Crystals of Phenylalanine-Specific Transfer Ribonucleic Acid

By *F. Cramer, F. v. d. Haar, W. Saenger,* and *E. Schlimme* [*]

On the basis of the base-pairing rules and the results of chemical and biochemical experiments, suggestions have been made concerning the secondary [1] and tertiary [2] structures of transfer ribonucleic acid (tRNA), the validity of which, however, can only be proved by X-ray structural analysis. Recently, microcrystalline spherulites of $tRNA^{F.\ Meth}_{E.\ coli}$ and $tRNA^{Ser}_{yeast}$ have been obtained [3]; however, single crystals are essential for an X-ray structural analysis. In this communication we wish to report on the crystallization of a tRNA from brewers' yeast.

$tRNS^{Phe}_{yeast}$ was isolated from a commercially available (Boehringer, Mannheim) soluble yeast-RNA. The working-up involved a partition step, as described by *Khym* [4] and subsequent chromatography on benzoylated DEAE-cellulose [5,6]. The $tRNA^{Phe}_{yeast}$ (82% aminoacylatable) thus obtained was first dialyzed against 10^{-2} M EDTA and then against 10^{-3} M Mg^{2+} and 10^{-2} M K^+.

The non-bonded metal ions were subsequently removed by dialysis against distilled water. Dioxane, from a solution of dioxane/water (35:100 v/v) was distilled *via* the vapor phase into a 1.5% solution of tRNA in dioxane/water (20:100 v/v) at room temperature in a dessicator. Crystals of rhombohedral form (Fig. 1) were formed along the vessel wall at the surface. The crystals were about 0.15 mm in length, about 0.07 mm wide, and were considered to be of a thickness of 0.01–0.02 mm.

In polarized light extinction was observed at each 90° interval, thus suggesting an orthorhombic system. On excitation by light of 325 nm wavelength the crystals exhibited strong blue fluorescence, as does the $tRNA^{Phe}_{yeast}$ itself. After redissolution of the crystals, the $tRNA^{Phe}_{yeast}$ was aminoacylatable to the same extent as the starting material.

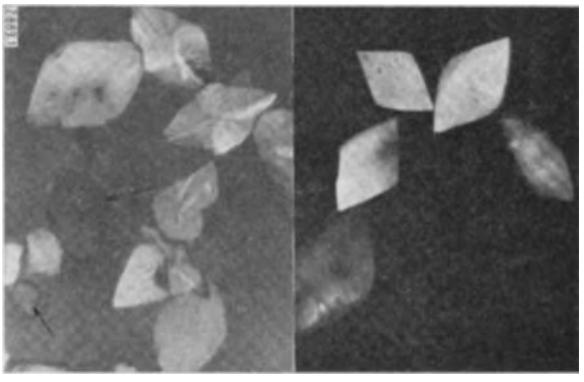

Fig. 1. Crystals of $tRNA^{Phe}_{yeast}$ yeast in polarized light.
The crystals were kept in the upper part of the Debye-Scherrer type crystallization tube (4mm diameter) for the photographic recording. The crystals situated at the places marked by arrows are oriented such that they do not rotate the plane of the polarized light. (Magnification approx 133×.) [**]

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[**] We thank *Dr. V. Neuhoff* for the photomicrographs.

Fourth International Catalysis Congress[*]

The Moscow Catalysis Congress from June 23 to 29, 1968 was the fourth in a series of four-yearly international congresses on heterogeneous catalysis. The kinetics and mechanisms of special reactions, new research methods, and the properties of little-known catalysts were dealt with in six plenary lectures and 86 discussion lectures, but the principal topic was the relation between the chemical composition, crystalline and electronic structure, and the activity and selectivity of catalysts.

1. The Active Center

Though many systems are now known in which the entire catalyst surface is uniformly active, the particularly high activity of special centers on the surface of others is partly due to geometric or topochemical factors. Uniformly active surfaces have been found on metal oxides in simple combustions and on metals in simple hydrogenations. This is so *e.g.* according to *P. C. Aben, J. C. Platteeuw,* and *B. Stouthamer* (Netherlands) (31) in the hydrogenation of benzene on Pt, Pd, and Ni catalysts supported on SiO_2, Al_2O_3, Al_2O_3–SiO_2, and MgO–SiO_2, and according to *M. Kraft* and *H. Spindler* (Leuna) (69) in the dehydrogenation of cyclohexane with Pt on Al_2O_3. However, these authors also found that the surface of the same catalyst is not uniformly active in the dehydrocyclization reaction of *n*-heptane. *R. van Hardeveld* and *F. Hartog* (Netherlands) (70) also point out that a catalyst can have several types of centers, which can act differently in different reactions; nickel on aerosil is reported to have a uniformly active surface in the deuteration of benzene to give cyclohexane, but not in the H/D exchange between benzene and D_2. Apart from crystallite corners, edges, surfaces, and lattice defects, active centers in metal catalysts include crystallite steps of atomic height (B_5 sites), as was described by *G. C. Bond* (England) (67).

The importance of the topochemical factor was discussed by *G. Parravano* (USA) (11) for the $^{12}C/^{14}C$ exchange in CO_2/CO mixtures and for the decomposition of H_2O_2 and N_2O on cobalt ferrites having the composition Co_{3-x} Fe_xO_4 (x = 1.9 ... 2.1). Whereas the stoichiometric ferrite (x = 2.0) gives a minimum rate for the first reaction, it is found to be the optimum catalyst for the other two reactions; this is attributed to the change in the distribution of ion vacancies with the Co/Fe ratio. *B. V. Erofeev, N. V. Nikiforova, I. I. Urbanovich,* and *L. D. Dmitrieva* (USSR) (47) reported that Cu and Mo on Al_2O_3, MgO, SiO_2, BeO, ZnO, and some spinels are particularly effective in the dehydrogenation of cyclohexane or the dehydrocyclization reaction of *n*-hexane if the metals are atomically dispersed and situated in cation sites of supports with octahedrally arranged anions. According to *K. Tarama, S. Yoshida,* and *Y. Doi* (Japan) (13), Cr^{5+} ions, which are characterized by an unusual crystal field, are active in the copolymerization of ethylene on chromic oxide.

A geometric factor is particularly important for systems in which multi-point adsorption of the reacting materials occurs. For example, according to *O. V. Krylov* and *E. A. Fokina* (USSR) (64), the activity of metal oxides in the reaction of acrolein with methanol increases with the lattice constant. *O. N. Bragin* and *A. L. Libermann* (USSR) (27) showed that the hydrogenolysis of alkylcyclopentanes and cyclohexane on Ru, Rh, Os, and Ir, which proceeds by two-point adsorption, yields a large number of products, whereas on Pt, owing to six-point adsorption, only the alkylcyclopentanes, and not the cyclohexane, react. According to *H. Noller, P. Andréu, E. Schmitz, S. Serain, O. Neufang,* and *J. Girón* (Hannover and Venezuela) (81), two-point adsorption is also responsible for the stereospecific action of many catalysts in the dehydrochlorination and dehydrobromination of 2,3-dichloro- or 2,3-dibromobutane to form 2-halogenobutene. For example, while KBO_2 and K_2CO_3 give a high *cis-trans* ratio in the end products, $CaCl_2$ and $Ca_3(PO_4)_2$ give a low ratio; this is explained by differences in the adsorption of substrate halogen on the catalyst cation and of substrate hydrogen on the catalyst anion.

In most insulating catalysts and in reactions with uncharged adsorbed intermediates, acid groups on the catalyst surface act as active centers. This was shown by *T. Yamaguchi* and *K. Tanaba* (Japan) (80) in the hydrolysis of dichloromethane on $NiSO_4$, ZnS, SiO_2, and Al_2O_3–SiO_2, by *Y. Noto, K. Fukuda, T. Onishi,* and *K. Tamaru* (Japan) (37) and *J. M. Criado, J. Dominguez, F. González, G. Munuera,* and *J. M. Trillo* (Spain) (38) in the dehydration of formic acid on Al_2O_3, SiO_2, Cr_2O_3, and TiO_2 and by *B. D. Flockhart, S. S. Uppal, I. R. Leith,* and *R. C. Pink* (Ireland) (79) in the H/D exchange between *n*-propane and D_2 on Al_2O_3. According to *H. Bremer* and *K. H. Steinberg* (Merseburg) (76), *T. V. Antipina, O. V. Bulgakov,* and *A. V. Uvarov* (USSR) (77), and *T. Nishizawa, H. Hattori, T. Uematsu,* and *T. Shiba* (Japan) (55), acid groups also bring about the dehydrogenation of isopropanol on MgO–SiO_2 and cracking processes, as well as the polymerization of ethylene and propylene and double bond migrations in 1-butene on partly fluorinated or hydrofluorinated Al_2O_3 catalysts. In all these cases the activity increases with the concentration of Lewis- or Brønsted centers.

2. The Catalyst-Substrate Bond

A knowledge of the nature and strength of the chemisorption bond is particularly useful for the establishment of reaction mechanisms and for the estimation of reaction rates. As was emphasized by *J. L. Garnett, R. J. Hodges,* and *W. A. Sollich-Baumgartner* (Australia) (1), there is an analogy between homogeneous and heterogeneous catalysis, as a result of which the interaction between individual substrate molecules and isolated catalyst structural units also approximately describes the chemisorption on the surface of solid catalysts. In the H/D exchange of monohalogenobenzenes, alkylbenzenes, and polycyclic aromatic compounds with D_2O on Pt, for example, the analogy is attributed to the π-complex mechanism occurring in homogeneous and heterogeneous catalysis. *V. S. Feldblium* (USSR) (15) referred to the analogy in the dimerization and isomerization of α-olefins on Ziegler catalysts. *P. Cossee, P. Ros,* and *J. H. Schachtschneider* (Netherlands) (14) presented results of quantum-chemical calculations that give a detailed picture of the energy relationships of the catalyst-substrate complex in the first-mentioned case. *A. Cimino, V. Indovina, F. Pepe,* and *M. Schiavello* (Italy) (12) studied the action of isolated catalyst structural units on the decomposition of N_2O on solids containing atomically dispersed Cr_2O_3 as catalyst doped with

[*] In this report, the lecture number is given (in parentheses) in each review, cf. Proc. IV. Internat. Congress Catalysis, Moscow 1968, in press.

various amounts of Li_2O in a catalytically inactive MgO matrix.

H. H. Dunken and *C. Opitz* (Jena) (2) calculated the chemisorption bond of CO, HCN, OH, and hydrocarbons on metals by the MO–LCAO method. The authors did not examine only the interaction between substrate molecules and isolated metal atoms, but also considered small metal domains. The results correspond qualitatively to a number of important experimental results.

Some authors also examined the interactions between substrates and the solid's electrons. However, an electronic factor can be expected only with semiconducting catalysts and possibly with metallic catalysts, but not with insulators, and also only in reactions with complete electron exchange between substrate and catalyst (ionosorption). It is therefore not surprising *e.g.* that *F. Bozon-Verduraz* and *S. J. Teichner* (France) (6) found no change in the rate of hydrogenation of ethylene on ZnO whose electron concentration was varied by doping, since the rate-determining step in this case is not associated with an electron exchange. On the other hand, *T. Freund, S. R. Morrison,* and *W. P. Gomes* (USA) (4) found that in the oxidation of formic acid to H_2O_2 and CO_2 on ZnO exposed to light, the concentration of electrons and holes on the catalyst surface determines the reaction rate.

According to *J. M. Criado, J. Dominguez, F. González, G. Munuera,* and *J. M. Trillo* (Spain) (38), the rate of dehydrogenation of formic acid on Cr_2O_3 and on TiO_2 also increases with the electron concentration, which is varied by doping. *C. Borgianni, F. Cramarossa, F. Paniccia,* and *E. Molinari* (Italy) (7) found that p-semiconductors (Cr_2O_3, NiO) are more active than n-semiconductors (ZnO, Fe_2O_3) in the combustion of H_2. *E. G. Schlosser* and *W. Herzog* (Frankfurt/Main) (9) presented a semiquantitative interpretation of the electronic factor on the basis of the combustion of CO and H_2 on doped NiO catalysts. Taking into account the space-charge layers on the catalyst surface, they were able to show that both the increase in reaction rate with increasing hole concentration and the decrease in reaction rate with decreasing hole concentration are much smaller than expected. *J. Scheve* and *I. W. Schulz* (Berlin) (84) believe that the electronic factor is due to energetic excitation of adsorbed molecules as a result of collision with electrons of the solid. The best catalyst is accordingly characterized by maximum energy transfer with agreement between the thermal energy of the electrons and special energy term differences of the molecule, as was shown for the decomposition of N_2O on CuO/Cr_2O_3 mixed catalysts.

N. P. Keyer (USSR) (8) mentioned that the "field effect", in which changes in the electron concentration on the surfaces of solids are brought about by an electric field, should be particularly useful for the investigation of electronic factors, since the catalyst mixture does not change in this case. Results have already been obtained for the decomposition of isopropanol on TiO_2. On the basis of investigations on the hydrogenation of benzene on Cu/Ni alloys, *D. A. Cadenhead, N. J. Wagner,* and *R. L. Thorp* (USA) (26) warn against overestimation of the electronic factor. Whereas the decrease in the reaction rate observed in this case with increasing Cu content had previously been attributed entirely to the filling of the electron vacancies in the 3d band, the authors now believe that the only important factor is the Ni concentration on the catalyst surface, which can differ from that in the interior as a result of a separation effect.

3. Catalytic Activity and Thermodynamic Quantities

As was shown by *W. M. H. Sachtler, G. J. Dorgelo, J. Fahrenfort,* and *R. J. H. Voorhoeve* (Netherlands) (34) for the oxidation of benzaldehyde to benzoic acid on MnO_2, V_2O_5, and V_2O_5/SnO_2 mixed catalysts, by *V. E. Ostrovsky* and *N. N. Dobrovolsky* (USSR) (46) for the combustion of H_2 on Cu, Ag, and Au, and by *A. Cimino, V. Indovina, F. Pepe,* and *M. Schiavello* (Italy) (12) for the decomposition of N_2O on Cr_2O_3/MgO mixed catalysts doped with Li_2O, the activity of the catalysts increases as the chemisorbed oxygen becomes more loosely bound. This is not surprising, since the reaction consists essentially of two steps, *i.e.* the combination of the organic substrate or of hydrogen with chemisorbed oxygen and the re-chemisorption of oxygen on the catalyst, the first step being rate-determining. Similar relationships were found by *G. K. Boreskov, V. V. Popovsky,* and *V. A. Sazonov* (USSR) (33) in the $^{16}O/^{18}O$ exchange in oxygen isotope mixtures on oxides of the first series of transition metals and in the combustion of H_2 and methane on cobaltites and chromites. *D. G. Klissurski* (Bulgaria) (36) confirmed these findings in the oxidation of methanol to formaldehyde on transition metal oxides and on Sb_2O_3, WO_3, and SnO_2, and *K. Kochloefl, M. Kraus,* and *V. Bažant* (ČSSR) (85) mentioned in this connection the dehydration of secondary alcohols on SiO_2, TiO_2, ZrO_2, and Al_2O_3.

In all these cases there is a linear relationship between the logarithm of the reaction rate or the activation energy and the bonding energy of the surface oxygen *i.e.* the free energy of surface oxygen release. This linear relationship, which is also known as the linear free energy relationship (LFER), may according to *V. A. Roiter, G. I. Golodetz,* and *Y. I. Pyatnitzky* (USSR) be regarded as a solid analog of the Hammett or Taft relationship found for homogeneous organic reactions. The authors also showed in the combustion of H_2 and propane on transition metal oxides that the activity cannot be increased indefinitely by the use of catalysts having very low oxygen-binding energies; on the contrary, there is an optimum catalyst for which the oxygen-binding energy is roughly equal to half of the enthalpy of the overall reaction. If the oxygen-binding energy is further decreased the catalyst activity decreases again, since the oxidation of the catalyst now becomes rate-determining instead of its reduction. A plot of the activity against the oxygen-binding energy gives a diagram having the volcano shape described by *Balandin.*

R. A. Gardner (USA) (83) also assessed the catalytic activity from the strength of the catalyst-substrate bond by evaluation of special bond strengths of the intermediates, which affect the IR vibration frequency, as shown for the combustion of H_2 and the combination of H_2 and CO.

4. Statistical Methods for the Discovery of Catalysts

The work of *I. I. Joffe, V. S. Fyodorov, B. Y. Gurevitch, M. A. Ustrayh, I. S. Fux,* and *K. M. Muhenberg* (USSR) (63) may be of special practical interest. The authors use the parameter calculation method known from statistics to find active and selective catalysts, *e.g.* for the oxidation of hydrocarbons, and illustrated the process in the case of the combustion of CO on metal oxides. It was found that out of 20 tabulated physicochemical quantities of the catalysts, only eight are significant for the catalytic activity. These quantities in order of increasing influence, are density, color index, melting point, vacancy volume, electronic structure factor, susceptibility, concentration of d-electron vacancies, and ionization potential of the metal. On the basis of these quantities, a number of metal oxides that have not yet been tested were chosen as promising catalysts for the combustion of CO.

D. A. Dowden, C. R. Schnell, and *G. T. Walker* (England) (62) showed how active and selective catalysts for complicated reactions can be found by the use of an arrangement scheme by means of which a large volume of experimental data can be taken into account, *e.g.* catalysts for the steam reforming of paraffins.

[VB 169 IE]

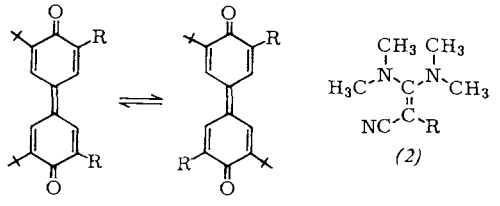
German version: Angew. Chem. *80*, 917 (1968)

Use of Nuclear Magnetic Resonance to Detect Intramolecular Rotations

By *H. Kessler* [*]

Isomerizations at CC and CN double bonds have been followed by NMR spectroscopy.

Rotation about CC double bonds can take place *e.g.* in quinonemethides [1] and in *o*-diphenoquinones [2] *via* a diradical transition tate. This is also the case with *p*-diphenoquinones of the type *(1)* ($\Delta G^{\ddagger}_{144\,°C}$ = 23.6 kcal/mole for R = C_6H_5) [3].



(2)

R = CH_3, C_6H_5 *(1)*

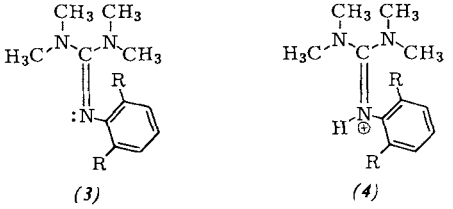
On the other hand, an ionic mechanism occurs in the rotation about the CC double bond in substances of the type *(2)* [4]. Hindrance of rotation about both CN single bonds is also observed (Table 1).

Table 1. Free enthalpies of activation $\Delta G_c^{\ddagger}$ for intramolecular rotations in 1,1-bisdimethylamino-2-cyanoethylenes *(2)*.

	R	$\Delta G_c^{\ddagger}$ (kcal/mole)			
		C=C	C–N [a]	C–N [b]	C-Aryl
(a)	CN	[c]	10.3	10.3	–
(b)	COC_6H_5	15.3	11.1	[d]	–
(c)	$COOC_2H_5$	13.5	13.9	[d]	–
(d)	C_6H_5	21.0	11.6	12.1	< 10
(e)	*p*-Cl–C_6H_4	20.1	11.8	12.3	< 10
(f)	*p*-Br–C_6H_4	20.2	12.0	12.4	< 10
(g)	*p*-CH_3CO–C_6H_4	17.8	12.9	13.2	10.3
(h)	*p*-NO_2–C_6H_4	16.2	13.9	13.8	10.9

[a] Methyl groups evaluated at low field. [b] Methyl groups evaluated at high field. [c] Not interpretable NMR spectroscopically for symmetry reasons. [d] Down to –60 °C the signal of the dimethylamino group at high field does not split.

The $\Delta G_c^{\ddagger}$ values of *(2d)–(2h)* can be correlated with the Hammett σ_p constants, two ρ values being obtained for the C–N rotations. It is therefore concluded that the *p*-substituent has different effects on the *cis* and on the *trans* positions. The *syn-anti* isomerization in phenylguanidines *(3)* proceeds



(3) *(4)*

Table 2. Free enthalpies of activation $\Delta G_c^{\ddagger}$ of the *syn-anti* isomerization of *(3)* and the rotation about C=N⊕ in *(4)*.

	R	Reaction	$\Delta G_c^{\ddagger}$ (kcal/mol)
(3a)	H	Inversion	12.1
(3b)	CH_3	Inversion	11.9
(4a)	H	Rotation	12.6
(4b)	CH_3	Rotation	14.4

via a linear transition state (inversion) [5]. This becomes particularly clear from a comparison of the steric effects of two *o*-substituents in the phenyl ring of *(3)* with the effect in the guanidinium salts *(4)*. In the salts, the free electron pair on the nitrogen is fixed by the protonation, so that only rotation is now possible. The steric effect hinders rotation, but facilitates inversion (Table 2).

Lecture at Isny/Allgäu on July 24, 1968 [VB 168 IE]
German version: Angew. Chem. *80*, 971 (1968)

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Chemisches Institut der Universität
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[1] *A. Rieker* and *H. Kessler*, Tetrahedron *24*, 5133 (1968).
[2] *H. Kessler* and *A. Rieker*, Tetrahedron Letters *1966*, 5257.
[3] *A. Rieker* and *H. Kessler*, unpublished.
[4] In this connection cf. also: *G. Isakson*, *J. Sandström*, and *I. Wennerbeck*, Tetrahedron Letters *1967*, 2233; *I. Shvo*, *E. C. Taylor*, and *J. Bartulin*, *ibid.* *1967*, 3259.
[5] *H. Kessler*, Tetrahedron Letters *1968*, 2041.

Phenyllithium Complexes of Transition Metals

By *Brigitte Sarry* [*]

Either of two types of organometallic compounds may be formed on treatment of anhydrous transition-metal halides with an ethereal solution of phenyllithium.

In the case of iron(III) chloride reduction to Fe(0) occurs, with binding of five molecules of phenyllithium in a complex compound $Fe(C_6H_5Li)_5$ analogous – though only formally so – to iron pentacarbonyl. This product is readily soluble in benzene; it is black and extremely sensitive to oxygen and moisture; it is quantitatively decomposed by water, the course of the hydrolysis depending on the conditions used:

$$Fe(C_6H_5Li)_5 + 7\,H_2O \xrightarrow{a} Fe(OH)_2 + 5\,LiOH + H_2 + 5\,C_6H_6$$
$$\text{(1)} \qquad \xrightarrow{b} Fe(OH)_2 + 5\,LiOH + 7/2\,H_2 + 5/2\,(C_6H_5)_2$$

(a: below –80 °C; b: at room temperature).

Oxidation of *(1)* by iodine causes attack only at the ligands and separation of elemental iron occurs according to the equation:

$$(1) + 5/2\,I_2 \rightarrow Fe + 5\,LiI + 5/2\,(C_6H_5)_2$$

However, in the reaction of *(1)* with mercury(II) chloride for determination of the phenyl groups, the iron is also oxidized:

$$(1) + 6\,HgCl_2 \rightarrow FeCl_2 + Hg + 5\,LiCl + 5\,C_6H_5HgCl$$

On the contrary, reduction of the pentabromides of niobium, tantalum, and tungsten by phenyllithium proceeds only to oxidation state +2 of the transition metal. The resulting diphenylmetals bind additional phenyllithium in neutral complexes of the general formula

$$[M(C_6H_5)_2(C_6H_5Li)_4]\cdot n(C_2H_5)_2O.$$

Their IR spectra show the phenyl groups to be bound to the central atom by σ-bonds.

From comparative investigations of various reactions carried out under the same conditions with phenyllithium complexes on the one hand and with pure, solid, solvate-free isolated phenyllithium on the other, conclusions can be drawn about the nature of the bonding of the phenyllithium to the transition-metal atom. Oxidation of phenyllithium in ethereal solution by dry oxygen leads to phenol and bi-

phenyl; reaction in the solid state gives also *o*-, *p*-, and, in small amounts, *m*-terphenyl. After treatment of phenyllithium with benzophenone and subsequent hydrolysis, triphenylmethanol is the only detectable product.

In contrast thereto, the corresponding reactions of phenyllithium complexes lead in all cases to triphenylene as an essential product along with biphenyl and in some cases some *o*-terphenyl. Thence it is concluded that in the complexes the lithium and the transition metal are bound in *ortho*-positions to the benzene nucleus.

Lecture at Berlin (Germany), on June 20, 1968 [VB 172 IE]
German version: Angew. Chem. *80*, 972 (1968)

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SELECTED ABSTRACTS

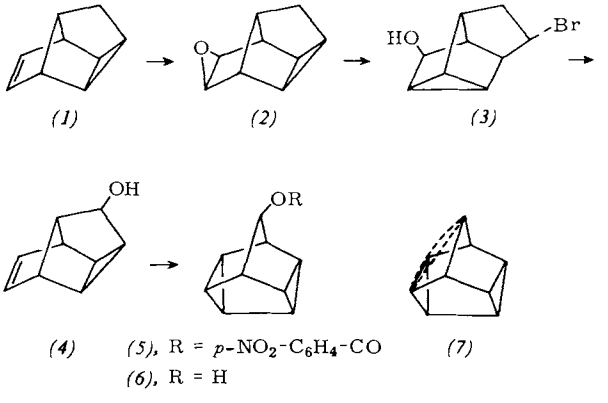
Some reactions of the species C_4 have been described by *R. F. Harris* and *P. S. Skell*. Small quantities of C_4 are present in carbon vapor, which can be produced with a high-vacuum arc. On co-condensation of the vapor with one of the substrates hexane, *cis*-2-pentene, *tert*-butyl chloride, methanol, ethanol, 1- and 2-propanol, and *tert*-butanol (all of which contain hydrogen) on a surface cooled with liquid nitrogen, a mixture of 1-butyne, 1,2- and 1,3-butadiene, and 1-buten-3-yne (vinylacetylene) is obtained from each substrate except pentene and *tert*-butanol, with which no vinylacetylene could be detected. The yields of C_4 hydrocarbons were around 1–2 %. Experiments with ^{14}C-enriched electrodes showed that the C atoms of the products all came from the electrode material. Carbon vapor from an electrically heated carbon filament, surprisingly, does not give the reactions described. / J. Amer. chem. Soc. *90*, 4172 (1968) / –Kr. [Rd 911 IE]

The decomposition of aromatic compounds in the focus of a laser beam has been studied by *R. H. Wiley* and *P. Veeravagu*. The impulse (3.5 ± 0.5 J or 10.0 ± 0.5 J) of a ruby laser was focused by means of a lens on an area of about 0.8 mm² of the sample, which had previously been frozen in liquid nitrogen. 1–3 mg of sample was decomposed. Gas-chromatographic analysis of the decomposition products showed mainly methane and acetylene, together with small quantities of ethane, ethylene, propane, propene, allene, diacetylene, and vinylacetylene, but no butadiene. Hydrogen and carbon monoxide were also detected in a few cases. Polycyclic hydrocarbons (naphthalene, anthracene, phenanthrene, biphenyl) gave a low methane/acetylene ratio (4:85), while monocyclic compounds (toluene, xylene, mesitylene) gave a higher ratio (40:10). Several observations indicate that plasma-like conditions prevail with excited carbon atoms in the reaction zone, *e.g.* the formation of large quantities of acetylene from entirely different substances and the substantial independence of the product distribution when the decomposition is carried out in the presence of nitrogen, oxygen, or hydrogen. / J. physic. Chemistry *72*, 2417 (1968) / –Hz. [Rd 922 IE]

Strongly exothermic heats of solution of palladium in molten tin have been found by *J. R. Guadagno* and *M. J. Pool*. This points to the formation of a compound even in the liquid state. The partial heat of solution of Pd does not change measurably in the concentration range from pure tin to the solubility limit (approx. 26 kcal/g-atom of Pd); it thus differs only slightly from the heats of solution of the known solid Pd–Sn compounds PdSn (–28.84 kcal/g-atom of Pd), $PdSn_2$ (–31.35), and $PdSn_4$ (–33.85). It can therefore be concluded that the bonding is similar and each Pd atom has four tin neighbors in the liquid state. It can be estimated from density measurements on a liquid alloy of 4 % of Pd in Sn that the Pd–Sn distance in a tetrahedral $PdSn_4$ molecule is practically the same as that found in the solid intermetallic compounds. / J. physic. Chemistry *72*, 2535 (1968) / –Hz. [Rd 924 IE]

The transfer of electronic excitation energy from a complex cation (hexaureachromium(III)) to an anion (hexacyanochromate(III)) has been observed by *H. Gausmann* and *H. L. Schläfer*. When the compound $[Cr(ur)_6][Cr(CN)_6]\cdot 3H_2O$ *(1)* [(ur)=$CO(NH_2)_2$] is irradiated with light of a wavelength that is absorbed practically only by the cation (*e.g.* 436 nm), the characteristic phosphorescence of the anion is emitted at 800–880 nm (at about 77 °K). The characteristic emission of the cation at 700–760 nm is not observed. Since the absorption spectrum of *(1)* is practically identical with the superimposed spectra of $K_3[Cr(CN)_6]$ and $[Cr(ur)_6]Cl_3$, there is only very weak coupling of the two chromium(III) centers in *(1)*. In this case it is possible to follow the path of the electronic excitation energy. It is absorbed by the cation (excited state, based on octahedral symmetry, $^4T_{1g}$) and passes nonradiatively into the lowest excited state of the system as a whole, *i.e.* the ^2E_g state of the anion, whence it is emitted as phosphorescence. / J. chem. Physics *48*, 4056 (1968) / –Hz. [Rd 923 IE]

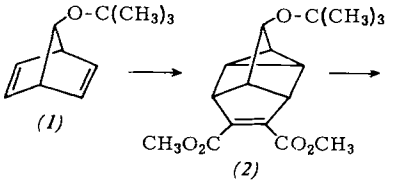
9-Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonyl *p*-nitrobenzoate *(5)* has been synthesized by *R. M. Coates* and *J. L. Kirkpatrick* from *(1)* ("deltacyclene") *via* the intermediates *(2)*–*(4)*. The solvolysis of *(5)*, m.p. 153.5–154.5 °C, in 65 % aqueous acetone at 125 °C exhibits first order kinetics with k = (7.0 ± 0.2)



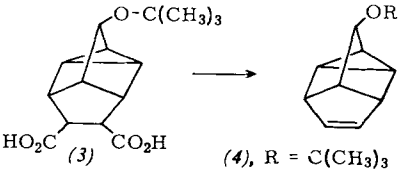
(1) *(2)* *(3)* *(4)* *(5)*, R = *p*-NO_2-C_6H_4-CO *(6)*, R = H *(7)*

×10^{-5}sec^{-1} (for comparison, k for 7-norbornadienyl *p*-nitrobenzoate is (5.8 ± 0.1) × 10^{-4} sec^{-1}). On solvolysis of [9-D]-*(5)* with *(6)*, one third of the D content is retained on C-9, and the remainder is found in two equivalent positions. The result suggests that the solvolysis proceeds *via* the cation *(7)*. / J. Amer. chem. Soc. *90*, 4162 (1968) / –Kr. [Rd 912 IE]

The tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-en-5-yl cation *(7)* does not rearrange, as was found by *P. von R. Schleyer* and *R. E. Leone*. The cation occurs in the solvolysis of the *p*-toluenesulfonate *(5)*, which was obtained from 7-norbornadienyl *tert*-butyl ether *(1)* *via* the intermediates *(2)*–*(4)*. On solvol-

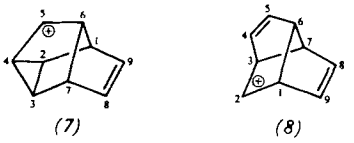


(1) (2)



(3)

(4), R = $C(CH_3)_3$
(5), R = p-CH_3-C_6H_4-SO_2
(6), R = $COCH_3$



(7) (8)

ysis of [5-D]-(5) in buffered CH_3COOH (10% excess of CH_3COONa, 110 °C, 3 hours), only the [5-D]-acetate (6) was found. This result is all the more surprising in that a rearrangement of (7) into (8) is readily conceivable, and the corresponding saturated [8-D]-cation rearranges readily into the [4-D]-cation [1]. / J. Amer. chem. Soc. *90*, 4164 (1968) / –Kr. [Rd 913 IE]

Di-*tert*-butyl thioketene (1) and di-*tert*-butyl thioketene *S*-oxide (2) have been prepared by *E. U. Elam, F. H. Rash, J. T. Dougherty, V. W. Goodlett,* and *K. C. Brannock.* (1) is formed from di-*tert*-butyl ketene or 2-*tert*-butyl-3,3-dimethylbutyryl chloride with P_2S_5 in pyridine. (1) was obtained in yields of 41 and 64% respectively as a purple-red oil boiling at 59 to 60 °C/6 torr.

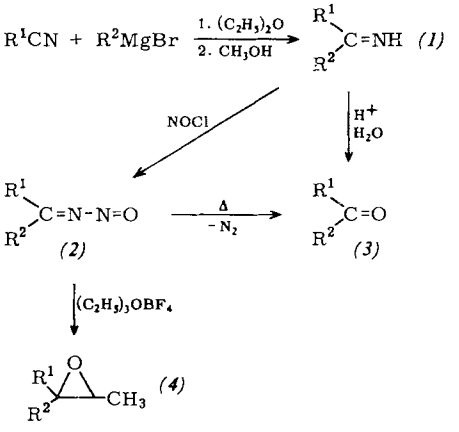
$$[(CH_3)_3C]_2C{=}C{=}O + P_2S_5 \rightarrow [(CH_3)_3C]_2C{=}C{=}S \quad (1)$$

$$[(CH_3)_3C]_2CH{-}COCl + P_2S_5 \rightarrow [(CH_3)_3C]_2C{=}C{=}S$$

Compound (1) does not dimerize or polymerize on storage at room temperature. It reacts with H_2O_2 or monoperphthalic acid to give the thioketene *S*-oxide $[(CH_3)_3C]_2C{=}C{=}S{=}O$ (2), which forms colorless crystals having m.p. 34–35 °C. Compound (2), which is the first known substance of this class, has roughly the same stability as aromatic thioketone *S*-oxides. / J. org. Chemistry *33*, 2738 (1968) / –Kr. [Rd 914 IE]

[1] *P. K. Freeman* and *D. M. Balls*, Tetrahedron Letters *1967*, 437.

N-Nitrosoketimines (*N*-nitrosoalkylidenamines) (2) have been synthesized by *C. J. Thoman* and *I. M. Hunsberger* from nitriles and Grignard compounds. The resulting alkylidenamines (1) were then treated with NOCl to form (2). Examples: $R^1 = R^2 = C_6H_5$, blue, m.p. 50–53 °C (25% yield); R^1 = *p*-tolyl, R^2 = *o*-tolyl, purple-red, m.p. 43 °C (68%); $R^1 = p$-Cl–C_6H_4, $R^2 = o$-Cl–C_6H_4, purple-red, m.p. 69 to 71 °C (76%).



Some nitrosoketimines could be kept only in solution. The compounds with bulky substituents or (in the case of the benzophenone derivatives) with electron-attracting substituents are more stable than the others. The decomposition to form the ketone (3) exhibits first order kinetics. Some nitrosoketimines can be converted by triethyloxonium tetrafluoroborate into oxiranes (4). / J. org. Chemistry *33*, 2852 (1968) / –Kr. [Rd 915 IE]

New adsorbents suitable for thin layer chromatography, according to *G. Hesse, H. Engelhardt,* and *R. Kaltwasser,* are polyacrylamide (1), *N*-acetylpolyacrylamide (2), and polyacrylonitrile (3). Suspensions of the finely divided materials in alcohol give strongly adhering layers on glass, on which water-soluble substances and substances containing hydrogen bonds can be separated. (1) and (2) have been found suitable for the separation of amino acids and dicarboxylic acids (both with alkaline eluents). Benzenesulfonic and toluenesulfonic acids were separated for the first time on (1) in *n*-butanol/water/methylamine (30% in H_2O) (80:6:15). (1), (2), and (3) can be successfully used for the separation of mono- and disaccharides. The separatory action is strongly dependent on the eluent. / Chromatographia *1*, 302 (1968)/ –Kr. [Rd 916 IE]

BOOK REVIEWS

Organometallic Compounds, Methods of Synthesis, Physical Constants and Chemical Reactions. Edited by *M. Dub.* Volume II: Compounds of Germanium, Tin and Lead. Including Biological Activity and Commercial Applications. Edited by *R. W. Weiss.* Springer Verlag, Berlin-Heidelberg-New York 1967. 2nd enlarged Edition. vii, 695 pp., 216 tables, DM 98.–.

The second edition of this meritorious book has been enlarged considerably and reviews the literature from 1937 to 1964 (1st Edition: 1937 to 1958). Thus, a complete survey of the literature concerning this important branch of organometallic chemistry, from the days of *E. Frankland,* is now available: Up to 1936 through the excellent critical treatment by *E. Krause* and *A. v. Grosse* (published by Borntträger, Berlin 1937, reprinted by Sändig, Wiesbaden 1965), from 1964 to 1966 through the annual literature surveys by *D. Seyferth* and *R. B. King* (published by Elsevier, Amsterdam), and finally through Part B of Organometallic Chemistry Reviews.

The book provides a complete collection of the literature. The seemingly overwhelming material has been presented in

a clear and readily usable form through skillful use of a system of tables and summaries. The tables, which are arranged according to groups of substances, provide information on methods of preparation and – as far as is known – yields; further, on physical properties and reactions, and in many cases also references to spectroscopic measurements, physiological effects, and proposed or actual technical applications of the individual substances. Critical evaluation of the subject matter is naturally left mainly to the reader himself – as is the case, for example, in "Beilstein". For instance, all the methods given for preparation of a substance in the literature of the period reported are listed alongside one another, complete with the often varying values for physical properties reported by the original authors. Since the work is not intended as a text book for students, but as a comprehensive, noncritical source of information for the specialist, this feature is certainly no drawback.

W. P. Neumann [NB 742 IE]

Strahlenchemie. Grundlagen – Technik – Anwendung. (Radiation Chemistry. Principles – Techniques – Applications.) Edited by *K. Kaindl* and *E. H. Graul*. Dr. Alfred Hüthig Verlag, Heidelberg 1967. 1st Edit., 645 pp., 236 figs., 95 tables, plastic cover, DM 92.–.

This book contains the contributions of seven well-known authors and is arranged in 12 chapters. Particular attention is given to the possibilities of quantitative treatment of radiation chemical processes, and the most important units and conversion factors are therefore discussed extensively. Another section shows the considerable progress that has been made in the last 20 years in the development of nuclear reactors, accelerators, and other sources of radiation. Only chemical dosimetry has been considered on the whole for the quantitative determination of the energy absorbed by a system that has been subjected to ionizing radiation.

The importance of radiation chemical reactions in water and aqueous solutions is clearly indicated. The main emphasis in the treatment of organic molecules has been placed on the polymerizations induced by irradiation – one of the main fields of radiation chemical research and of technical utilization – and it is satisfying to see that the kinetics of the processes have not been neglected. In addition, radiolysis of organic reactor coolants has been considered. A later edition should if possible indicate the possibilities of radiation chemical synthesis of low-molecular organic products.

Radiolytic effects in frozen solutions, important for the chemistry of radicals, are treated briefly. There are some excellent chapters on the radiation chemistry of solids and the influence of radiation on catalysts, outlining some possibilities of irradiated catalysts. The last chapter, written in English, deals with radiation-induced reactions in gases. All chapters have an index to the literature, arranged in alphabetical order of the authors' names.

In general, it can be said that the high standard of this work does credit to the authors and editors. The book fills a gap in an important field that has been somewhat neglected in Germany, and it can therefore be recommended to every scientist and engineer interested in radiation chemistry.

H. Drawe [NB 750 IE]

Comprehensive Biochemistry. Volume 26: "Extracellular and Supporting Structures". Parts A and B. Edited by *M. Florkin* and *E. H. Stotz*. Elsevier Publishing Company, Amsterdam-London-New York 1968. Part A: xvi, 295 pp., many figures and tables, Dfl. 47.50; Parts B: xii, 297 pp., many figures and tables, Dfl. 47.50.

Volume 26 of "Comprehensive Biochemistry"[1] deals with the molecular structure and the biochemical function of the extracellular supporting structures. Two of the planned total of three subvolumes have so far been published. The first one considers the substances and tissues occurring in microorganisms and plants, and the second one those found in vertebrates. In spite of their briefness, the various sections are treated thoroughly and are up to date. The complete volume will contain almost 1000 pages. This fact is an indication both of the great interest in this subject and of the biological importance of the cell-supporting structures, which are of paramount importance for contact with the environment.

Isolation, chemical and physical characterization, biosynthesis, and physiological function are treated in the individual sections, the literature up to 1966 having been reviewed in an excellent manner. The respective authors have either aimed at providing a complete bibliography or made an excellent choice of the most important publications. Once again it has proved possible to engage authors of international standing.

A terse and exhaustive account of the polysaccharides, polyuronides, and lignin of plant cells is given by *S. M. Siegel. J. M. Ghuysen, J. L. Strominger*, and *D. J. Tipper* display their mastery in a skillfully written review of the cell-wall structures of gram-positive bacteria; the same applies to *O. Lüderitz, K. Jann*, and *R. Wheat*, the authors of the extremely thorough, expert article on the antigenes of gram-negative cells. The interesting topic of shell formation by mussels, snails, and birds is summarized in a comparative manner by *K. M. Wilbur* and *K. Simkiss. A. J. Bailey* provides a detailed and scholarly guide through the broad and complex field of the collagens, and *B. J. Barrett* through that of cartilaginous tissue. In both these chapters the subject matter is viewed from the most varied aspects, starting from the structure and the biosynthesis and going through to aging, so that a unique review has resulted that is certainly worthy of the series. In their section on silk and other spun fibers, *F. Lucas* and *K. M. Rudall* consider all the available material from a number of different points of view. Fittingly, there follows a brief and yet exhaustive section on intracellular fibrous proteins and keratinization (*K. M. Rudall*).

Together, the two subvolumes cover the fields considered in a series of varied, competent, and contemporary articles. *M. Florkin* and *E. H. Stotz* have once again succeeded in bringing out a work that continues this remarkable monographic text- and hand-book in the expected manner. Without doubt these eminently successful volumes again deserve the highest praise; they maintain the excellent quality of their predecessors.

L. Jaenicke [NB 741a IE]

Comprehensive Biochemistry. Volume 27: Photobiology, Ionizing Radiations. Edited by *M. Florkin* and *E. H. Stotz*. Elsevier Publishing Company, Amsterdam-London-New York 1967. 1st Edit., xvi, 356 pp., 104 figures, 23 tables, Dfl. 55.00 / 114 s.

This extensive handbook of biochemistry now enters the realm of molecular biology proper with the fifth section, which is to embrace eight volumes. The present volume 27 shows that radiation effects of the most widely varying kinds are approachable from a biochemical angle and are no longer the exclusive domain of radiologists and physiologists, and analyzes the detection and biochemical and biophysical applications of radiations of all kinds. The first seven chapters, which deal with photobiology as such, are certainly of the standard expected of this competent work.

Photomechanical reactions of plants are described in the contributions on phototropism (*K. V. Thimann*), photosynthesis (*L. N. M. Duysens* and *J. Amesz*), phytochrome and photoperiodism (*S. B. Hendricks* and *H. W. Siegelman*); the treatment of photosynthesis is, however, rather categorical, this probably being attributable in part to a desire to avoid duplication of material in earlier volumes, and hardly considers the outstanding work of *H. T. Witt*. On the other hand, *J. K. Setlow* gives a detailed and most useful account of the

[1] Cf. Angew. Chem. *79*, 627 (1967); Angew. Chem. internat. Edit. *6*, 646 (1967).

effects of ultraviolet radiation on proteins, nucleic acids (pyrimidine dimerization), and nucleoproteins. However, a more rigorous treatment of fundamentals, and of photochemical and photophysical primary processes as an introduction, which will certainly be missed by the biologist, would have been welcomed. The other chapters are concerned with biochemistry of vision (*C. D. B. Bridges*), bioluminescence in various organisms (*F. H. Johnson*), and the photosensitization of biological material (*M. I. Simon*). One will miss references to the important work done on quinone-catalyzed photooxidation in this section.

In spite of the broad field covered in comparison with the preceding articles, the final chapter by *P. Alexander* and *J. T. Lett* on the effects of ionizing radiation on biological macromolecules gives more the impression of an appendix, and by no means provides an adequate treatment of the available knowledge in this field, particularly more recent work. However, one can always argue about how much space should be devoted to these things in such a comprehensive work: they could even occupy a separate volume. On the whole, this book gives a well balanced impression and summarizes a topic that has been the ground of various diverging disciplines for much too long. The literature has been covered up to 1966, thus making this volume a highly informative and desirable standard work. *L. Jaenicke* [NB 741b IE]

Atomic Absorption Spectroscopy and Analysis by Atomic Absorption Flame Photometry. By *J. Ramírez-Muñoz*. Elsevier Publishing Company, Amsterdam-London-New York 1968. 1st Edit., xii, 493 pp. 156 figs., 23 tables, bound, Dfl 80.—.

The analytical technique of atomic absorption spectroscopy, which has been described in four monographs in English within the space of two years, deserves special consideration. The present work is one of those four monographs and, from its size, the fullest. The author, who is a spectroscopist employed by a firm of instrument makers, divides his book into five chapters which are unfortunately very uneven in treatment. Within this framework, the fundamentally simple theory of atomic absorption spectroscopy is mentioned only briefly but quite sufficiently. Most of the space is taken up by description of instrumental details. It is in this section that the danger exists that, without a critical selection, which is lacking in this work, the details may obscure the whole. Light sources and burners are certainly important parts of the apparatus, but it is not justifiable to devote a fifth of the book to them. The very wide expositions on sensitivities and detection limits unfortunately do not clarify these important aspects of analysis. The experimental methods, so long as they deal with general details like solutions for calibration, preparation of diluted solutions, and calculation of the results, are treated very fully. On the other hand, there is no special reference to the possibility of interference and its avoidance.

The actual application of atomic absorption spectroscopy to the quantitative determination of particular elements in the presence of others is treated too briefly. The author often limits himself to a literature reference, without going further into the analytical directions or the relevant range of concentration. This last part, which deals specifically with applications (40 pp.), should be enlarged. The volume of literature quoted certainly justifies a wider treatment.

The bibliography, which comprises 950 citations up to about 1966, has been compiled very carefully. References that are difficult to obtain, and older reports of symposia, have been conscientiously recorded.

For those concerned with the apparatus side of atomic absorption spectroscopy, the present book with its ample collection of material will be an excellent aid. For the practising analyst confronted every day with new problems that he might wish to solve by this method, the present volume offers too little that would give information and advice in the laboratory.

In spite of these limitations, this is still the most comprehensive monograph on the subject. The rather one-sided emphasis or preference for some aspects does not diminish the great service that the author has rendered in making a considerable contribution to the further diffusion of a new analytical technique. *J. Ringhardtz* [NB 755 IE]

Clathrate Compounds. By *V. M. Bhatnagar*, S. Chand & Co., Delhi-New Delhi-Jullundur-Lucknow-Bombay-Calcutta-Madras 1968. 1st Edit., viii, 244 pp., many Figures and Tables, Rs. 20.00 / $ 8.00.

The book is a – not completely exhaustive – collection of the literature concerning inclusion compounds, in which the various types of inclusion compounds (urea, gas hydrates, deoxycholeic acids, cyclodextrins, *etc.*) are reviewed. Unfortunately, the extremely interesting theoretical aspects of bonding in these substances are not discussed at all. The division of the subject matter appears arbitrary. For instance, the term clathrate compound (title of the book) is not defined until page 60 of a total of 132 pages of text. The bonding, the essentially new feature of these compounds, is dismissed in a single sentence: ".....very weak forces like those of H bonds and of the van der Waals type, which are normally not capable of joining molecules together, may contribute to hold the two components in the inclusion compounds together". That is rather meager! The catalytic action of inclusion compounds, and inclusion compounds in biochemical reactions and in protein chemistry, are not considered at all. The claims made in the foreword – "This book is designed to gather together in one place the total literature pertaining to clathrate compounds", or "it will be the first book to give a detailed catalogue of all the work on clathrates from the origin to date" – appear to the reviewer to be at least unjustified. The book contains no subject and author index. Technical production is poor. The information that it contains can probably be obtained more readily and more cheaply from review articles written by competent researchers.

F. Cramer [NB 743 IE]

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Olefin Alkylation in Biosynthesis

BY J. W. CORNFORTH [*]

Stereochemical studies, made possible by asymmetric labeling with hydrogen isotopes, have led to the hypothesis that enzymic association of C_5 units in polyisoprenoid synthesis is not a concerted process but proceeds in two steps: a trans 1,2-addition to an olefin followed by a trans 1,2-elimination. It is shown that similar mechanisms can also explain the cyclization of squalene epoxide to tetracyclic and pentacyclic triterpenoids.

1. Introduction

It is difficult, though perhaps not impossible, to imagine a chemical basis for life in which connected carbon atoms play no part. Recent experiments on the genesis of "life-like" molecules from substances, such as methane and hydrogen cyanide, which might be presumed to have been abundant on the prebiotic earth, have indicated several natural non-biotic mechanisms for carbon-carbon bond formation. The hypothesis underlying such experiments is that the first life on earth was organized from existing, complex chemical species, and a necessary consequence is that mechanisms for biosynthesis evolved before the available supply was exhausted: mechanisms for carbon-carbon bond formation along with the rest.

In the biosynthetic reactions leading to proteins, carbohydrates, nucleic acids, and most lipids, condensations of the aldol and Claisen type predominate: an enolate anion, formed by removal of hydrogen (or sometimes carboxyl) α to a carbonyl group, attacks another carbonyl group. The *alkylation* of enols, so common in organic synthesis, is curiously rare in biosynthesis; it is probably true that the nucleophilic carbonyl group and the electrophilic enolate ion generate, by reaction with each other, most of the carbon-carbon bonds found in nature.

This is one reason why the enzymes of terpenoid biosynthesis [1] are of especial interest: although (*R*)-mevalonic acid *(1)*, the starting-point for all terpenoid biosynthesis, is formed by Claisen condensation of three molecules of acetyl-coenzyme A, neither the aldol nor the Claisen condensation is of any further importance in forming the many additional carbon-carbon bonds of the terpenoids. Instead, we have a type of reaction which can be classed as olefin alkylation.

The "leaving" group for the first alkylation [*(4)* + *(3)* → *(7)*] is pyrophosphate ion. Mevalonic acid 5-pyrophosphate *(2)* is produced by two successive phosphoryl transfers to (*R*)-mevalonic acid *(1)* from adenosine triphosphate. The double bond required for further alkylation is then generated by a concerted elimination reaction, also requiring adenosine triphosphate; the four products obtained in this step are inorganic phosphate, adenosine diphosphate, carbon dioxide, and isopentenyl pyrophosphate *(3)*. The leaving group is then activated further by a prototropic exchange which produces dimethylallyl pyrophosphate *(4)*. The increased electrophilic activity of the allylic pyrophosphate *(4)*, compared with the homoallylic isomer *(3)*, is seen for example in its sensitivity to aqueous acid. Below pH 5 pyrophosphate ion is rapidly eliminated and water is alkylated; the major product is the alcohol *(5)* presumably formed from the intermediate allylic carbonium ion *(6)*. The sequence of enzymic reactions leading from *(1)* to *(4)* was first indicated in soluble preparations from yeast, and then from liver. The four enzymes responsible have been extensively purified. Each of them can be separated from the other three, though none of them has yet been obtained completely pure.

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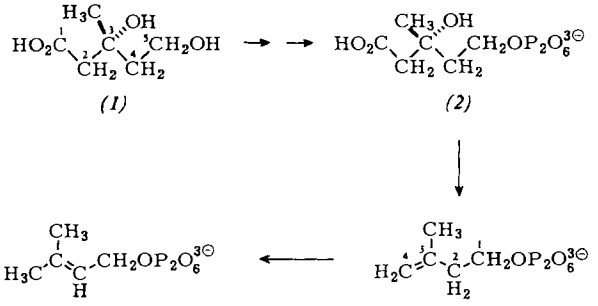
Kent (England)

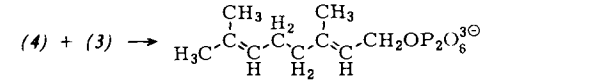
[1] An excellent review of terpenoid biosynthesis is that by *R. B. Clayton*, Quart. Rev. (chem. Soc. London) *19*, 168, 201 (1965).

Combination of the intermediates *(3)* and *(4)* is the first and characteristic step in the biosynthesis of polyisoprenoids. In this enzymic reaction, a molecule of dimethylallyl pyrophosphate and one of isopentenyl pyrophosphate react, with loss of a proton and of a pyrophosphate anion, to form a new allylic pyrophosphate. In the soluble liver and yeast preparations which so far have been the most extensively studied, the product is geranyl pyrophosphate *(7)*. This allylic pyrophosphate can then react, apparently on the same enzyme, with another molecule of isopentenyl pyrophosphate *(3)* to produce the C_{15}-derivative farnesyl pyrophosphate *(8)*. Further chain-lengthening to geranylgeranyl pyrophosphate does not proceed at a measurable rate with this enzyme system.

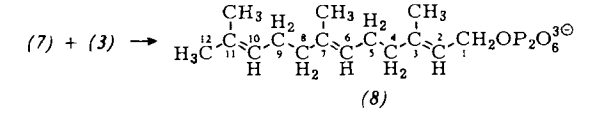


(1) *(2)* *(3)* *(4)*

(5) *(6)*



(7)



(8)

The formation of *(7)* can be interpreted as proceeding by way of two carbonium-ion intermediates, thus:

$$\underset{(4)}{\text{R–OPP}} \rightarrow \text{R}^+ + \text{OPP}^- \qquad (1)$$

$$\text{R}^+ + \underset{(3)}{\text{H}_2\text{C=C(CH}_3\text{)CH}_2\text{CH}_2\text{OPP}} \rightarrow \text{RCH}_2\overset{+}{\text{C}}\text{(CH}_3\text{)CH}_2\text{CH}_2\text{OPP} \qquad (2)$$

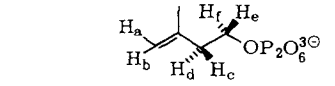
$$\text{RCH}_2\overset{+}{\text{C}}\text{(CH}_3\text{)CH}_2\text{CH}_2\text{OPP} \rightarrow \underset{(7)}{\text{RCH}_2\text{C(CH}_3\text{)=CHCH}_2\text{OPP}} + \text{H}^+ \qquad (3)$$

R = dimethylallyl

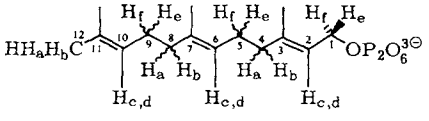
The isomerization of isopentenyl pyrophosphate to dimethylallyl pyrophosphate can also be interpreted by equations (2) and (3), if H^+ replaces R^+.

2. Stereochemical Considerations

To know what actually happens on the enzyme, more information is needed than is ascertainable by present methods. Some insight can be gained, however, by studying the stereochemistry of the condensation; and during the last few years *Popják* and the writer, at Milstead Laboratory, have examined the stereochemistry of polyisoprenoid, and particularly of squalene, biosynthesis.



(9)



(10)

It is not immediately apparent that anything can be learned in this way, for the optical asymmetry present in mevalonic acid and its phosphates is lost in isopentenyl and dimethylallyl pyrophosphate. However, in isopentenyl pyrophosphate there are three methylene groups. Assuming that it is possible to distinguish between the two hydrogen atoms on each methylene group, as in *(9)*, and also to trace the fate of each hydrogen atom in the products of the enzymic reactions leading, for example, to farnesyl pyrophosphate *(10)*, then several conclusions are possible concerning what happens on the enzymes. Let us suppose that in the stereochemical sequence rules [2] H_a ranks higher than H_b and H_e ranks higher than H_f. Then

1) If the hydrogen-ion eliminations in the isomerization and in the two coupling reactions are stereospecific, positions 2, 6, and 10 in *(10)* will be occupied by H_c or H_d according to the stereochemistry. Nonstereospecific reactions would lead to mixtures of H_c and H_d at these positions.

2) Displacement of pyrophosphate anion is necessary to form the carbon-to-carbon bonds between positions 4–5 and 8–9. If these displacements occur with inversion of configuration the absolute configurations at C-5 and C-9 in *(10)* will be (*S*); if retention of configuration is the rule, then these absolute configurations will be (*R*). If these displacements are nonstereospecific (as carbonium-ion reactions often are), then (*RS*)-configurations will result at C-5 and C-9.

3) The two sides (above and below the plane of the projection *(9)*) of the double bond in isopentenyl pyrophosphate are not equivalent in an asymmetric environment. If the new carbon-carbon bond is formed from *below* the plane of this double bond, the absolute configurations at C-4 and C-8 in *(10)* will be (*S*); if it

[2] *R. S. Cahn, C. K. Ingold,* and *V. Prelog,* Experientia *12,* 81 (1956).

is formed from *above* that plane, the absolute configurations will be (*R*).

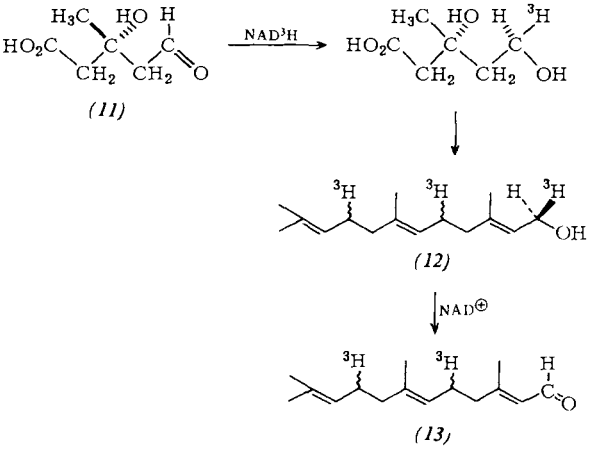
These three potentially stereospecific processes define the stereochemical behavior of all atoms in the substrates which undergo permanent changes in bonding as a result of the coupling reaction. The isomerization is not so completely defined, for the transformation of isopentenyl pyrophosphate *(3)* into dimethylallyl pyrophosphate *(4)* requires the uptake of a hydrogen ion. The terminal methylene group in *(3)* can take up the ion from above or below the plane of the double bond, but the resulting pattern of substitution (*e.g.* the C-12 methyl group in *(10)*) has no chirality unless the entering hydrogen can be distinguished from *both* H_a and H_b. Since the only practical way of distinguishing between the two hydrogen atoms in each pair (H_{ab}, H_{cd}, H_{ef}) is to label one of them with a hydrogen isotope, it follows that chirality could only be introduced at the methyl group of dimethylallyl pyrophosphate by using all three known isotopes of hydrogen, and the stereochemistry of hydrogen addition could only be solved by devising some method of recognizing this chirality.

2.1. Preparation of Isotopically Labeled Compounds

Experimentally, it is not convenient to label isopentenyl pyrophosphate *(3)* directly with hydrogen isotopes. Its precursor mevalonic acid *(1)* is a better subject, for the principal reason that mevalonic acid already possesses a center of asymmetry at C-3, and that only (*R*)-mevalonic acid is accepted as a substrate by the enzyme that phosphorylates it [3, 4].

If a hydrogen atom at the 4- or 5-position of mevalonic acid is replaced stereospecifically by deuterium or tritium, this configuration will persist at the corresponding position (2 and 1 respectively) of the isopentenyl pyrophosphate *(3)* formed from it enzymically, since at neither of these carbon atoms is the bonding altered. If, however, mevalonic acid is labeled stereospecifically at the 2-position with isotopic hydrogen, the relationship between the chirality at C-2 of mevalonate with the geometry at C-4 in isopentenyl pyrophosphate depends on the mechanism of the elimination reaction *(2)* → *(3)*. Therefore, it is necessary to determine the orientation of isotopic hydrogen at C-4 of the isopentenyl pyrophosphate – it is not sufficient, as it is with C-1 and C-2, to know the configuration of the parent mevalonate.

Introduction of labeled hydrogen (both deuterium and tritium) into C-5 of mevalonic acid was done enzymically [5]. An enzyme extractable from pig liver, mevaldate reductase [6], transfers hydrogen from NAD^2H and NAD^3H to mevaldic acid *(11)*, the aldehyde of mevalonic acid; NADH itself can easily be labeled with deuterium or tritium. Curiously, the enzyme reduced both the (*R*)- and the (*S*)-forms of mevaldic acid, but this lack of stereospecificity is at a site remote from the center of action. Tritium-labeled mevalonic acid, prepared in this way, was converted by a preparation of soluble enzymes from rat liver into



(11) *(12)* *(13)*

farnesyl pyrophosphate, which could be hydrolyzed enzymically (alkaline phosphatase) to farnesol. When this labeled farnesol *(12)* was oxidized to farnesal *(13)* by NAD^+ in the presence of liver alcohol dehydrogenase, one-third of the tritium, *i.e.* all the tritium at C-1, was lost.

The orientation of the hydrogen removed from primary alcohols by liver alcohol dehydrogenase has been determined, for ethanol, as pro-*R*. If the stereospecificity of alcohol dehydrogenase is the same for farnesol as for ethanol (as would be expected) then the isotopic hydrogen introduced into mevalonate by mevaldate reductase should also produce this (5*R*) configuration. Confirmation of this was obtained [7] from experiments with geraniol as a model for farnesol, showing that liver alcohol dehydrogenase removes the pro-*R* hydrogen from geraniol; later, a direct correlation of the specificities for geraniol and for ethanol was obtained [*] by chemical degradation of geraniol, labeled with tritium by reduction of geranial with NAD^3H in the presence of liver alcohol dehydrogenase, to ethanol containing the same primary hydroxyl group. On liver (or yeast) alcohol dehydrogenase this ethanol lost all its tritium.

For the stereospecific labeling at the 4- and 2-positions of mevalonic acid, chemical methods were used. The acid *(14)* and the lactone *(15)* [8] were first converted into the geometrically isomeric benzhydrylamides *(16)* and *(17)*. Each of these was epoxidized and subsequently reduced by $LiBD_4$ to give, after alkaline hydrolysis, two specimens of mevalonic acid labeled with deuterium at position 4.

Because of the method of synthesis, these two specimens of mevalonic acid must be composed of different molecular species. The epoxidation of a double bond by a peroxy-acid is a *cis* addition of oxygen; the

[3] *F. Lynen* and *M. Grassl*, Hoppe-Seylers Z. physiol. Chem. *313*, 291 (1958).

[4] *R. H. Cornforth*, *J. W. Cornforth*, and *G. Popják*, Tetrahedron *18*, 1351 (1962).

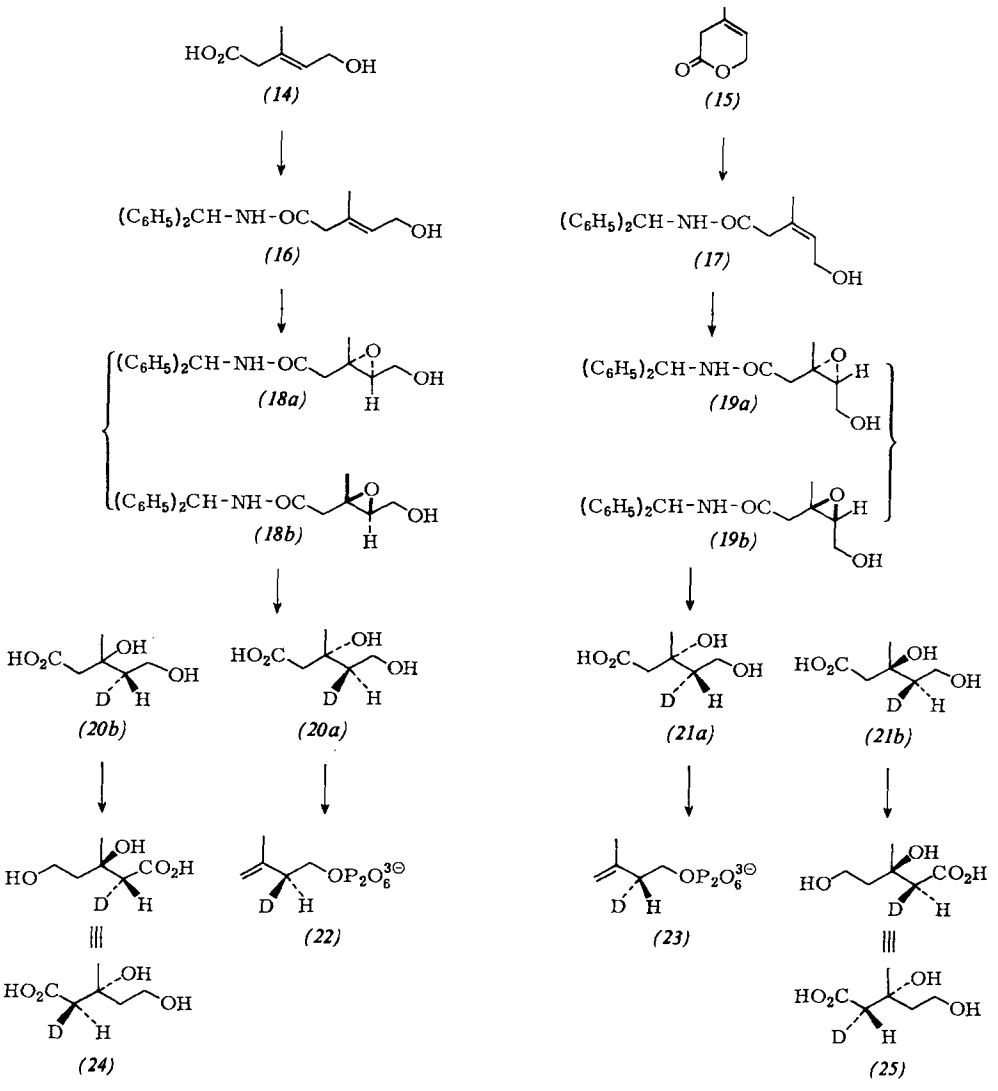
[5] *C. Donninger* and *G. Popják*, Proc. Roy. Soc. (London), Ser. B *163*, 465 (1966).

[6] *M. J. Schlesinger* and *M. J. Coon*, J. biol. Chemistry *236*, 2421 (1961).

[7] *C. Donninger* and *G. Ryback*, Biochem. J. *91*, 10 P (1964).

[*] *D. Arigoni* and *H. Weber*, private communication.

[8] *J. W. Cornforth*, *R. H. Cornforth*, *G. Popják*, and *I. Y. Gore*, Biochem. J. *69*, 146 (1958).



reduction of an epoxide by a metal hydride produces inversion of configuration at the center from which oxygen is displaced. Hence the benzhydrylamide *(16)* produced a racemic mixture of the enantiomeric epoxides *(18a)* and *(18b)*, and from this by reduction and hydrolysis the racemic mixture *(20a)* and *(20b)* was formed; whereas the benzhydrylamide *(17)* gave the racemic mixture *(21a)* and *(21b)* *via* the racemic epoxide *(19a)* and *(19b)*. Further, because mevalonic kinase phosphorylates only the (3*R*) form of mevalonic acid, the racemic mixtures *(20)* and *(21)* will behave enzymically as though each consisted exclusively of one molecular species *(20a)* and *(21a)*. When the sequence of enzymic reactions has proceeded as far as isopentenyl pyrophosphate, the asymmetry at C-3 of mevalonate is destroyed but the asymmetric labeling persists, *(20a)* giving exclusively the (2*S*) enantiomer *(22)* and *(21a)* giving exclusively the (2*R*) *(23)* [9].

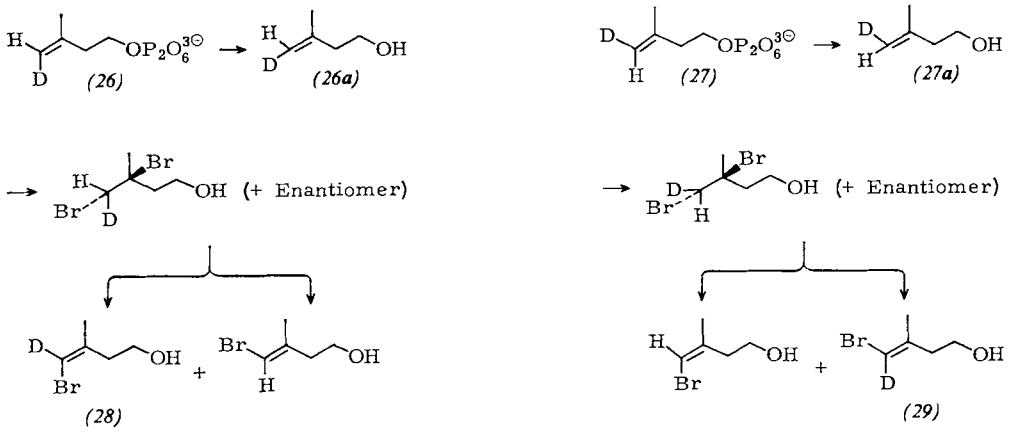
The diastereoisomeric mevalonic acids *(20)* and *(21)* were also useful in solving the problem of labeling position 2 of mevalonic acid asymmetrically with hydrogen. For if the carboxyl and hydroxymethyl functions of mevalonic acid are exchanged, the product is still mevalonic acid with the difference that C-4 has become C-2 and a (3*R*)-mevalonic acid has become (3*S*). Thus the enzymically inactive component *(20b)* gives enzymically active (3*R*) [2*R*-2-D_1]mevalonic acid *(24)*. Similar treatment of the racemic mixture *(21)* will give *(25)* as the sole enzymically active molecular species.

The necessary inversion of functional groups was effected [10] in three stages: 1) C-4 labeled mevalonates were esterified by reaction of methyl iodide with the silver salts; 2) the methyl mevalonates were oxidized by zinc permanganate in cold acetone to methyl hydrogen 3-hydroxy-3-methylglutarates; 3) reduction of the lithium salts with lithium borohydride then gave C-2 labeled mevalonates.

The enzymic reaction leading from mevalonic acid 5-pyrophosphate *(2)* to isopentenyl pyrophosphate *(3)* is a *trans* elimination of water and carbon dioxide; so that (3*R*)[2*R*-2-D_1]mevalonate generates *cis*-[4-D_1]-isopentenyl pyrophosphate *(26)* and (3*R*)[2*S*-2-D_1]mevalonate generates *trans*-[4-D_1]-isopentenyl pyrophosphate *(27)*. However, this was not known *a priori* and the geometry of the two deuterioisopentenyl pyrophosphates, prepared enzymically from the two mevalonates, had to be ascertained [10]. This was done by enzymic hydrolysis of both compounds to isopentenol *(26a)* and *(27a)*, addition of

[9] *J. W. Cornforth, R. H. Cornforth, C. Donninger*, and *G. Popják*, Proc. Roy. Soc. (London), Ser. B *163*, 492 (1966).

[10] *J. W. Cornforth, R. H. Cornforth, G. Popják*, and *L. S. Yengoyan*, J. biol. Chemistry *241*, 3970 (1966).



bromine to the double bond, and elimination of hydrogen bromide by methanolic alkali in conditions favoring the E_2 reaction. The main product is a mixture of *trans*-4-bromoisopentenol with a lesser amount of the *cis* isomer. Since addition of bromine to a double bond is specifically *trans*, and the E_2 elimination preferentially *trans*, it follows that the deuterium in *cis*-[4-D_1]isopentenol will be retained in the *cis*-4-bromoisopentenol and absent from the *trans*; the converse will be true with *trans*-[4-D_1]isopentenol. By separation of the geometrically isomeric bromoisopentenols (by gas-liquid chromatography) and examination of each isomer for deuterium (by mass spectrometry) it could be shown that deuterium was retained in the *cis*-4-bromoisopentenol *(28)* derived, ultimately, from (3*R*)[2*R*-2-D_1]mevalonate *(24)* and in the *trans*-4-bromoisopentenol *(29)* derived from (3*R*)[2*S*-2-D_1]-mevalonate *(25)*. From the other two bromoisopentenols, the deuterium was largely lost. Thus the enzymic formation of isopentenyl pyrophosphate was established as a *trans* elimination, and the stereochemical correlation between C-2 labeled mevalonates and C-4 labeled isopentenyl pyrophosphates was secured.

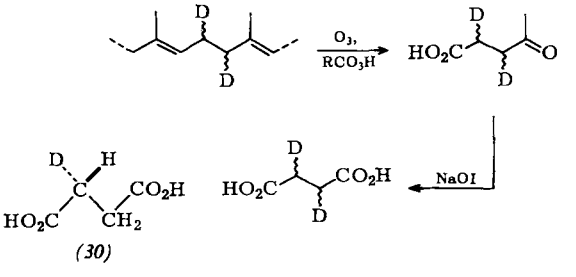
3. Formation of Polyisoprenoids from C_5 Units

The stereochemistry of the alkylation step leading to polyisoprenoids was defined by tracing the fate of deuterium or tritium when these stereospecifically labeled mevalonates were used as substrates for cell-free preparations of rat liver. Sometimes farnesyl pyrophosphate was chosen as the end-product for examination; sometimes squalene.

When farnesyl pyrophosphate is synthesized enzymically from three mevalonate units, three hydrogen atoms are eliminated which were originally attached to C-4 of mevalonate. By mass-spectrometric examination of farnesol derived by enzymic hydrolysis from biosynthetic farnesyl pyrophosphate, it was found[9] that when (3*R*)[4*R*-4-D_1]mevalonate was the precursor all three deuterium atoms were retained, but that deuterium-free farnesol was formed when (3*R*)[4*S*-4-D_1]mevalonate was the precursor. This result was confirmed by examination of squalene, biosynthesized from either C-4 deuteriated or C-4 tritiated mevalonates; the 4*R* hydrogen was completely retained and all of the 4*S* hydrogen was lost.

When mevalonates labeled at the 2- and 5-positions were the precursors, only deuterium could be used as the labeling isotope. Farnesol or squalene derived enzymically from these labeled precursors was degraded by ozonolysis; the levulinic acid, which contained the potentially asymmetric centers to be investigated, was oxidized by alkaline sodium hypoiodite to give as main products iodoform and succinic acid.

We had already prepared, for a different purpose, asymmetrically labeled monodeuteriosuccinic acid of known absolute configuration, and had shown that its optical activity in the ultraviolet is easily measurable by a modern spectropolarimeter; $[\alpha]_{250nm}$ is $\pm 18°$, so that a few milligrams of pure succinic acid suffice to determine the direction and extent of asymmetric labeling. Squalene made biosynthetically



(30)

from (3*R*)[5*R*-5-D_1]mevalonate[9], and farnesol from (3*R*)[2*R*-2-D_1]mevalonate[10], were degraded to succinic acid as described. Each of these succinic acids was found to consist essentially of [2*R*-2-D_1]succinic acid *(30)*, the optical activity corresponding to the deuterium content of the specimen, as measured by mass spectrometry of the methyl ester or the anhydride[11].

Assume that a molecule of isopentenyl pyrophosphate, which is to be alkylated by a molecule of a primary allylic pyrophosphate *(31)*, is oriented on the enzyme as represented in *(32)*. The two carbon atoms of the double bond and the four atoms attached to them are in the plane of the paper. Then our results show (i) that complete inversion of configuration occurs at the primary allylic carbon atom (C-2) when pyrophosphate ion is displaced and the new C–C bond is formed, (ii) that this bond is formed from *below* the plane of the double bond in isopentenyl pyrophosphate, and (iii) that the 2*R* hydrogen atom of the isopentenyl pyrophosphate is eliminated to form the new, *trans*, double bond.

[11] *G. Popják* and *J. W. Cornforth*, Biochem. J. *101*, 553 (1966).

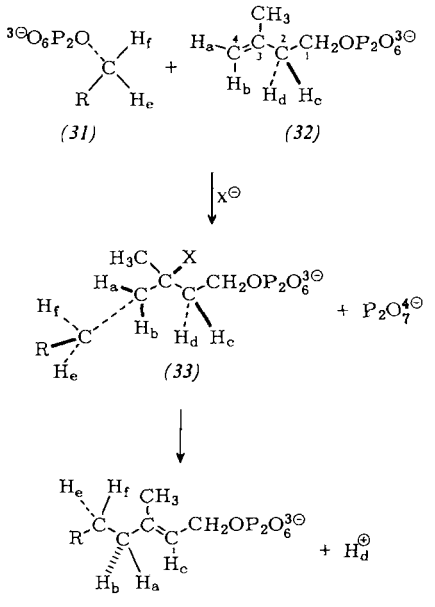
From (i) the conclusion may be drawn that the condensation cannot be initiated by formation of a carbonium ion from the allylic pyrophosphate, unless (a) the carbonium ion is spatially so restricted that rotation about the $C-CH_2^+$ bond is forbidden, or (b) formation of the new C–C bond occurs so rapidly that there is insufficient time for this rotation to occur. The simplest explanation, requiring no such special hypotheses, is that the new bond is formed as the old bond breaks: a reaction of S_N2 type where inversion of configuration is normal. This makes the C–C bond formation a concerted process.

Is it possible to extend this concept and to represent the whole condensation as a concerted process, a continuous drift of electrons starting from the $C-H_R$ bond at position 2 of isopentenyl pyrophosphate and ending with the departure of pyrophosphate anion? If the stereochemical requirements (ii) and (iii) are considered together, this appears unlikely. For since a *trans* double bond is being generated in the product, the entire isopentenyl pyrophosphate molecule must be oriented for a concerted reaction, as shown, with H_R on C-2 (that is, H_d) *below* the plane of the paper. Since the electrons of the $C-H_R$ bond are being used to form the new double bond, C-3 of the isopentenyl pyrophosphate is having electrons supplied to it (to form the new double bond) and withdrawn from it (to form the C–C bond) on the same side; effectively, a nucleophilic substitution with retention of configuration. This seems energetically far less favorable than a concerted mechanism in which electrons are supplied to, and withdrawn from, opposite sides of C-3; but in the present case this would lead either to a *cis* double bond or to the elimination of H_S: both contrary to experiment. Indeed, when rubber (which has *cis* double bonds) is biosynthesized, it is H_S which is eliminated, not H_R.

These considerations have led us to postulate a two-stage mechanism for the alkylation, in which an electron-donating group X is supposed to participate. This group might be part of the enzyme, but it might also be an enzyme-bound water molecule, or an oxygen atom of the pyrophosphate group in isopentenyl pyrophosphate (a hypothesis put forward by *Johnson* [12] before the stereochemical details were known). The first stage is then a *trans*-addition of the allylic group and of X to the double bond of isopentenyl pyrophosphate; the second stage is a *trans*-elimination of X and H_R from the intermediate *(33)* to generate the new double bond. If the group X has a formal negative charge, its binding to C-3 might not at any stage be more than that in a close ion-pair.

This mechanism accounts satisfactorily for the observed stereochemistry of the condensation. However, an alternative explanation is possible.

In a classical publication [13], *Eschenmoser*, *Ruzicka*, *Jeger*, and *Arigoni* showed how the cyclization of *trans*-squalene could lead without formation of stable intermediates to all known types of tetracyclic and pentacyclic triterpenes by a series of stereospecific steps. The cyclizations, which are all classifiable as olefin alkylations, were assumed to proceed by "antiparallel"

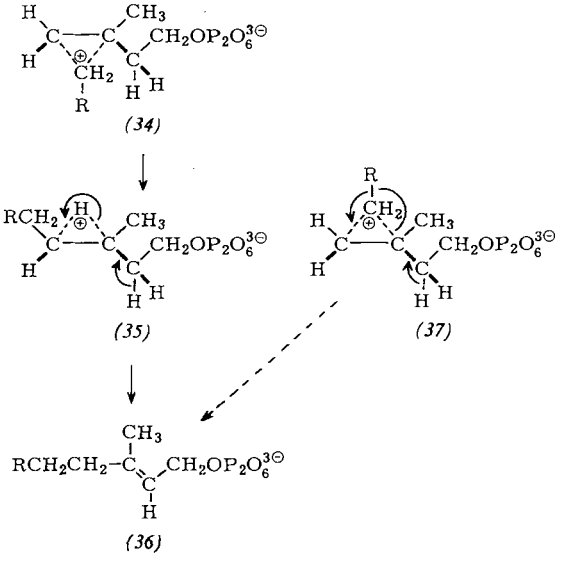


(31) *(32)* *(33)*

(*trans*) addition, to a double bond, of a carbonium ion and an electron-donating group (in this case the π-electrons of another double bond).

In order to derive the observed stereochemical arrangement of the final product, it was always necessary to postulate one or more stereospecific intramolecular rearrangements of non-classical carbonium ions. Sometimes, two successive stereospecific rearrangements of the same complex cation had to be assumed.

An analogous mechanism could account for the observed stereochemistry of alkylation of isopentenyl pyrophosphate. According to this, the first step would be the formation of the non-classical carbonium ion *(34)*; next, this would undergo intramolecular rearrangement to another non-classical ion *(35)* which would allow the now stereochemically favorable elimination of H_R to give the final product *(36)*. It is a logical disadvantage of this mechanism that formation of the non-classical carbonium ion from the other side of the double



(34) *(35)* *(37)* *(36)*

[12] *W. S. Johnson* and *R. A. Bell*, Tetrahedron Letters No. 12, 27 (1960).

[13] *A. Eschenmoser*, *L. Ruzicka*, *O. Jeger*, and *D. Arigoni*, Helv. chim. Acta *38*, 1890 (1955).

bond [as in *(37)*] would allow a mechanistically similar formation of *(36)* without need to postulate an intermediate rearrangement.

One might regard the mechanism *(34)* → *(36)* as equivalent to the "X-group" mechanism in which the electrons of a C–H bond act as an X-group. The essential difference between this and the true "X-group" mechanism is spatial. The rearrangement of *(34)* to *(35)* entails a large displacement in space of the allylic group R (or alternatively of the whole isopentenyl pyrophosphate molecule). This displacement must occur (since no stable intermediate is permitted) at the "active center" of the condensing enzyme, to which the substrates have already been bound for the initial stage of the reaction. When it is also considered that the group R may be large, and that its allylic double bond leaves it little flexibility at the point of attachment to isopentenyl pyrophosphate, the difficulty of postulating intramolecular rearrangement of *(34)* to *(35)* becomes obvious. This can be regarded as an argument in favor of the X-group mechanism, since the capacity of the active center of an enzyme to bind a specific substrate in a specific conformation favorable for reaction should be greater, the less movement of the substrate is necessary during the enzymic reaction. In the X-group mechanism, little movement is necessary.

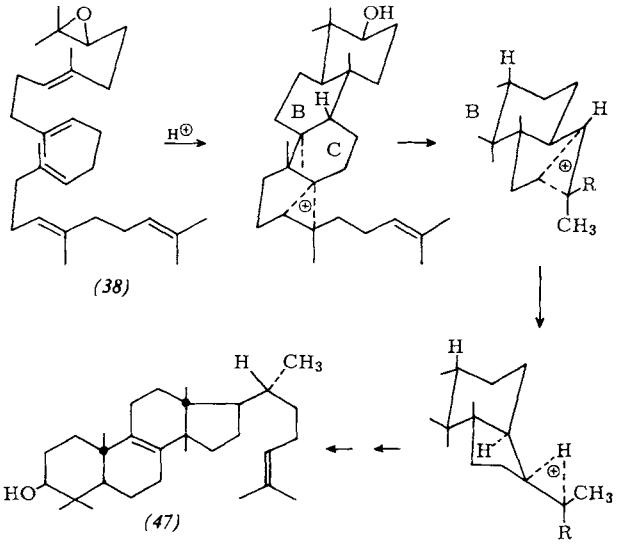
4. Cyclization of Squalene to Triterpenoids

It is instructive to examine whether the cyclization of squalene to tetracyclic and pentacyclic triterpenoids can be formulated with X-group mechanisms in place of the original concept of stereospecific intramolecular rearrangements of carbonium ions. This turns out to be possible. The first three postulates of the original scheme can be retained: that all-*trans* squalene is the starting-point, that the substrate molecules assume definite conformations for cyclization, and that (to paraphrase the third requirement) whenever electrons are abstracted from a particular substituted carbon atom, the deficiency is always made good from the opposite side. The fourth postulate, that no stable intermediate intervenes between squalene and the final product, is not acceptable for X-group mechanisms. It was an intellectual *tour de force* to show that every known type of triterpenoid could arise from squalene by a "non-stop" mechanism, but this view tends to require incompatible properties in the enzyme mediating a cyclization.

Since no stable intermediate is permitted, the whole process has to be supposed to occur on a single enzyme. This enzyme must be able, at the same active center, to impose a particular conformation on the squalene chain and to allow considerable freedom of movement in this chain during rearrangements; and to control stereochemically the intramolecular, space-demanding rearrangements of carbonium ions without participating in them chemically. If, in contrast, the formation of stable intermediates allows the participation of more than one enzyme, the spatial requirements of the active center of each enzyme can be less exacting.

4.1. Formation of Lanosterol from Squalene

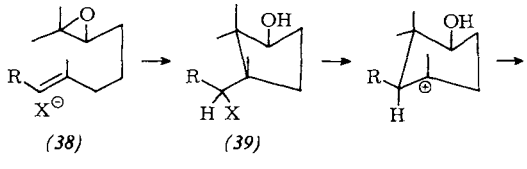
More evidence is available on the transformation of squalene to lanosterol than on the formation of any other cyclic terpenoid. This is not a "non-stop" reaction, since squalene epoxide *(38)* appears to be an obligatory intermediate[14,15]. The classical theme of cyclization, adapted to start from this intermediate, is as shown (Scheme 1).



Scheme 1.

We can consider whether it is useful to postulate an X-group mechanism for any of these ring-closures and subsequent rearrangements.

Formation of rings A and B: Here, the only way to involve an external X-group is to postulate that the initial cyclization leads to a cyclopentane ring [*(39)*, exemplified for ring A], and that rearrangement to a cyclohexyl cation precedes further cyclization.



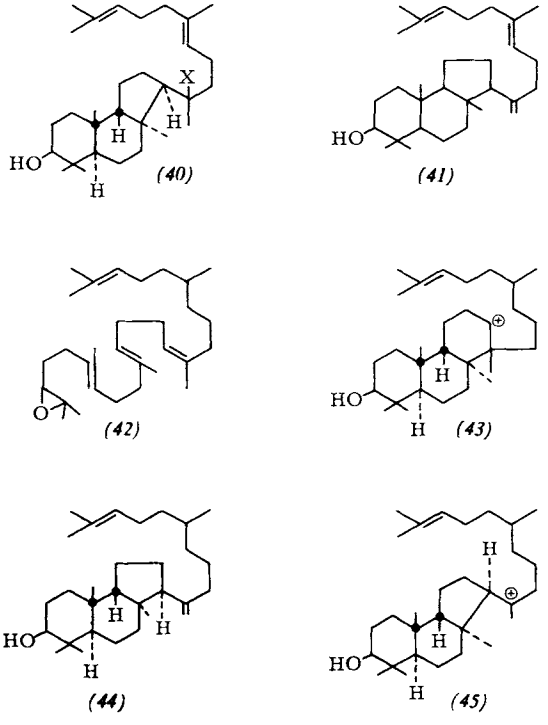
There seems to be no reason here why rings A and B should not be closed by a concerted process, the π-electrons of the next double bond playing the part of the X-group, and six-membered rings being formed *ab initio*. Moreover, the alternative is an anti-Markovnikov addition to the double bond and is to this extent energetically unfavorable.

Formation of ring C: Here, the intervention of an X-group does lead to a cyclization in the Markovnikov sense, and formation of the intermediate *(40)* would be favored (though rearrangement to the energetically

[14] *E. J. Corey, W. E. Russey,* and *P. R. O. de Montellano,* J. Amer. chem. Soc. *88*, 4750 (1966).

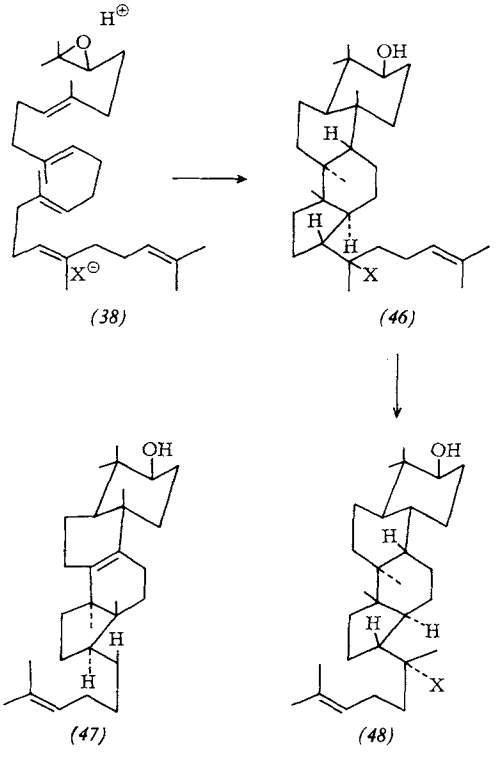
[15] *E. E. van Tamelen, J. D. Willett, R. B. Clayton,* and *K. E. Lord,* J. Amer. chem. Soc. *88*, 4752 (1966).

less favored cyclohexyl cation must still occur if the cyclization is to continue). Secondly, it has been shown that non-enzymic cyclization of squalene epoxide does yield as one product a cyclopentanonaphthalene derivative *(41)*, an indication that this mode of cyclization is energetically favorable[16]. Thirdly, the dihydrosqualene epoxide *(42)* can be partially cyclized enzymically to a mixture of products, a major component of which is probably the alcohol *(44)*[17]. This of course could arise from an intermediate *(40)* by simple elimination of HX.



To decide whether this finding is evidence for an intermediate such as *(40)*, we can consider the "normal" mechanism in which a six-membered ring C is formed directly by a continuation of the concerted cyclization that closed rings A and B. This is an anti-Markovnikov cyclization, but on the enzyme it might be promoted by the stereochemical arrangement of the substrate, the π-electrons of the next double bond being available to complete the addition only in the anti-Markovnikov sense. If these π-electrons were not available, as in the dihydrosqualene epoxide *(42)*, the cyclization may be assumed to proceed as far as the cation *(43)*. In the absence of an electron-donating group this cation would tend to rearrange to the more stable tertiary form *(45)*. Loss of a proton from this cation could well give mainly the olefin *(44)* since one hydrogen atom in the methyl group would always be in a stereochemically favorable position for the final elimination. One has to conclude that the intervention of an X-group in the closure of ring C, though quite possible, is not on the evidence a necessary postulate.

Formation of ring D: This is a cyclization in the Markovnikov sense and there is no incentive to suppose that a six-membered ring might be formed first and rearrange to a five-membered ring. (The objections to the sequential rearrangement of non-classical cations, as formulated in Scheme 1, have already been stated.) The alternative is to postulate an electron-donating group X which completes the addition. Accepting that the other cyclizations are concerted, one then has a multiplex electron-shift leading from squalene epoxide *(38)* to the intermediate *(46)*. Little displacement of any part of the molecule is required for this cyclization.



The rearrangement to lanosterol can proceed directly from the final non-classical cation pictured in Scheme 1, the four migrating groups and the proton finally to be eliminated already having the favorable *trans-anti-trans-anti-trans* arrangement. For analogous rearrangement of the intermediate *(46)*, a preliminary rotation through 120° is necessary about the single bond joining the side-chain to ring D. This gives the conformation *(48)* and might occur in one of three ways:

1) Rotation is confined to the side-chain and occurs without detachment of *(46)* from the enzyme on which it was formed. For example, the group X might be a water molecule attached to an anionic site on the enzyme; after cyclization, the resulting –OH group might swing to a cationic site where its separation, initiating rearrangement, would be facilitated. This mechanism would also require 120° movement of the rest of the side-chain; but this is a part of the molecule which does not need to be bound at the active center,

[16] *E. E. van Tamelen, J. D. Willett, M. Schwartz*, and *R. Nadeau*, J. Amer. chem. Soc. *88*, 5937 (1966).

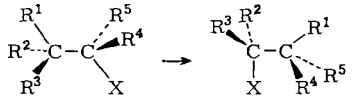
[17] *E. E. van Tamelen, K. B. Sharpless, R. Hanzlik, R. B. Clayton, A. L. Burlingame*, and *P. C. Wszolek*, J. Amer. chem. Soc. *89*, 7151 (1967).

and which apparently can be altered considerably without affecting the cyclization [18].

2) The intermediate *(46)* is held to the enzyme by its X-group while the rest of the molecule is reoriented, perhaps on an adjacent part of the enzyme, in the configuration favorable to rearrangement.

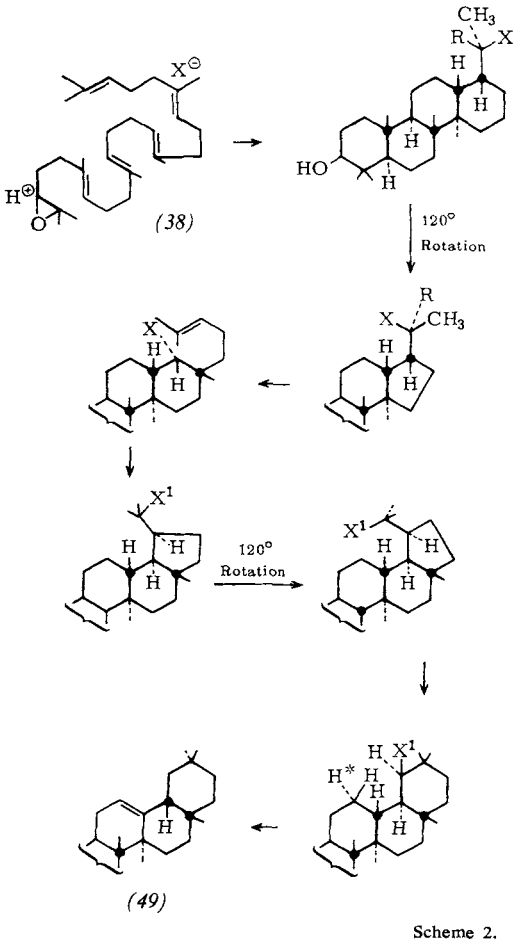
3) The intermediate *(46)* dissociates from the enzyme, and rearrangement with elimination of HX and formation of lanosterol *(47)* occurs on another enzyme.

Also in the case of pentacyclic triterpenoids, X-group mechanisms can explain the various structures and stereochemistry, but it is necessary to assume the intervention of two X-groups, and also to postulate double 1,2-rearrangements of the following type:



Several examples of this type of rearrangement are already known; *e.g.*, the rearrangement of 5α,6β-dibromocholestane and of other vicinally disubstituted steroids [19].

The postulated course of the cyclization can be represented as in Scheme 2 for the case of β-amyrin *(49)*. It is clear that this process could not be considered to take place on a single enzyme, and therefore that if the X-group mechanism is correct at least one intermediate between squalene epoxide and β-amyrin remains to be found. Recognition of such an intermediate will also decide between the "non-stop" mechanism originally proposed and the stepwise mechanism to which our stereochemical studies have led us.



Scheme 2.

[18] *E. E. van Tamelen, K. B. Sharpless, J. D. Willett, R. B. Clayton*, and *A. L. Burlingame*, J. Amer. chem. Soc. *89*, 3920 (1967).

[19] *D. H. R. Barton* and *J. F. King*, J. chem. Soc. (London) *1958*, 4398.

Received: May 20, 1968 [A 669 IE]
German version: Angew. Chem. *80*, 977 (1968)

Crystallization during Polymerization

BY B. WUNDERLICH[*]

This paper is dedicated to Prof. Dr. E. Husemann on the occasion of her sixtieth birthday

Simultaneous as well as successive polymerization and crystallization is possible. While crystallization after polymerization usually produces folded chain lamellar crystals, crystallization during polymerization frequently produces fibrillar extended chain crystals.

1. Introduction

A polymerization reaction leading from small monomer molecules to linear high polymer may be one of two types, a step reaction or a chain reaction[1]. A step reaction proceeds by random coupling of bifunctional molecules and results in a gradual increase in molecular weight (see Fig. 1).

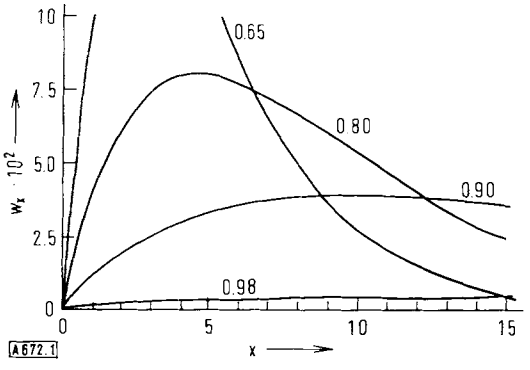


Fig. 1. Molecular weight distribution during a step reaction polymerization. The weight fraction of molecules made of x monomers is w_x. The degree of completion of the reaction is expressed by p which varies between 0 and 1. Mathematically the curves are represented by

$w_x = x(1-p)^2p^{x-1}$

An example of a step polymerization is the reaction of ε-aminocaproic acid in the molten state. The possible reactions are represented by equation 1:

$$\underset{x\text{-mer}}{H[-NH-(CH_2)_5-CO-]_xOH} + \underset{y\text{-mer}}{H[-NH-(CH_2)_5-CO-]_yOH} \rightarrow \underset{(x+y)\text{-mer}}{H[-NH(CH_2)_5-CO-]_{x+y}OH} + H_2O \quad (1)$$

x and y may take any value above zero. The step reaction is thus a typical chemical reaction. A chance of rearrangement of chemical bonds exists on any collision of the reactive partners. Any two steps contributing to the growth of the same polymer molecule are completely uncorrelated. If the reaction is speeded up by a catalyst, each step is catalyzed separately.

A completely different picture is presented by a chain reaction polymerization, which leads to linear high polymers in a one dimensionally cooperative process. The growth of a polymer molecule can proceed only after initiation and then goes sequentially by addition of one monomer unit at a time. Thus, the reaction mixture contains only monomer molecules and growing or completed polymer molecules. The termination or transfer of a growing chain determines, in conjunction with the initiation, the molecular weight. Ethylene polymerization (equation 2) is an example of free

$$\text{Initiation:} \quad R-O-O-R \rightarrow 2\,R-O\cdot \quad (2)$$

$$\text{Propagation:} \quad R-O\cdot + CH_2=CH_2 \rightarrow R-O-CH_2-CH_2\cdot$$

$$\underset{x\text{-mer}}{R-O(-CH_2-)_{2x-1}CH_2\cdot} + \underset{\text{monomer}}{CH_2=CH_2} \rightarrow \underset{(x+1)\text{-mer}}{R-O(-CH_2-)_{2x-1}CH_2\cdot}$$

radical chain reaction polymerization. Any two steps contributing to the growth of the same polymer molecule are correlated.

Crystallization is in principle a three dimensional cooperative polymerization reaction since any molecule of more than about 1000 atoms may be called a high polymer and any crystal grain can be looked upon as a single molecule. Most crystals studied in the past have bonds of similar strength in all three directions of space. All ionic crystals and all metals fall into this category. Crystals of linear high polymers represent an exception, for the bonds along the backbone chain are stronger by a factor of 10 to 100 than the secondary bonds which hold the crystal together. This difference in bond strength allows the separation of the formation of a linear high polymer crystal into two stages, the polymerization which sets the primary bonds, and the crystallization which sets the secondary bonds. Many of the presently common linear high polymers have a ceiling temperature[2] sufficiently above the melting temperature that on melting or dissolution no primary bonds are broken.

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Troy, N.Y., 12181 (USA)

[1] *R. W. Lenz*: Organic Chemistry of Synthetic High Polymers. Interscience Publ., New York 1967.

[2] The ceiling temperature is the temperature of the polymer-monomer equilibrium above which only monomer is thermodynamically stable.

2. Categories of Crystallization and Polymerization

Crystallization before the polymerization is completed may be separated into two categories, simultaneous and successive polymerization. Simultaneous polymerization and crystallization is indicated if the covalent primary and secondary bonds are set at the same time. The description of such a process is identical with ordinary crystallization. A pattern unit, which may be part or all of the monomer molecule, is positioned on a lattice point on the surface of an already existing crystal. Covalent bonds are rearranged simultaneously with the formation of secondary bonds which may be hydrogen bonds, dipole bonds, or van der Waals bonds. The heat of transition contains contributions from the heat of polymerization as well as the heat of crystallization. Analogously the entropy is the sum of two such contributions.

Successive polymerization and crystallization is the process in which crystallization occurs somewhat later than polymerization, but before the polymer molecule is completely formed. In this case a detailed kinetic description of the steps leading to crystal formation is necessary to understand the influence of the polymerization step on solidification and *vice versa*. If the reaction is carried out close to the ceiling temperature, it may be possible to distinguish between simultaneous and successive polymerization on the basis of purely thermodynamic arguments. For example, crystalline polyoxymethylene has a lower formaldehyde vapor pressure than the less ordered polymer. Determination of the formaldehyde vapor pressure or the formaldehyde equilibrium concentration during polymerization should thus indicate the physical state of the chain ends. The closer the polymerization and crystallization sites approach, the lower should be the vapor pressure or concentration of formaldehyde [3].

Simultaneous polymerization and crystallization was suggested as early as 1927 by *Staudinger et al.* [4] for the formation of fibrous polyoxymethylene from gaseous formaldehyde. Also an early suggestion was that in an ideal single crystal of polyoxymethylene grown during polymerization of formaldehyde the molecular length should be identical with the crystal dimension in the chain direction [5].

In addition to the two categories of crystallization during polymerization, one must consider the case in which the polymer molecule is completed in the dissolved or molten state before crystallization commences. The usual crystallization from polymer melt and solution [6,7] are such processes. There is no question about the separate treatment of polymerization and crystallization step. Complications, however, are still possible if the polymer molecules are produced in a special non-equilibrium conformation and crystallization begins before equilibration. Interesting examples are the formation of metastable, supersaturated solutions of polyamide in chloroform at low temperature using the Schotten-Baumann reaction [8], and of silk fibroin in the silk glands of *Bombyx mori* [9]. Both metastable solutions can be broken up by spontaneous precipitation. In such cases of very large supercooling, a crystallization different from crystallization close to the melting or dissolution temperature is to be expected.

The three categories of crystallization of flexible linear high polymers are summarized in Fig. 2.

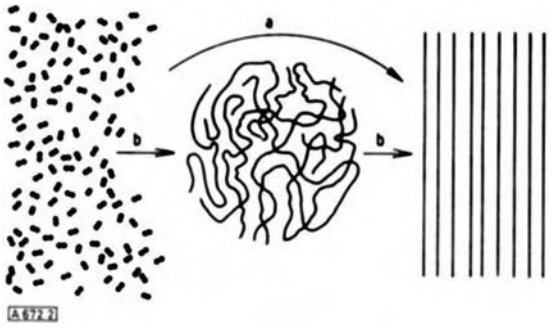

Fig. 2. Schematic representation of the paths from the monomer to the crystalline polymer. a) Simultaneous and successive polymerization and crystallization; b) separate polymerization and crystallization.

3. Nucleation and Crystal Growth

Crystal growth can occur only after a nucleus of sufficient size has been produced. The free energy of formation of a homogeneous nucleus of quadratic cross section normal to the chain direction can be estimated from equation 3:

$$\Delta\Phi = a^2 l \Delta f + 4al\sigma_s + 2a^2\sigma_e \qquad (3)$$

The free energy of crystallization is represented by Δf, a negative quantity below the melting or dissolution temperature. σ_s and σ_e are the positive surface free energies of the side and end surfaces respectively. The molecular chain length in the nucleus is l while a is the width of the quadratic cross section. Figure 3 shows the change of $\Delta\Phi$ as a function of a and l for a certain set of parameters. The path of minimum free energy to a large crystal goes across the saddle point at which the size of the critical nucleus is reached, further growth is accompanied by a decrease in free energy and is thus a spontaneous process.

From the different examples of crystallization during polymerization five nucleation paths have been derived [10]: A. an intermolecular nucleation followed by simultaneous polymerization and crystallization near

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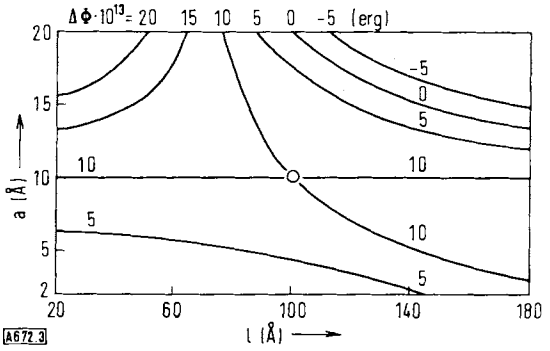


Fig. 3. Graph of the free energy of formation, $\Delta\Phi$, of a polymer crystal nucleus of length l in the chain direction and width a, assuming a quadratic cross section. Parameters assumed are σ_e = 50 erg/cm², σ_s = 5 erg/cm², $\Delta f = -2 \cdot 10^8$ erg/cm³ which corresponds to polyethylene 25—30 °C supercooled.

the ceiling temperature; B. an intermolecular nucleation followed by simultaneous polymerization and crystallization far from the ceiling temperature; C. an intermolecular nucleation followed by successive polymerization and crystallization; D. an intramolecular nucleation followed by simultaneous polymerization and crystallization; and finally E. an intramolecular nucleation followed by successive polymerization and crystallization. Only path A is close enough to the polymerization equilibrium that one may assume reversibility of the polymerization step. In all other cases the depolymerization reaction is probably small. If the ceiling temperature of a simultaneous polymerization and crystallization is below or at the melting or dissolution temperature of the crystal, and if the reaction is carried out close to the ceiling temperature, one can expect a perfect coupling of polymerization and crystallization (case A). Nucleation is then also a prerequisite for high molecular weight polymer. The examples best studied of such reactions are the formation of metaphosphate by dehydration of orthophosphate [11] and the polymerization of formaldehyde in aqueous or alcoholic solution [12].

The formation of lithium metaphosphate by dehydration of the acid orthophosphate is typical for all alkali metaphosphates and metaphosphoric acid [13].

$$x\ HO(-\overset{\overset{O}{\|}}{\underset{\underset{O^{\ominus}}{|}}{P}}-O-)H \longrightarrow HO(-\overset{\overset{O}{\|}}{\underset{\underset{O^{\ominus}}{|}}{P}}-O-)_xH + (x-1)\ H_2O \qquad (4)$$

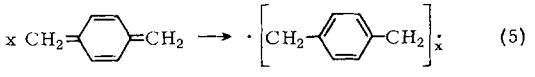
Although the metaphosphate is stable at lower temperature it does not form below 210 °C on stepwise heating because of nucleation difficulties. At 210 °C, 0.65 moles of water are lost per mole of LiH_2PO_4, and oligomers up to nonaphosphate have been identified by thin-layer chromatography in the almost completely amorphous reaction product [13]. The oligomers were formed by a step reaction and one expects a distribution of molecular weights as shown in Fig. 1. The step reaction sequence is interrupted as soon as the crystalline linear high polymer phase is nucleated. At this moment further polymerization proceeds by addition of small molecules to the crystal surface, the step reaction pattern has changed to a chain reaction sequence. The chain reaction kinetics is a cooperative polymerization scheme and as such the only one compatible with crystallization.

The type A nucleation and crystal growth of metaphosphates by dehydration is thus a random step reaction to form oligomers of sufficient length to nucleate the crystalline phase, followed by simultaneous polymerization and crystallization. From the degree of polymerization at the temperature of first nucleation and the results of thin layer chromatography it can be estimated that the chain length of the critical nucleus is about ten PO_3-units [10]. The molecular weight distributions shown in Fig. 1 apply only for the prenucleation period. For the crystalline metaphosphates of potassium, molecular weights up to several million have been reported [14, 15]. The molecular weight was found to be quite uniform, increasing in uniformity with time of reaction [14].

A similar mechanism has been shown to govern the formation of polyoxymethylene from formaldehyde in aqueous or alcohol solution. In these solvents the monomer is largely present as diol or hemiacetal, respectively, where the C=O double bond is already replaced by two single bonds. This reduces the major driving force of polymerization of formaldehyde ($\Delta G = -3.7$ kcal/mole) to little more than the driving force for crystallization ($\Delta G = -0.4$ kcal/mole) [12]. The initial stages of the reaction are again a step reaction until oligomers of about ten monomer units are reached, then spontaneous nucleation of solid polyoxymethylene takes place and further growth occurs *via* chain reaction by simultaneous polymerization and crystallization [12]. All polymer produced is completely crystalline as in the case of metaphosphates. Polyoxymethylene precipitates spontaneously out of a clear formaldehyde solution if it reaches a supersaturation of 4 to 8 weight percent formaldehyde. High molecular weight has only been achieved by control of nucleation [12].

Both the metaphosphate and the polyoxymethylene can be crystallized close to equilibrium by properly adjusting concentration of monomer and temperature. The reversibility of polymerization and crystallization under these conditions allows a rejection of defects and generation of perfect crystals. Further from the ceiling temperature (case B) it is more difficult to achieve more perfect crystals. The polymerization rate must first be matched to the nucleation, then to the crystallization rate. Since any polymerization may be slowed down by concentration change, temperature variation, or even a moving temperature gradient [16], it should still be possible to grow good crystals. The polymerization of *p*-xylylene and cellulose may be examples for type B nucleation followed by simultaneous polymerization and crystallization.

The formation of poly-*p*-xylylene is an example of conversion of a gaseous monomer into a crystalline polymer [17]. The monomer can be produced in 100% yield by vapor phase pyrolysis of di-*p*-xylylene at 550—600 °C [18]. Solid polymer has only been observed on surfaces cooled below 30 °C [18],



(5)

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despite a 420 °C melting point of the polymer [19]. Special nucleation difficulties exist because of the relative instability of the dimer and trimer diradicals with relatively weak central bonds [17]. In terms of equation 3, $\Delta\Phi$ must be particularly large for small values of l because of a large σ_e caused by the free radical ends. If nuclei are once formed, polymerization and crystallization is fast and the crystallinity is only about 80%, probably due to the large supercooling. Increasing the supercooling gives rise to even smaller crystallinity [19]. The more interesting experiment, to raise the temperature after nucleation to about 400 °C in order to carry out the crystallization more slowly, has not, as yet, been performed.

The biosynthesis of cellulose by *Acetobacter xylinum* is the other probable example of type B nucleation and crystal growth [10]. Simultaneous polymerization and crystallization has been assumed [20] when it was shown that no oligomers are present in the vicinity of actively polymerizing cellulose fibers [21]. Intermolecular nuclei have been observed after an initial induction period [22]. In cellulose, very little or no growth occurs in the direction normal to the molecular chain axis after nucleation. The measured diameter of the fibers is 100–250 Å [23]. This polymer is far from completely crystalline, probably as the result of a large degree of supercooling.

Type C nucleation and crystal growth differs from types A and B by showing successive polymerization and crystallization. The originally polymerized oligomers do not crystallize completely, but leave active chain ends in the amorphous phase. Such an intermolecular crystallization presents a number of problems: 1. On going from the crystallized to the amorphous portion of the molecule there is an increase in space requirement which can only be accommodated by a fibrous morphology. 2. Different polymerization rates of chains contributing to the same crystal should lead to defects and folds [24] (see Fig. 4.). 3. The distribution of active chain ends in solution or melt or on a solid surface should be of influence upon crystallization. 4. Solubility or crystallization temperature of chain ends, polymerization rate, density of chain ends, and molecular weight should be variables of the process.

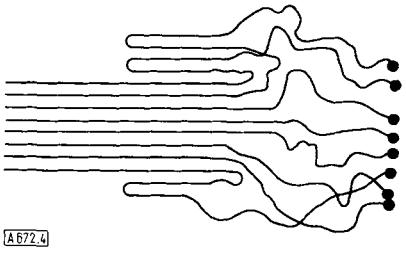

Fig. 4. Schematic representation of the fibrous habit caused by increased space requirement of the amorphous portion of molecules and the introduction of defects and folds by molecules of different polymerization rate (see also ref. [24]).

Many examples of type C nucleation and crystal growth are known [10]. Of particular interest have been the vinyl polymerizations involving Ziegler-Natta catalysts and ionic chain reactions.

A Ziegler-Natta catalyst usually consists of the reaction product of an organometallic compound (like triethylaluminum) and a transition metal compound (like titanium tetrachloride) slurried in a dry, oxygen free, inert hydrocarbon solvent (like heptane) along with the monomer to be polymerized. Such catalysts are capable of producing stereoregular (crystallizable) polymers so that conditions are set for crystallization during polymerization.

$$\text{Catalyst-CH}_2\text{-CHR}' + x\,\text{CH}_2\text{=CHR} \rightarrow \text{Catalyst}(-\text{CH}_2\text{-CH}(\text{R})-)_x\text{CH}_2\text{-CHR}' \quad (6)$$

Bulkiness of the catalyst in homogeneous catalysis and sparsity of reaction sites in the case of heterogeneous catalysis precludes simultaneous polymerization and crystallization. In all cases of high active site concentration fibrillar crystals have been observed. The best perfection was obtained by room temperature polymerization of ethylene on glass-supported $VCl_3/Al(C_2H_5)_3$ catalyst in heptane [25]. Intermediate perfection was found with $TiCl_3/Al(C_2H_5)_3$ catalyst in heptane and toluene between 0 and 40 °C [26]. The least perfect fibrils grew at the highest reaction temperature and the best solvents, 85 to 110 °C with $TiCl_3/Al(C_2H_5)_3$ catalyst in toluene and xylene [27].

Examples of homogeneous ionic polymerization and crystallization of the type C include the formaldehyde [12] and probably also the trioxane polymerization to polyoxymethylene [28, 29], the lactam polymerization to polyamide [30], and the decomposition of diazomethane to polymethylene [31]. In all these cases a complicated reaction intermediate precludes polymerization on a crystal surface. Very little is known in these cases about the crystal morphology, nothing is known about the nucleus size.

The polyamide crystallinity was varied by changing reaction conditions. If the reaction is carried out very fast an amorphous "virgin polymer without thermal history" can be produced [32]; in contrast, on careful slow zone polymerization, a highly crystalline polyamide was made [33]. A considerable reduction in crystallinity was found for polymethylene when the polymerization temperature of diazomethane was reduced to −50 °C. The amorphous polyamide was produced so fast, that even nucleation was avoided, while the low crystallinity polymethylene was probably less perfect because the polymerization rate exceeded the crystallization rate.

Nucleation and crystal growth of type A to C have an intermolecular nucleation step in common. Oligomers of short enough length must crystallize before high polymer can be produced. If the oligomer is formed *via* a chain reaction, it is possible to have such a low concentration of oligomers that intermolecular

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nucleation becomes impossible. The oligomer grows into a high molecular weight polymer and after reaching sufficient size may nucleate a crystal intramolecularly. Figure 3 indicates that this is only likely in a folded chain conformation since both dimensions, *a* and *l*, must have a reasonable value, larger than several atomic diameters. Since chain folding ought to increase σ_e, an elongated nucleus, similar to the one assumed in calculation of the data given in Fig. 3, is expected. After nucleation, further crystal growth can occur by simultaneous polymerization and crystallization (type D) or by successive polymerization and crystallization (type E). The reaction site is at the surface of the crystal and since the nucleation difficulty has been overcome, further crystal growth should increase dimensions *a* and *l* following approximately the valley of Fig. 3. At later times oligomers can add to the growing crystal so that the molecular weight may be less than the crystal weight.

Type D or E nucleation and crystal growth should be of particular importance for free radical polymerization of crystallizable monomers since free radical oligomers would rather terminate than nucleate a crystal. Concentrations of free radicals of 10^{-8} to 10^{-9} M are common in such polymerizations, a concentration much too low to yield sufficient oligomer for intermolecular nucleation.

The most probable example of intramolecular nucleation is the free radical polymerization of tetrafluoroethylene[10]. The resulting polymer is recovered as a granular powder or as a dispersion. The molecular weight may be as high as 10^8 and the crystallinity is estimated to be 97%[35]. Single dispersion particles (diameter $\approx$ 0.2 μ about 200 molecules) have given rise to discrete electron diffraction patterns[7].

The main conclusions to be drawn here then are that the first nucleation and later crystallization steps must be matched to polymerization rate to yield a perfect crystal. The nucleus size for several polymers has been estimated to be about 20 Å in the chain direction. Five types of nucleation and crystallization seem to describe the presently known cases of crystallization during polymerization.

The importance of nucleation is illustrated by the polymerization of ε-aminocaproic acid from the gas phase[36]. In a closed vessel ε-aminocaproic acid crystals were shown to cover their surfaces with polymer. The monomer evaporates to build up the vapor pressure of 0.2 torr. From the gas phase ε-aminocaproic acid is able to polymerize after nucleation of the crystalline state. This nucleation is greatly enhanced on the monomer crystal surface, so that despite a much larger glass vessel surface the largest portion of polymer, crystallized during polymerization, is found on the surface of the monomer crystal. A direct polymerization of the crystalline monomer seems impossible probably because the monomer exists in the form of zwitterions. The polymerization of the gaseous monomer is a successive crystallization and polymerization[10].

Several problems of crystallization are connected with crystallization during polymerization. Besides the crystal perfection mentioned above the directiveness of polymer chains presents a major difficulty. Polymers like cellulose, polycaprolactam, and poly-β-hydroxybutyrate[37] can fit only in antiparallel arrangement onto an ideal crystal. If such polymer chains are produced from an active center such that it grows only in one direction, the most stable crystalline arrangement cannot be achieved. Experiments on caprolactam seem to bear out this fact, the X-ray diffraction diagram indicates a less perfect arrangement for crystals grown during polymerization than for antiparallel folded chain crystals grown from solution[33].

A special type of polymerization is the reaction of crystalline monomer[38]. The numerous examples studied can be separated into the categories, polycondensations, free radical reactions, and ring opening polymerizations. Polycondensations of amino acids and oligoamides[39] have led only to successive polymerization and crystallization with a loss of the initial orientation. Some of the reactions were topochemical since they followed a reaction path only possible for crystalline monomer, but none of the cases investigated demonstrated topotacticity, a solid state path from the crystalline monomer to the crystalline polymer.

Free radical polymerization from crystalline monomers is even more difficult. Besides the general conditions for a topotactic polymerization (to provide the proper geometry for monomer approach for reaction and to have a continuous path to the crystal structure of the polymer) an additional condition exists: the need to protect the radicals from mutual termination. Only in clathrates have all these conditions been fulfilled and simultaneous polymerization and crystallization has been achieved for 2,3-dimethylbutadiene and 2,3-dichlorobutadiene in thiourea[40], and for butadiene and vinyl chloride in urea[41]. Figure 5 represents schematically the

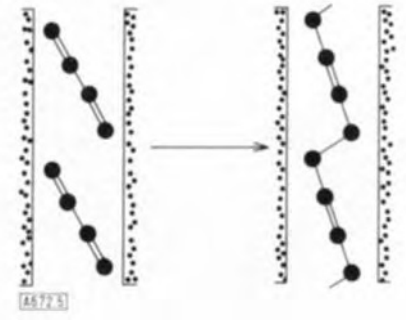

Fig. 5. Schematic representation of simultaneous polymerization and crystallization of butadiene urea clathrates. The reaction is free radical initiated by ionizing radiation.

reaction conditions. The geometry is just right for the parallel approach of the planar sp^2 hybrid of the double bond and the planar free radical, only a minimal adjustment of the position of the monomer is necessary to give polymer inside the urea

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or thiourea channels. The final group of solid state monomers which have been polymerized are ring type monomers such as trioxane, trithiane, tetroxane, 3,3-bis(chloromethyl)-oxetane, and β-propiolactone[10]. In this group topotactic polymerization reactions seem to be possible (simultaneous polymerization and crystallization). The favorable factors are a small heat of reaction and a small volume change since the number of covalent bonds stays constant.

4. Comparison of Crystal Forms from Different Crystallization Paths

The discussion of nucleation and crystal growth has shown that crystallization during and after polymerization may be very different; as a consequence different crystal forms are expected. Crystal growth from the already polymerized melt or solution has been studied in great detail[6,7]. In all careful homopolymer crystallizations lamellar crystals similar to the one shown in Fig. 6 were found with the small dimension of the

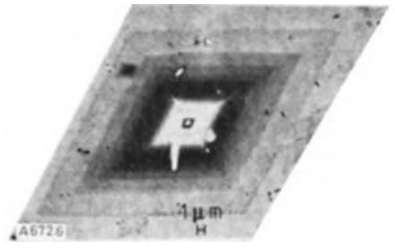

Fig. 6. Chain folded lamellar polyethylene crystal. The chain direction is normal to the plane of the micrograph, a growth spiral of many lamellae is shown.

lamellae being in the chain direction; the usually much longer chains are accommodated by chain folding. Typical lamellar thicknesses (chain fold lengths) on crystal growth from solution are 50 to 200 Å, from the melt 100–500 Å.

A lamellar crystal of only 100 Å thickness has a specific surface area of about 10^6 cm²/g. Such a large surface area makes the folded chain crystal lamellae metastable, they melt usually 5 to 30 °C below the melting point of extended chain crystals[33,42,43]. If the metastable lamella melts without reorganization[44], the melting temperature lowering, ΔT, can be described by the Thomson equation[45], first applied to melting of lamellae by *Tammann*[46]:

$$\Delta T = 2\,\sigma_f T_m^\circ / \Delta H_u \cdot \rho \cdot l \qquad (7)$$

σ_f is, as shown above, the surface free energy, in this case of the fold surface. T_m° is the melting point of a very thick lamella, H_u is the heat of fusion per cm³ of polymer, ρ is the crystalline density, and l the lamellar thickness, the fold length. From measurements of ΔT, values of 40 to 90 erg/cm² have been derived for some typical polymers[33,43,47].

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The reason for the metastable lamellar habit is an intramolecular secondary nucleation for each new chain crystallizing. Figure 3 shows that after the saddle point has been overcome, the path of lowest free energy would call for an increase of both a and l. If, however, each new molecule must be nucleated anew on the growth face of the crystal, new folds with a small value of l are set up during crystal growth. Crystal growth in the l-direction is only possible as a second step going on in the solid state. It involves a rearrangement of folded chain portions of the crystals to larger fold lengths in a thickening process – a process which is often kinetically hindered.

Proof of this crystal growth sequence has come, *inter alia*, from direct experiments with extended chain polyethylene crystals. Lamellae of up to 10 µ in the chain direction and 100 µ at right angles were grown by crystallization from the melt at elevated hydrostatic pressure[48,49]. Under these conditions the

Fig. 7. Extended chain polyethylene crystal. Electron micrograph of a fracture surface. The molecular chains are in the plane of the micrograph, parallel to the visible striations.

thickening after folded chain crystal growth is enhanced relative to the crystal growth. Figure 7 shows such an extended chain lamella viewed at right angles to the chain direction. Attempts to use these high melting crystals as seeds for crystallization of extended chain crystals failed, only folded chain lamellae grow on extended chain nuclei as is shown in Fig. 8[50,51]. Once folded chain lamellae were formed, they could be made to extend somewhat by annealing at the crystallization or higher temperature[51]. Crystallization of polyethylene over extended periods of time has led to crystals up to 2000 Å in fold-length[52].

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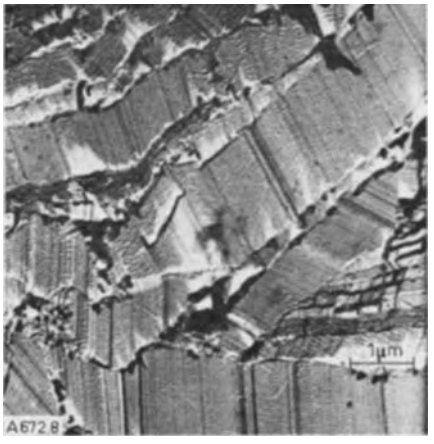

Fig. 8. Folded chain lamellae grown on the surface of extended chain polyethylene crystals. Electron micrograph of a surface replica. The chains are in the plane of the micrograph at rigth angles to the upper and lower lamellar surfaces.

All these difficulties do not exist in crystallization during polymerization if the random polymeric state is avoided before crystallization. The size of the nucleus for simultaneous polymerization and crystallization of polyoxymethylene, metaphosphates, and possibly also poly-*p*-xylylene seems to indicate that the surface free energy of the intermolecular critical nucleus is less than that of a folded chain polymer nucleus. After reaching the critical size, further growth in the chain direction by addition of more monomer units proceeds without difficulty. A problem might be the converse, growth of further layers parallel to the chain direction which calls for new, secondary nucleation. If this is the case, a fibrous habit as found in the Kurrol's salts [11], in cellulose (from *Acetobacter xylinum*) [53], in several differently polymerized polyoxymethylenes [54] and polytrithianes [55], and in the polyolefins from Ziegler catalysis [56], must be the natural result.

A comparison of density of extended chain crystals grown from the melt at varying pressures with folded chain crystals grown from solution at different temperatures is shown in Fig. 9. Both forms can show a high degree of perfection [48, 57]. A difference is seen, however, in the melting behavior, as predicted by equation 7. Crystals grown during polymerization of comparable or greater perfection than crystals grown after polymerization melt at higher temperatures. Measurements were performed on polytetrafluoroethylene [58], polyethylene [59], polycaprolactam [33], polytrithiane [55], and the clathrate polymers [40,41]. Even more characteristic seems to be the fact that extended chain crystals melt so slowly, that with standard thermal analysis heating rates temporary superheating beyond the melting point is possible [42].

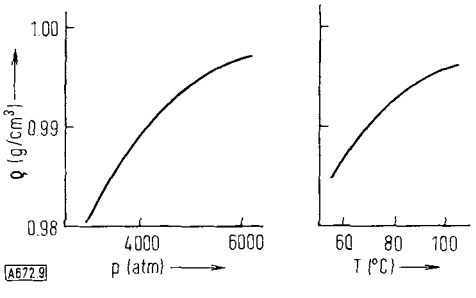

Fig. 9. a) The density of extended chain crystals of polyethylene approaches the X-ray density above 3000 atm crystallization pressure. b) The density of folded chains of crystals of polyethylene also approaches the X-ray density if the crystallization temperature is close to the dissolution temperature. (The ideal X-ray density of polyethylene at 23 °C is 1.000 g/cm³.)

Most of the comparison of different crystallization paths has been concerned with the two limiting cases: folded chain and extended chain crystals. The discussion of Ziegler type crystallization during polymerization has indicated that on successive polymerization and crystallization considerable distances may exist between the sites of polymerization and crystallization. In such cases chain folding may be induced because of introduction of randomized chain portions and because of unequal polymerization rates as was illustrated in Fig. 4.

Overall it seems possible to conclude that all chain conformations in solid polymers are schematically represented by the area of the triangle in Fig. 10.

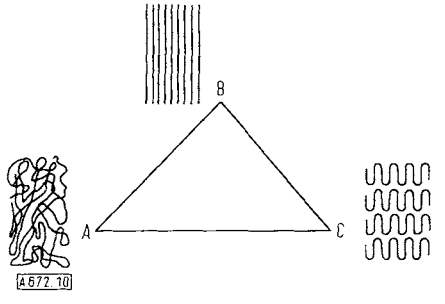

Fig. 10. Schematic representation of polymer chain conformations in the solid state. A, glassy (or molten) random chains. B, extended chains. C, folded chains.

For crystallizable polymers the chain conformations around A can be produced by quenching polymer melts or solutions as well as by very fast polymerizations into the glassy state. Crystals with more extended chain conformation can be produced by crystallization during polymerization or occasionally by special annealing after crystallization from the melt. Morphologies of folded chain conformation can be produced by separate polymerization and crystallization. On faster crystallization, usually at higher degrees of supercooling, poorer crystals with conformations tending toward A are produced.

A final note concerns the X-ray structure of polymer crystals grown during polymerization. Most examples reported seem to have the same crystal structure as the

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polymer crystallized from melt or solution [10]. Occasionally a less stable or low temperature structure can be produced. An example is the polycaprolactam made by zone polymerization which has not the ideal orthorhombic crystal structure, but a paracrystalline structure which has a less perfect alignment of H-bonds [33]. The metaphosphates can be produced in a low temperature crystal form first which converts into the high temperature modification at higher temperature [13]. Polyoxymethylene may under certain conditions of crystallization during polymerization form orthorhombic instead of hexagonal crystals [12]. Poly-*p*-xylylene also crystallizes during polymerization first as a metastable orthorhombic structure, to change at about 240 °C into the stable, denser hexagonal crystal structure [19].

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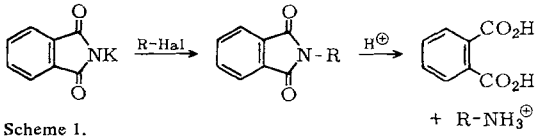
The Gabriel Synthesis of Primary Amines

BY M. S. GIBSON AND R. W. BRADSHAW[*]

Reaction of potassium phthalimide with halogenoalkanes and with a variety of other alkylating agents leads to the N-alkylphthalimide. N-Substituted phthalimides may be converted into the corresponding primary amine by hydrolysis or hydrazinolysis. The scope and limitations of these reactions, which together constitute the Gabriel Synthesis of primary amines, are reviewed.

1. Introduction

The Gabriel Synthesis of primary amines and amino compounds may be summarized schematically as follows:



Scheme 1.

Potassium phthalimide is generally used for the first stage but (a) sodium phthalimide and (b) phthalimide and potassium carbonate or sodium carbonate have been used to some extent; the second stage is normally accomplished by hydrolysis or hydrazinolysis [1]. The importance of the Gabriel Synthesis lies in (i) the absence of secondary or tertiary amine contamination of the primary amine, (ii) the toleration of a very wide range of other functional groups in the molecule, and (iii) the mild conditions now available for accomplishing both stages. High yields of primary amines are generally obtainable, rendering the synthesis attractive, *inter alia*, for the preparation of isotopically labeled amines and amino acids [2].

The successful conversion of methyl and ethyl iodides into the *N*-alkylphthalimides by reaction with potassium phthalimide at 150 °C was reported by *Graebe* and *Pictet* in 1884 [3]. It was already known that *N*-alkylphthalimides could be hydrolyzed to phthalic acid and the primary amine, but it was *Gabriel* who appreciated the significance of these reactions and formulated the Synthesis which bears his name [4]. The scope of the synthesis was explored by *Gabriel* and his colleagues in Berlin for over 30 years.

In the early days, examples slowly accumulated of the preparation of primary alkylamines and aralkylamines from alkyl bromides (including allyl bromide) [5] and aralkyl chlorides and bromides [4,6]. However, from the beginning, greater interest attached to applications of the reaction to bi- and poly-functional halogeno compounds (with potassium phthalimide) and to transformations, including hydrolysis, of the products. In the aralkyl series, early examples included the chloromethylnitro- and chloromethylcyano-benzenes [4,7]. Reaction occurred readily (with potassium phthal-

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[4] *S. Gabriel*, Ber. dtsch. chem. Ges. *20*, 2224 (1887).

[5] a) *A. Neumann*, Ber. dtsch. chem. Ges. *23*, 994 (1890); b) *S. Gabriel*, *ibid. 24*, 3104 (1891).

[6] *H. Strassmann*, Ber. dtsch. chem. Ges. *21*, 576 (1888).

[7] a) *S. Gabriel* and *H. Hendess*, Ber. dtsch. chem. Ges. *20*, 2869 (1887); b) *H. K. Günther*, *ibid. 23*, 1058 (1890).

imide) and control of temperature was important; sometimes the reactions were necessarily moderated by diluting the reactants with sodium chloride [8] or (in one case) benzyl cyanide [9], but years were to elapse before the use of solvents became commonplace.

With the *N*-(cyanobenzyl)phthalimides, the vigorous treatment used for hydrolysis led to the corresponding amino acid [10]. In the aliphatic series, such bi- and poly-functional compounds as monochloroacetone, ethyl chloroacetate and 1,3-dichloro-2-propanol [11], 1-bromo-2-phenoxyethane [12] and 4-bromobutanenitrile [13] were examined; acidic hydrolysis gave the expected amino compounds, the ester and nitrile groups also undergoing hydrolysis.

Greatest interest attached to the particular cases of 1,2-dihalogenoethanes and 1,3-dihalogenopropanes in which, by choice of conditions, one or both halogen atoms could be displaced in Stage 1. If both halogen atoms were replaced, completion of the Gabriel Synthesis gave ethylenediamine and trimethylenediamine respectively [4, 14]. If one halogen atom were displaced, the resulting *N*-(halogenoalkyl)phthalimide could be subjected to hydrolysis, giving halogenoalkylamine salts, or to metathetical reactions with various nucleophiles. Thus, reaction of *N*-(2-bromoethyl)phthalimide with (a) aniline [15], (b) potassium hydrogen sulfide [16], and (c) sodium benzenesulfinate [17] gave (a) *N*-(monoanilinoethyl)- and *N*-(dianilinoethyl)-phthalimides, (b) the *N*-(mercaptoethyl)phthalimide and *N*,*N*'-thiodiethylenediphthalimide, and (c) phenylsulfonylethylphthalimide respectively, which could be hydrolyzed to the corresponding amino compounds. Again, use of sodio derivatives of diethyl malonate and its monoalkylated derivatives provided syntheses of amino acids [18].

Other useful developments hinged on the stability of the phthalimido group under a variety of conditions which permitted the modification of other functional groups. These may be illustrated by the use of 3-phthalimidopropionyl chloride in the Friedel-Crafts acylation of benzene [19], the α-bromination of ω-phthalimidoalkylmalonic esters in the preparation of α,ω-diamino acids [20], and the oxidation of *N*-(ω-hydroxyalkyl)- and *N*-(ω-mercaptoalkyl)phthalimides to the corresponding carboxylic and sulfonic acids [16, 21].

The general usefulness of the Gabriel Synthesis was thus established, though limitations were imposed by the reaction conditions in common use. Most of the alkylation reactions (Stage 1) were carried out by heating the reactants together at temperatures in the range 120–240 °C for periods of up to several hours, even though such conditions were recognized as undesirable or even dangerous in some cases [22]. In this context, it is perhaps remarkable that *Beck*'s demonstration in 1893 that 1-chloromethyl-2-nitrobenzene reacted readily enough with potassium phthalimide in boiling ethanol [23] should have been overlooked.

The vigorous conditions of acidic hydrolysis (Stage 2) used at this time prevented extension of the synthesis to compounds containing acid-sensitive groups, although preliminary alkaline hydrolysis to the *N*-substituted phthalamic acid, followed by milder acidic hydrolysis to phthalic acid and the amine, permitted some variation. Again, the significant observation that hydrazine readily cleaved the phthaloyl group from ethyl phthalimidoacetate as phthalhydrazide under quite mild conditions (*Radenhausen*, 1895) [24] had either been missed or insufficiently appreciated. Approximately 30 years were to elapse before hydrazinolysis was introduced as a technique for accomplishing Stage 2 of the Gabriel Synthesis [25].

2. Stage 1: Formation of the *N*-Substituted Phthalimide

2.1. Displacement Reactions

2.1.1. Alkyl Halides

The most commonly used alkylating agents in the Gabriel Synthesis are the alkyl halides. As indicated above, a wide range of other functional groups are tolerated as substituents within the molecule, although it may be necessary or desirable to protect some functional groups in order to facilitate reaction; *e.g.* it is standard practice to use halogenoalkanoic esters (not the acids), and it seems necessary to protect phenolic groups [26].

The consensus of opinion is that the alkylation stage is an S_N2 reaction, the ambident phthalimide ion reacting at nitrogen, though this view rests largely on analogy with other nucleophilic reactions of alkyl halides [27]. Whilst in the main

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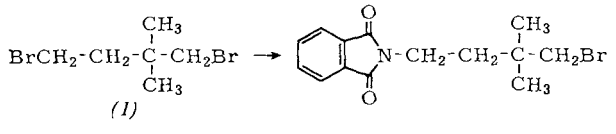
the products are those expected from the S_N2 mechanism, it is clear that this mechanism cannot apply in all cases.

There are indications that primary chloroalkanes are less reactive than the corresponding bromides or iodides in the Gabriel Synthesis (see *e.g.* [28–33]). However, since the reactions are carried out under such a wide range of conditions, the comparison must be interpreted cautiously. There is, nonetheless, a predisposition to accept this view of the relative ease of reaction of halides, borne out by the choice of bromide or iodide rather than chloride [34], the unreactivity of alkyl fluorides (illustrated by the preparation of 2-(fluoroethyl)phthalimide from 1-bromo-2-fluoroethane [35]), and the occasional use of iodide ion as additive [36] (for examples of other additives see Ref. [30a, 37–39]). Recently, the reactions of 1-chloro-, 1-bromo-, and 1-iodopropane with potassium phthalimide in dry dimethylformamide at 25 °C have been found to be first order, in halogenoalkane and in potassium phthalimide, the order of reactivity being RCl < RBr < RI; the rates of the first two reactions were not increased by addition of iodide ion [36c].

Primary halogenoalkanes not containing other functional groups, except sterically hindered compounds of the neopentyl type, react reasonably well with potassium phthalimide. Thus *(1)* shows very marked difference in reactivity of the two bromine atoms; a competing elimination reaction was noted in this case, although the by-product was not identified [40]. Examples in which this type of compound has been induced to react are provided by *(2a)*, *(2b)* [41] and



(1)

$H_3C-C(CH_2X)_3$ *(2a)*, X = *p*-$CH_3-C_6H_4-SO_3$
(2b), X = Br

$(CH_3)_2C(CH_2X)_2$ *(3a)*, X = $C_6H_5SO_3$
(3b), X = Br

$(CH_3)_nSi(CH_2X)_m$ *(4a)*, *n* = 3, *m* = 1, X = Cl
(4b), *n* = 2, *m* = 2, X = Cl

(3a) and *(3b)* [42]; in each case the reaction was carried out at high temperature. The analogous silicon compounds *(4a)* and *(4b)* have been successfully substituted using phthalimide and potassium carbonate [43a], and potassium phthalimide in dimethylformamide [43b].

Substitution has also been achieved with some secondary halogenoalkanes, though apparently with greater difficulty, and with attendant side reactions (elimination). 2-Bromopropane [5b] and 2-bromobutane [44] give the substituted phthalimide and apparently olefins; bromocyclohexane is reported to give cyclohexene [25]. Bromodiphenylmethane gives according to conditions, the substituted phthalimide or mainly tetraphenylethylene [45].

Systems involving differently environed halogen atoms react preferentially at the carbon which is more susceptible to S_N2 attack. An improved synthesis of the antimalarial drug primaquine, utilizes this idea in the treatment of 1,4-dibromopentane with potassium phthalimide in acetone to give 67% of the desired *N*-(4-bromopentyl)phthalimide [46]. In the case of 1,2,3-tribromopropane, the product is *N*-(2-bromoallyl)-phthalimide [47]. Elimination is also noted with 1,3-dichloro-3-methylbutane, which gives isopentenylphthalimide [48], and with 1,4-dibromopentane in ethanol, which gives polymeric material [46].

There are a considerable number of applications to cases of halogeno compounds bearing a ketonic [49], ester [49], or nitrile [50] function at the halogenated carbon atom; these relate to syntheses of aminoketones, amino-acids, or derivatives thereof. A particularly important case is that of diethyl bromomalonate, which gives the well-known diethyl phthalimidomalonate, starting point of the Sörensen amino-acid synthesis [51]. Scission of a benzoyl group has been reported during reaction of 2-bromo-1,3-diphenyl-1,3-propanedione with potassium phthalimide in ethanol (no cleavage is reported in benzene, or without solvent) [52]. Substances such as 2-chloropropionitrile give acrylonitrile and a small amount of the substituted

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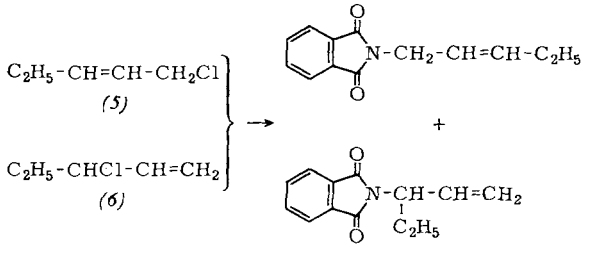
phthalimide when heated with potassium phthalimide[53]; however, acrylonitrile adds to potassium phthalimide under appropriate conditions[54].

Allylic halides react reasonably well with potassium phthalimide to give the corresponding substituted phthalimides[36a,55]. *N*-(*cis*-2-butenyl)- and *N*-(*trans*-2-butenyl)phthalimides have been made in this way[56]. *Meisenheimer* and *Link*[57] have investigated the allylic isomers *(5)* and *(6)* in this reaction, and obtained mixtures of virtually the same composition from each: the primary allylic phthalimide is the major component, and the overall yield of isomers was appreciably lower from the secondary halide. The reactions were conducted at 190–200 °C, and the absolute purity of the halides may perhaps be open to question. However,



the possibility of rearrangement remains, at least in some cases, and further investigation seems desirable. Propargylic halides have also been used in the Gabriel Synthesis[58], and are reported to give excellent yields of the derivative.

Gabriel occasionally utilized solvents in some of his reactions of halogenoalkanes with potassium phthalimide[9a,59], although he evidently preferred the absence of a diluent for most of his investigations in this field (see Ref.[9,23,25,45b,52a,55c,59–72] for examples of the solvents used and referred to in the older literature). Dimethylformamide is now widely employed as a solvent for Stage 1 of the Gabriel Synthesis[49] because potassium phthalimide is moderately soluble in this solvent, and relatively mild conditions suffice for the displacement of halogen by phthalimide ion. Moreover, yields are significantly enhanced[73,74], though again the presence of water may adversely affect some reactions[75]. However, other solvents continue to be employed, *e.g.* petrol[76], kerosene[42], acetamide[77], chlorobenzene[78], acetonitrile[79], amyl alcohol[80], diglycol[81], ethylene glycol[36b], and dimethylsulfoxide[82]. However, on occasions the absence of a solvent may still be preferred where yields are critical, as in the synthesis of $^{13}CH_3NH_2$, which proceeds in higher yield using the original method[83].

A recent preliminary account of the use of hexamethylphosphoramide (hexametapol)[84], indicates that Stage 1 of the Gabriel synthesis may be accomplished under conditions comparable with those reported for dimethylformamide. Indeed, it has been shown that sodium phthalimide can be generated *in situ* in this solvent, and that some reactions occur at room temperature with equally acceptable yields.

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[74] *H. K. Müller* and *G. Rieck*, J. prakt. Chem. (4) *9*, 30 (1959).

[75] *J. H. Billman* and *R. V. Cash*, Proc. Indiana Acad. Sci. *62*, 158 (1953); *A. N. Nesmejanow*, *K. G. Perevalova*, *L. S. Shilovtseva*, and *V. D. Tyurin*, Izvest. Akad. nauk. SSSR, Otdel. chim. Nauk. *1962*, 1997.

[76] *O. Riobé* and *H. Cottin*, C. R. hebd. Séances Acad. Sci. *240*, 1783 (1955).

[77] *W. Siedel* and *H. Nahm*, German Pat. 928711 (June 10, 1955) Farbwerke Hoechst A.G.; Chem. Abstr. *52*, 5471 (1958).

[78] *H. J. Barber*, *R. F. Fuller*, *M. B. Green*, and *H. T. Zwartouw*, J. appl. Chem. *3*, 266 (1953).

[79] *K. Wallenfels*, *F. Witzler*, and *K. Friedrich*, Tetrahedron *23*, 1845 (1967).

[80] *M. Ohara* and *T. Hattori*, J. pharmac. Soc. Japan (Yakugakuzasshi) *71*, 575 (1951); Chem. Abstr. *46*, 4548 (1952).

[81] *A. Weissberger*, *D. B. Glass*, and *P. W. Vittum*, US-Pat. 2552240 (1951), Eastman Kodak Co.; Chem. Abstr. *45*, 7900 (1951).

[82] *F. Sparatore* and *F. Pagani*, Farmaco (Pavia), Ediz. sci. *20*, 248 (1965); Chem. Abstr. *63*, 8344 (1965).

[83] *J. D. Cox* and *R. J. Warne*, J. chem. Soc. (London) *1951*, 1896.

[84] *H. Normant* and *T. Cuvigny*, Bull. Soc. chim. France *1965*, 1866.

From the discussion in Section 2.1.4. it is clear that the first stage of the Gabriel synthesis does not always involve direct substitution of halogen by phthalimide ion in these reactions. It may be mentioned in passing, however, that the proposed S_N2 mechanism does involve definite stereochemical implications. In a rare case of substitution at an asymmetric carbon atom, *Fischer*[85] noted that (−)ethyl 2-bromopropionate, when treated with potassium phthalimide at 125 °C for 5 hours, gave the phthalimido derivative with approximately 42% racemisation. Mild conditions are now available for carrying out the Gabriel Synthesis, and this point clearly requires investigation with optically stable materials.

2.1.2. Aryl Halides and Vinyl Halides

In the early days of the Gabriel Synthesis, it was noted that picryl chloride reacted readily (70 °C) with potassium phthalimide to give *N*-picrylphthalimide; 2-chloroquinoline, however, was observed not to react even at temperatures as high as 230 °C[12]. Later authors have expressed the view that picryl chloride is the only aromatic halide to react in the Gabriel Synthesis[86], though this is not in fact the case.

1-Chloroanthraquinone has been reported to react with phthalimide and sodium acetate in the presence of copper at temperatures near 200 °C, hydrolysis with sulfuric acid yielding 1-aminoanthraquinone. Similar results were obtained with 1,5-dichloroanthraquinone and other substituted anthraquinones[87]. Again, 2-bromofluorene, 1- and 2-chloroanthracenes, and 9-bromoanthracene react with potassium phthalimide in nitrobenzene under similar conditions, though in indifferent yields[62].

A number of aromatic systems bearing halogeno substituents and capable of facilitating delocalization of the negative charge during attack by phthalimide ion (*e.g.* $-NO_2$, $-CN$), have also been noted to react. Examples are provided by 1-fluoro-2,4-dinitrobenzene[88], and (less readily) 1-chloro-2,4-dinitrobenzene[88], 1-chloro-2-nitrobenzene[89] (although 1-chloro-4-methoxy-2-nitrobenzene is said not to react under the same conditions[89]), 1,3,5-trichloro- and 1,3,5-trifluoro-2,4,6-tricyanobenzenes[79].

Cyanuric chloride reacts with potassium phthalimide (1 equivalent) in acetone to give *N*-(4,6-dichlorotriazin-2-yl)phthalimide[90]. Acetonylacetone condenses with *N*-aminophthalimide to give *N*-(2,5-dimethylpyrrol-1-yl)phthalimide[91].

ω-Bromostyrene (with copper catalysis)[92] and tetrafluorobenzoquinone[93] provide examples of unsaturated halogeno compounds which react with potassium phthalimide. *Nesmejanow* and his co-workers have investigated the reaction of copper phthalimide with bromo- and chloroferrocene[94], when fairly good yields of *N*-ferrocenylphthalimide were obtained.

Recently, work has been performed on the direct phthalimidation of unsubstituted aromatic systems. For example *N*-chlorosulfonylphthalimide has been shown to react with biphenyl[95]; however, the product yield is low. Without the use of any catalyst, the major product of the reaction is *N*-(4-biphenylyl) phthalimide, whereas in the presence of cuprous chloride, the three isomeric monophthalimido-derivatives are produced in approximately equal proportions. This suggests that the reaction proceeds *via* a free radical mechanism, a view supported by the isolation of phthalimide itself from the reaction mixture. Since *N*-chlorophthalimide reacts with biphenyl to give only a trace of *N*-(4-biphenylyl)phthalimide, it is thought that this possible intermediate is not formed. The reaction has been extended to halogenated benzenes using either cuprous chloride, or cuprous naphthenate as catalyst.

2.1.3. Other Displaceable Groups

Although the metathetical reaction of alkyl tosylates with phthalimide ion was discovered in 1928[96], it was nearly 20 years later before *Sakellarios*[97] developed the use of these derivatives as alternatives to halogenoalkanes in the Gabriel Synthesis. This author discussed the advantages of tosylates over halides with respect to their lower volatility and greater thermal stability. It may be added that these derivatives are also more accessible in the pure state than the corresponding halogenoalkanes. Coupled with the fact that yields are often enhanced when sulfonates rather than the bromides are employed[41,42], it is perhaps surprising that relatively few examples of this modification of the Gabriel Synthesis are reported. Moreover, the reaction with potassium phthalimide and 2-chloroethyl tosylate gives *N*-(2-chloroethyl)phthalimide in excellent yield[97], at least suggesting that sulfonates are more reactive than the corresponding chlorides.

Other typical examples include such tosylates as *(7)*[98] and *(8)*[82], the sultones *(9)*[68] and *(10)*[99], and the neopentyl sulfonates *(2)* and *(3)*[41,42]. A case of elimination has

[85] *E. Fischer*, Ber. dtsch. chem. Ges. *40*, 489 (1907).

[86] *H. Krauch* and *W. Kunz*, Organic Name Reactions. Wiley, New York 1964, p. 182.

[87] *H. A. E. Drescher* and *J. Thomas*, US-Pat. 1528470 (March 3, 1925), Chem. Abstr. *20*, 424 (1926).

[88] *A. L. Beckwith* and *J. Miller*, Austral. J. sci. Res., Ser. A *5*, 786 (1952).

[89] *R. C. Elderfield*, *L. L. Smith*, and *E. Werble*, J. Amer. chem. Soc. *75*, 1245 (1953).

[90] *W. F. Beech*, J. chem. Soc. (London) (C) *1967*, 466.

[91] *R. Epton*, Chem. and Ind. *1965*, 425.

[92] *K. W. Rosenmund*, *M. Nothnagel*, and *H. Riesenfeldt*, Ber. dtsch. chem. Ges. *60*, 392 (1927).

[93] *K. Wallenfels* and *W. Draber*, Tetrahedron Letters *13*, 24 (1959).

[94] *A. N. Nesmejanow*, *V. A. Ssasonowa*, and *V. N. Drosd*, Chem. Ber. *93*, 2717 (1960).

[95] *R. A. Lidgett*, *E. R. Lynch*, and *E. B. McCall*, J. chem. Soc. (London) *1965*, 3754.

[96] *G. R. Clemo* and *E. Walton*, J. chem. Soc. (London) *1928*, 723.

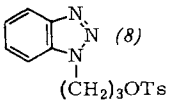
[97] *E. J. Sakellarios*, Helv. chim. Acta *29*, 1675 (1946).

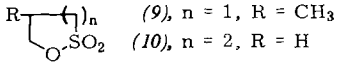
[98] *D. A. Shirley* and *J. R. Zeitz*, J. org. Chemistry *18*, 1591 (1953).

[99] *J. H. Helberger*, *G. Manecke*, and *R. Heyden*, German Pat. 901054 (Jan. 7, 1954), Böhme Fettchemie GmbH.

been noted with 2-cyanoethyl tosylate, when the main product of reaction is the volatile acrylonitrile[97], as with the corresponding 2-chloropropiononitrile under similar conditions[53]. Moreover, although *N*-(2-tosyloxyethylsulfonyl-*p*-phenyl)acetamide appears to react by displacement of the tosylate function[69], it is possible that this is an elimination-addition reaction.

(7) $n\text{-}C_{18}H_{37}OTs$ *(8)*

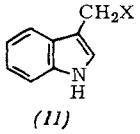




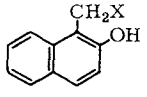
(9), n = 1, R = CH_3
(10), n = 2, R = H

Other types of ester have been occasionally employed. For example, potassium phthalimide and ethyl carbonate react to give *N*-(2-hydroxyethyl)phthalimide[100], as do γ-lactones[101,102], *e.g.* γ-butyrolactone affords 3-phthalimidobutyric acid[101]; trimethyl phosphate gives *N*-methyl-4-nitrophthalimide on treatment with potassium 4-nitrophthalimide[103]. *N*-Benzylphthalimide is formed from benzyl nitrate and potassium phthalimide in dimethylformamide[36c].

Mannich compounds and derived salts have also been employed in metathetical transformations involving the phthalimide ion. For instance, phthalimidomethyltrimethylammonium iodide and potassium phthalimide give diphthalimidomethane[104]. Base catalyzed reactions of phthalimide with *(11)* and *(12)* give the corresponding phthalimido derivatives[104,105]. Although *o*-nitro-β-(dimethylamino)propiophenone and β-(dimethylamino)propiophenone[106] may formally react by a displacement with phthalimide ion[107], the likelihood of an elimination-addition reaction still remains.



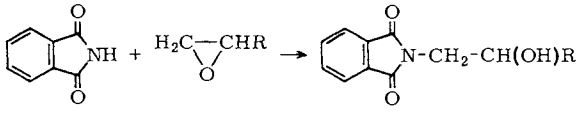
(11)



(12)

X = $N(CH_3)_2$, SC_2H_5

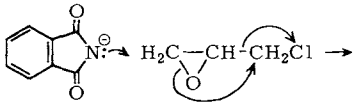
In 1917, *Gabriel* and *Ohle* demonstrated that epoxides could be used for direct alkylation of phthalimide itself[108]. In general, the product of reaction is the *N*-(2-hydroxyalkyl)phthalimide (see Scheme 2).



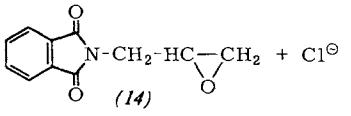
R = H, CH_3 [108], CH_2Cl [108,109], $CH_2OC_2H_5$, $CH_2OC_6H_5$ [110], $CH_2OC_6H_4NO_2$-(*p*) [111]

Scheme 2.

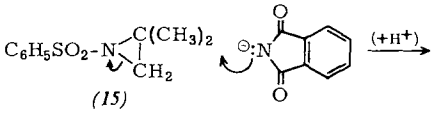
Although the reaction is usually conducted with phthalimide itself, it is evident that a small amount of phthalimide ion is required to initiate the process; pyridine can also be used as a base[111,112]. If potassium phthalimide is employed as the reagent, further reaction may occur. For example, epichlorohydrin *(13)* gives rise to the epoxy compound *(14)*[113], which may react further to give *N,N'*-(2-hydroxytrimethylene)-phthalimide as a by-product[11,109]. An analogous nitrogen heterocycle is the aziridine derivative (15), which on treatment with phthalimide and a catalytic amount of potassium phthalimide affords the sulfonamide *(16)*[114].



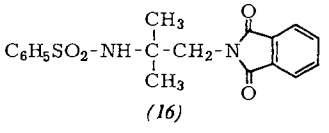
(13)



(14)



(15)



(16)

(Certain quaternary ammonium salts are also effective alkylating agents in the Gabriel Synthesis; these reactions are discussed in Section 2.1.4.[115].)

2.1.4. Neighboring Group Participation

In general, very few examples of genuine neighboring group effects in the Gabriel reaction have been investigated. Many cases where, in the light of present day knowledge[116], a participation would be expected to occur, are either qualitatively expressed as being fast, or no data concerning the relative rate of reaction are recorded. For example, compounds of the type

[100] *K. Yanagi* and *S. Akiyoshi*, J. org. Chemistry *24*, 1122 (1959).

[101] *M. Zaoral*, Chem. Listy *52*, 2338 (1958).

[102] *J. Bornstein, S. F. Bedell, P. E. Drummond*, and *C. L. Kosloski*, J. Amer. chem. Soc. *78*, 83 (1956).

[103] *J. H. Billman* and *R. V. Cash*, Proc. Indiana Acad. Sci. *63*, 108 (1954).

[104] *R. O. Atkinson*, J. chem. Soc. (London) *1954*, 1329.

[105] *F. Poppeldorf* and *S. J. Holt*, J. chem. Soc. (London) *1954*, 4094.

[106] *A. Butenandt* and *U. Renner*, Z. Naturforsch. *8b*, 454 (1953).

[107] *A. Butenandt, U. Renner, H. Henecka*, and *H. Timmler*, German Pat. 933339 (Sept. 22, 1955), Farbenfabriken Bayer AG.

[108] *S. Gabriel* and *H. Ohle*, Ber. dtsch. chem. Ges. *50*, 819 (1917).

[109] *E. Cherbuliez, B. Baehler, A. Yazgi*, and *J. Rabinowitz*, Helv. chim. Acta *43*, 1158 (1960).

[110] *W. R. Boon* and *T. Leigh*, J. chem. Soc. (London) *1951*, 1497.

[111] *V. Petrow* and *O. Stephenson*, J. Pharmacy Pharmacol. *5*, 359 (1953).

[112] *H. Ohle* and *E. Euler*, Ber. dtsch. chem. Ges. *69*, 1022 (1936).

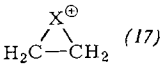
[113] a) *M. Weizmann* and *S. Malkowa*, Bull. Soc. chim. France (4) *47*, 356 (1930); b) *E. O. Titus, L. C. Craig, C. Golumbic, H. R. Mighton, I. M. Wempen*, and *R. C. Elderfield*, J. org. Chemistry *13*, 39 (1948).

[114] *V. I. Markow* and *S. I. Burmistrow*, Ž. obšč. Chem. *35*, 158 (1965).

[115] *M. S. Kharasch* and *C. F. Fuchs*, J. org. Chemistry *9*, 359 (1944).

[116] *B. Capon*, Quart. Rev. (chem. Soc. London) *18*, 45 (1964).

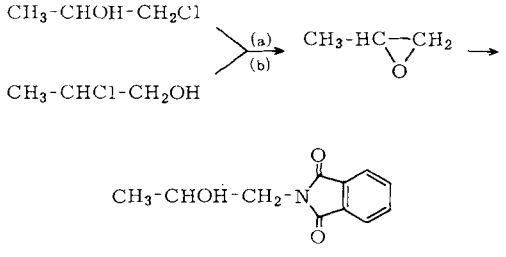
X–CH_2CH_2–Hal [where X is (substituted) nitrogen[117], sulfur[118], or possibly oxygen[29]], might be expected to react rapidly with phthalimide ion, as in fact do *N*-(2-bromoethyl)-*N*-methylaniline[119] and bis-(2-chloroethyl)amine[120]. The observed rapidity of reaction in these instances could well mean the involvement of intermediates of the general formula *(17)*, and the simple S_N2 mechanism may not apply.



(17)

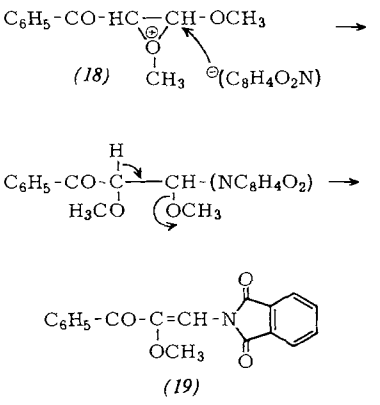
Halonium ions are also formally possible intermediates in certain cases of α,ω-dihalides. Participation may also arise with some substituted benzyl halides. Whereas the above examples must rest largely upon analogy, the following systems leave little doubt that participation is in operation.

Gabriel and *Ohle*[121] re-examined the product obtained from 2-chloro-1-propanol and potassium phthalimide, and found it to be identical with that from 1-chloro-2-propanol. The resulting material was identified as *N*-(2-hydroxypropyl)phthalimide, and it was concluded that the reaction proceeded *via* propylene oxide as an intermediate. Moreover, it was separately shown that phthalimide ion reacts with epoxides under similar conditions[108]. Even in the absence of further



information it is clear that reaction (a) involves neighboring group participation; this is probably true for reaction (b) also. However, not every reaction of a hydroxyalkyl halide with potassium phthalimide involves rearrangement even in cases where a cyclic ether intermediate may be formed; *e.g.* no rearrangement occurs in the case of 1-iodo-3-pentanol[122].

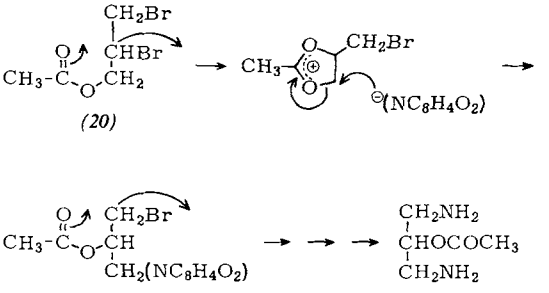
Reaction may also proceed *via* a three-membered ring in the case of 2,2′-diiododiethyl ether[29]. An interesting related example is provided by 2-bromo-3,3-dimethoxy-1-phenyl-1-propanone, which reacts readily with potassium phthalimide to give *(19)*[123]. Here, the oxonium salt *(18)* could function as intermediate.



(18)

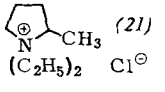
(19)

Philippi and *Seka*[124] examined the reaction between potassium phthalimide and 2,3-dibromopropyl acetate *(20)*, and suggested that 2 moles of potassium phthalimide were consumed, to give rise to the metathetical product, which on acid hydrolysis afforded the diamine. A parallel sequence with 2,3-dibromopropanol provided the same compound. However, *Fairburn* and *Cowdrey*[125] later examined the product from 1,3-dichloro-2-propanol, which they found to be identical with the compound examined by *Philippi* and *Seka*. In the light of present day knowledge, it is clear that the product is not the 1,2-diamine, but is the 1,3-analog, produced *via* at least one cyclic five-membered intermediate (cf. also[126, 73a]).



(20)

Similar effects are found in nitrogen- and sulfur-containing compounds; for instance, *N*,*N*-diethyl-*N*-(4-chloropentyl)amine gives only a trace of the metathetical product. The major component of the reaction with potassium phthalimide was found to be *N*-(4-diethylaminopentyl)phthalimide[115]. Here, the reaction was shown to proceed *via* the pyrrolidinium salt *(21)*.



(21)

Again, benzyl-2-chloro-2-cyanoethyl sulfide gave the metathetical product as the minor component of reaction, whereas the major product was found to be *N*-(2-benzylthio-2-cyanoethyl)phthalimide[127]. From the above examples of neighboring group

[117] *L. P. Walls*, J. chem. Soc. (London) *1934*, 104.

[118] *A. E. Cashmore* and *H. McCombie*, J. chem. Soc. (London) *1923*, 2884.

[119] *J. v. Braun*, *K. Heider*, and *E. Müller*, Ber. dtsch. chem. Ges. *51*, 273 (1918).

[120] *F. G. Mann*, J. chem. Soc. (London) *1934*, 461.

[121] *S. Gabriel* and *H. Ohle*, Ber. dtsch. chem. Ges. *50*, 804 (1917).

[122] *R. C. Elderfield* and *C. Ressler*, J. Amer. chem. Soc. *72*, 4059 (1950).

[123] *H. Shirahama* and *T. Matsuoto*, Bull. chem. Soc. Japan *38*, 1293 (1965).

[124] *E. Philippi* and *R. Seka*, Liebigs Ann. Chem. *433*, 88 (1923).

[125] *A. Fairburn* and *G. W. Cowdrey*, J. chem. Soc. (London) *1929*, 129.

[126] *G. W. Kilmer* and *H. McKennis*, J. biol. Chemistry *152*, 103 (1944).

[127] *K. D. Gundermann*, Liebigs Ann. Chem. *588*, 167 (1954).

participation, it can be seen that where such an effect is liable to occur, due caution must be placed in interpreting the course of the phthalimidation reaction.

2.2. Addition Reactions

In the presence of basic catalysts, phthalimide has been found to add readily to a variety of α,β-unsaturated systems [54, 128–134]. Such α,β-unsaturated com-

$$X{-}CH{=}CH_2 + C_8H_4O_2NH \rightarrow X{-}CH_2CH_2(NC_8H_4O_2)$$

X = CN, CHO, CO_2CH_3, $COCH_3$
$C_8H_4O_2NH$ = phthalimide

pounds may be intermediates in reactions of halogeno-compounds with potassium phthalimide. This elimination addition mechanism seems certain to apply in the reactions of phthalimide ion with γ-bromo-β-methoxybutyrophenone [135], and β-bromo-β,β-dinitroethylacetate [136] which give respectively 1-(2-oxo-2-phenylethyl)-*N*,*N*′-ethylenediphthalimide) and *N*-(2,2-dinitroethyl)phthalimide as the sodium salt.

A novel, but slow addition of *N*-bromophthalimide to isolated double bonds (which competes with allylic abstraction) has recently been reported [137]. Thus, 3,3-dimethyl-1-butene (CCl_4, reflux 120 hours) gives a 1:1 adduct [137]. However, it is reported that ethyl vinyl ether adds to *N*-bromophthalimide at 50 °C in two hours [138].

2.3. Condensation Reactions

Whereas secondary aliphatic amines and primary and secondary aromatic amines condense with formaldehyde and phthalimide to give *N*-alkyl (or *N*-aryl) aminomethylphthalimides [139], primary aliphatic amines give the *N*,*N*′-(alkylamino)dimethylenephthalimide. It is somewhat surprising that primary and secondary alcohols react with phthalimide to give condensation products, with the elimination of water [140]. A typical example is provided by the reaction of 3-morpholino-1-propanol, which gives a good yield of the corresponding phthalimido derivative. The high pressure condensation of phthalimide with acetone in the presence of hydrogen and an Al_2O_3/Pt catalyst, to give *N*-isopropylphthalimide [141] is presumably an example of reductive alkylation, and as such could be a new route to this type of primary amine.

3. Stage 2: Formation of the Primary Amine

3.1. Hydrolytic Methods

3.1.1. Acidic Hydrolysis

Hydrolysis of *N*-substituted phthalimides by hydrochloric acid has been widely practised in the Gabriel Synthesis. At first, fuming or concentrated acid was used, often at temperatures as high as 200 °C in sealed tubes (*e.g.* [4, 6, 7a, 9b, 22]). Such extreme conditions are probably unnecessary in many cases, and more acceptable conditions involve the use of concentrated or 20% acid at reflux temperature for several hours (*e.g.*, [16, 21, 55d, 68, 83, 113, 115]). In some cases, acetic acid is employed as co-solvent (*e.g.*, [8, 17, 29, 58a]). Typical examples of acid hydrolyses are provided by (2-mercaptoethyl)phthalimide [16, 142], *N*-acetonylphthalimide [143], *N*-(2-diethylaminoethyl)phthalimide [117], *N*,*N*′-iminodiethylenephthalimide [120], a variety of phthalimidoalkyl heterocycles [82, 144], tetraethyloxydiethyl-2,2-diphthalimido-2,2,2′2′-tetracarboxylate [145].

Similar hydrolytic procedures involve the use of hydrobromic (*e.g.*, [14, 15, 19, 40, 97, 146]), hydriodic (*e.g.*, [26, 47b]), and sulfuric (*e.g.*, [13b, 14, 23]) acids. The choice of acid is perhaps significant in the hydrolysis of *N*-(halogenoalkyl)phthalimides, when it is preferable to use the halogeno acid corresponding to the halogen atom in the side chain, so as to avoid the possibility of exchange [113a, 147–149]. The conversion

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of *N*-(4-bromobutyl)phthalimide to 4-iodobutylamine hydriodide by 55% hydriodic acid illustrates such exchange [150]. Sulfuric acid may also promote hydrolysis of the halogeno function in these cases [14].

A common complication is the hydrolysis of other functional groups, [13, 18–20, 36b, 39, 51c, 54, 69, 77, 124, 151, 152, 154–160]; although γ-lactone rings [153], and a number of ether bonds [145] survive. Moreover, electrophilic displacement of aryl iodine during acidic hydrolysis occurred in an unsuccessful attempt to prepare *p*-iodobenzylamine by the Gabriel method [161], and esterification of alcoholic functions may take place when concentrated halogen acids are used [73a, 108, 162]. Finally, some phthalimides resist acidic hydrolysis, or are decomposed under the reaction conditions (*e.g.*, [59c, 158, 163]). Whilst in such cases as amino-acid synthesis, the concomitant hydrolysis of *e.g.* ester and phthaloyl groups is convenient, the usefulness of acidic hydrolysis is otherwise limited by the susceptibility of other groups to attack.

3.1.2. Two Stage Hydrolysis

In this method the imide is hydrolyzed under alkaline conditions to the phthalamic acid, and the latter under acidic conditions to the amine. The first stage occurs very readily [50b, 164], and vigorous alkaline treatment is unnecessary unless other groups are to be hydrolyzed [51a]. Indeed, opening of the imide ring occurs to some extent under such mild conditions as are obtained in Schotten-Baumann acylations [165], and oxidations with $[Fe(CN)_6]^{3-}$ [160].

The second stage can usually be accomplished under milder acid conditions than those used for the substituted phthalimide [17, 166], a feature relevant where some of the more acid-sensitive groups are concerned [159a, 164a]. A major drawback is the loss of material through re-cyclization to the imide in the second stage (*e.g.*, [12, 159a, 160, 167]), though this can be recovered and re-cycled if necessary [168].

3.1.3. Alkaline Hydrolysis

Complete alkaline hydrolysis was advocated by *Putochin* [66, 169], particularly for the preparation of diaminoalkanes [170] from α,ω-diphthalimidoalkanes, and aminoalcohols [171] from ω-phthalimidoalkyl halides (with the reported exception of *N*-(4-chlorobutyl)-phthalimide which gives pyrrolidine [172]); the method was independently used for the preparation of certain allylic amines [61, 173]. More recent applications include syntheses of neopentyl type amines [41, 42]. The method has not been widely used, and is unsuitable for alkali sensitive molecules; for example, a Smiles rearrangement occurs during alkaline hydrolysis of *N*-[2-hydroxy-3-(*p*-nitrophenoxy)propyl]phthalimide [111], and its acetate [174].

3.2. Aminolytic and Hydrazinolytic Methods

3.2.1. Aminolysis

There were definite indications in early work on the Gabriel reaction that alkyl phthalimides reacted with primary amines with ring opening. Thus *Seitz* had noted *N*-phenylphthalimide as a product of reaction of *N*-(2-bromopropyl)phthalimide with aniline [31a], and *Ristenpart* had obtained the corresponding phthalimides from methylamine and ethylamine with *N*-(2-bromoethyl)phthalimide [175]. Alternative ring closure of such phthalamides will (a) regenerate the original phthalimide and (b) lead to the phthalimide derived from the amine reactant [176]. Such aminolytic reactions have led to complications in much of the synthetic antimalarial work based on reactions of *N*-(halogenoalkyl)phthalimides with primary amines [177]. Aminolysis of phthalimides either as the major [178] or

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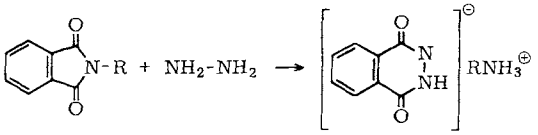
as the minor reaction [179] has been noted in other instances. Thalidomide (α-phthalimidoglutarimide) also apparently reacts with certain diamines, notably putrescine and spermidine, very readily [180].

3.2.2. Hydrazinolysis

Hydrazinolysis, introduced by *Ing* and *Manske* [25, 181] in 1926, has largely but not entirely superseded hydrolytic methods for accomplishing the second stage of the Gabriel Synthesis. In the original method, the substituted phthalimide was treated with hydrazine in hot ethanolic solution, when an uncharacterized (and incorrectly formulated) intermediate was readily produced. This was decomposed by heating with hydrochloric acid, when phthalhydrazide was precipitated and the amine hydrochloride usually remained in solution. The comparatively mild conditions of reaction and ease of separation of products presented obvious attractions and constituted an important advance, but it was not until nearly 20 years later that such technical innovations as conducting the hydrazinolysis [184] or acidic decomposition [70] stages at room temperature were employed in one or two cases, and that the intermediate was recognized as the amine salt of phthalhydrazide *(22)* [176b].



(22)

Manske applied the technique to the Curtius and related reactions [182]. Thus, substituted urethanes and ureas react with phthalic anhydride to give the corresponding phthalimides which can then be hydrazinolyzed; isocyanates can likewise be converted in two steps into the primary amine [183].

Inherent merits in the method were apparent in cases of difficult hydrolysis, for example *N*-(3-*p*-acetamidophenoxypropyl)phthalimide [163], and in avoidance of side reactions [159a, 185]. In 1946 *Mosher* [177] queried the necessity of boiling the hydrazinolysis intermediate with hydrochloric acid prior to isolation of the amine, and he illustrated an alternative procedure in which the intermediate was rendered alkaline and the expected amine isolated directly by solvent extraction. Independently, *Barber* and *Wragg* [176b] had recognized the hydrazinolysis intermediate in these reactions as *(22)*; formation of the amine or its hydrochloride, depending on whether *(22)* was treated with potassium hydroxide or hydrochloric acid, was thus immediately intelligible.

The use of an excess of hydrazine and the separation of the expected amine as the free base has been used occasionally [144b], and specifically recommended for some peptides where it would be otherwise difficult to remove residual hydrazine hydrochloride from the peptide hydrochloride [186]. However, the presence of residual hydrazine in some cases may pose problems of purification [187], requiring the use of *e.g.* salicylaldehyde for its removal [35, 73a].

The conditions available for hydrazinolysis are sufficiently mild to allow the preservation of many functional groups (*e.g.* [56, 73e, 189, 191, 192]), including most of those which are sensitive to hydrolysis. Thus, α,ω-aminoalkanenitriles are available through hydrazinolysis [193]. Carboxylic ester functions generally survive [49, 73b, 190], though there are indications that this group is somewhat sensitive [194], as indeed are xanthates [195].

Hydrazinolysis has frequently been practised in boiling ethanol, and under such conditions, reaction is likely to be fast. Nevertheless, reported reaction times vary considerably, and some quoted periods are probably excessive. Intermediate temperatures have also been employed [188], and occasionally necessitated by the sensitivity of another part of the molecule to attack, as for example with certain 2-aminothiazole derivatives [189]. Finally, hydrazinolysis has been accomplished for a considerable number of compounds, including peptides (which may be hydrazinolyzed in aqueous solution [190]), at room temperature [184, 191].

Moreover, the hydrazinolysis procedure cannot generally be applied to molecules containing (a) halogenoalkyl [196], or (b) aldehyde or ketonic groups, although the latter may often be protected by conversion into acetals and thioacetals [102, 197], or ketals and thioketals [132b, 198]. For molecules containing

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acid sensitive groups (*e.g.* acetal), isolation of the amine by basification may be necessary for the group to be preserved [102]. In this connection, use of an excess of hydrazine to permit direct isolation of amines may be used [144b]. If the expected amine is base-sensitive, a carefully controlled hydrazinolysis followed by acidic work-up may provide the only possibility of isolation of the hydrochloride [111] (for examples see [165, 199]).

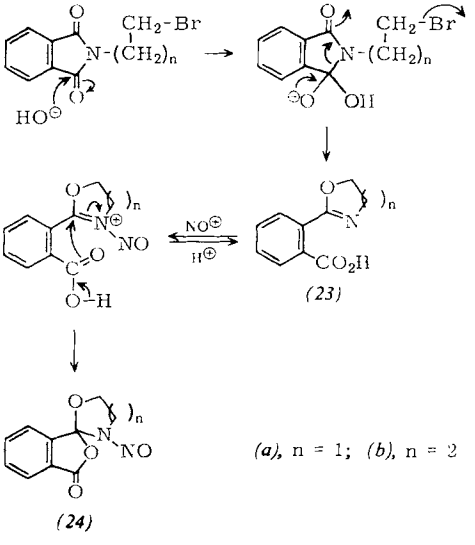
3.2.3. Phenylhydrazinolysis

Phenylhydrazinolysis was introduced for removing phthaloyl groups in one stage, particularly from peptide derivatives [200], so avoiding the final acid treatment of the Ing-Manske hydrazinolysis procedure. The technique has not been widely used and has been reported as unsuccessful when applied to *cis*-2-butenylphthalimide [56a] and *N*-(5-sulfamoyl-2-thienyl)-phthalimide [201]; the last compound is reported to suffer decomposition on attempted hydrazinolysis.

3.3. Neighboring Group Participation

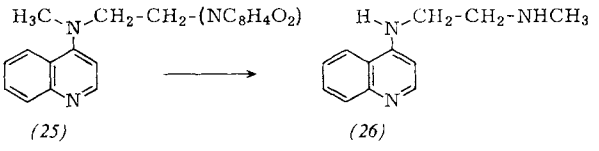
Neighboring group participation effects are observable in the alkaline hydrolysis of *N*-(2-bromoethyl)- and *N*-(3-bromopropyl)phthalimide, in which the *N*-nitroso compounds *(24a)* and *(24b)* resp. are formed [203]. *Gabriel* postulated the formation of intermediate products having 8- and 9-membered rings [202] respectively. These reactions have recently been reinvestigated, and the intermediate products recognized as the oxazolene *(23a)* and 1,3-oxazine derivative *(23b)* respectively, presumably in the zwitterionic form.

Similar considerations probably apply for example, in the reaction of *N*-(2-bromoethyl)phthalimide with



potassium pyrrole with subsequent hydrazinolysis, which leads not to *N*-(2-aminoethyl)pyrrole [204] but to pyrrole itself and a product that may be equated with that subsequently obtained by hydrazinolysis of *(23a)* [203a]. This apparently anomalous result is readily explained by assuming that pyrrole anion, like hydroxide ion, reacts with the phthalimide to give an intermediate product, which then reacts with hydrazine in the expected way (cf. also [205]).

Artefacts are frequently obtained in hydrolysis and hydrazinolysis reactions where the generated primary amino group can interact with other functional groups in the molecule. Examples are provided by the formation of pyrrolene derivatives in (a) the acidic hydrolysis of *N*-(4-oxo-4-phenylbutyl)phthalimide [154]



(25) *(26)*

and (b) the hydrazinolysis of methyl 3-phthalimidocrotonate [206]; formation of analogous six-membered rings has also been noted [207]. The involvement of cyclic transition states may also lead to rearranged products. Thus the alkaline hydrolysis of *N*-[2-hydroxy-3-(*p*-nitrophenoxy)propyl]phthalimide involves an O→N aryl migration [111, 174]; O→N acetyl migration has been noted during hydrazinolysis and work-up of 3-methoxy-1-(*p*-nitrophenyl)-2-phthalimidopropyl acetate [208]. An example of N→N migration is afforded by the reaction *(25)*→*(26)* [164d].

4. Conclusions

Finally a few limitations of the Gabriel Synthesis should be noted. For example, *sym*-dichloroacetone is reported to react with potassium phthalimide to give phthalimide itself [209]. Difficulties have also been noted with certain pentaerythritol derivatives such as *(27)*, which, with potassium phthalimide also produces phthalimide and probably an oxetane [73a]. Further *(28)* gives an unidentified compound rather than the metathetical product [210].

$(YCH_2)_2C(CH_2X)_2$ *(27)*: X=Br, Y=OH
(28): X=Y=Br, I

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Most of the reported failures in the second stage of the synthesis are largely concerned with the inherent instability of either the generated amine, or some other sensitive part of the molecule. Examples of the former category are encountered in systems of the type *(29)–(31)*, which do not survive hydrolysis or hydrazinolysis, and usually decompose *inter alia* to formaldehyde and ammonia. The latter group includes some examples of *N*-thienylphthalimides, in which the heterocyclic ring decomposes, and gives rise to hydrogen sulfide [201].

$X(CH_2\text{–}NC_8H_4O_2)_n$

(29) X = RS–; n = 1 [211]
(30) X = N; n = 3 [212]
(31) X = NO_2; n = 1 [213]

Despite these minor limitations, the Gabriel Synthesis will doubtless continue to be exploited for the preparation of primary amines, but more complete understanding of the reactions involved must await further mechanistic studies.

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Kinetic Studies on Substitution Reactions of Carbonylmetal Complexes [1]

BY H. WERNER [*]

Kinetic studies of substitution reactions of carbonylmetals and of carbonylmetal derivatives in which other ligands (n or π donors) besides CO are bound to the metal atom have recently attracted great interest, and the results of these investigations throw a new light on theoretical and preparative problems. The substitution mechanism is determined mainly by steric and electronic factors.

1. Introduction

It is known from the classic work of *Hieber* and his school that metal carbonyls undergo substitution reactions of type (1) when thermal or photochemical

$$M(CO)_x + yL \rightarrow M(CO)_zL_y + (x-z)CO \qquad (1)$$

energy is supplied. The ligand L may be varied within wide limits, and may be either an n donor (*e.g.* amine, phosphine, arsine, stibine, isocyanide, thioether) or a π donor (*e.g.* olefin, aromatic compound). Carbonylmetal derivatives in which one or more other groups X (*e.g.* NO, H, halogen, alkyl) are bound to the metal atom besides CO also react readily with donors L. The course of the substitution is in many cases determined by the nature of the non-CO ligands, their donor and acceptor properties being particularly important.

General observations of this type were until recently based almost exclusively on the results of preparative studies [2]. Kinetic studies on the mechanism of substitutions of carbonylmetal compounds have only recently been initiated, and are now being carried out in rapidly growing numbers.

The first study in this field was reported in 1959 and was concerned with the kinetics of the reactions of carbonylphosphinenickel complexes which are important in industry [3]. This report referred to the use of spectrophotometric methods for the determination of the concentration of carbonylmetals, and so provided a decisive stimulus to further development.

Photochemical reactions will not be discussed in the present article, since a review of this topic has recently been published [4].

2. Possible Reaction Courses

There are two possible courses for the reaction [eq. (1)] of a carbonylmetal $M(CO)_x$ with a donor L (y = 1, $z = x-1$).

(a) The first step is the cleavage of an M–CO bond to form an intermediate in which the coordination number has been reduced by 1, which then reacts with L.

$$M(CO)_x \xrightarrow[-CO]{} M(CO)_{x-1} \xrightarrow{+L} M(CO)_{x-1}L \qquad (2)$$

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[1] *H. Werner*, Habilitationsschrift, Technische Hochschule München, 1966.

[2] For a review, see *T. A. Manuel*, Advances organometallic Chem. *3*, 181 (1965).

[3] *L. S. Meriwether* and *M. L. Fiene*, J. Amer. chem. Soc. *81*, 4200 (1959).

[4] *W. Strohmeier*, Angew. Chem. *76*, 873 (1964); Angew. Chem. internat. Edit. *3*, 730 (1964); see also *E. O. Fischer* and *M. Herberhold*, Experientia, Suppl. *1964*, 259.

(b) The first step is a direct attack of L on the central atom of the original complex to give an activated complex and possibly also an intermediate in which the coordination number has been increased by 1, and from which the reaction product is formed by loss of a CO group.

$$M(CO)_x \xrightarrow{+L} M(CO)_xL \xrightarrow[-CO]{} M(CO)_{x-1}L \qquad (3)$$

If the first step is rate-determining, as is usual in substitution reactions of complexes, the rate equations are:

$$\text{for (a)} \quad \frac{d[M(CO)_{x-1}L]}{dt} = k[M(CO)_x] \qquad (4)$$

$$\text{for (b)} \quad \frac{d[M(CO)_{x-1}L]}{dt} = k[M(CO)_x]\,[L] \qquad (5)$$

According to the nomenclature established by *Ingold*[5], a reaction course of the type (a) is an S_N1 mechanism, while course (b) is S_N2.

Following a suggestion by *Langford* and *Gray*[6], an S_N1 mechanism might also be called a D mechanism ("dissociative mechanism") and an S_N2 an A mechanism ("associative mechanism"). This terminology avoids the use of the word "nucleophilic", which seems undesirable in view of the fact that very many donors L have not only electron donor, but also electron acceptor properties as complex ligands.

The substitution reactions of carbonylmetal compounds do not always obey the simple rate equations (4) and (5). It has been found that several parallel steps as well as several consecutive steps can be rate-determining. Such processes give rate equations of fractional order, the interpretation of which will be explained with the aid of some examples in Section 4.

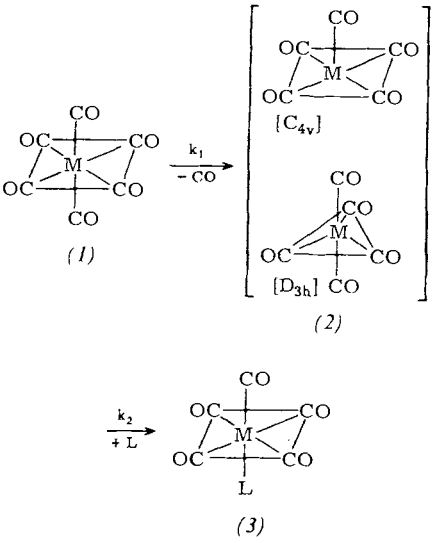
3. Methods of Investigation

As was mentioned above, the concentration determinations required for the calculation of rate data are mainly based on spectrophotometric methods in the reactions of carbonylmetal compounds. IR spectroscopy is particularly widely used, since the CO stretching frequencies are generally very intense, and so reflect accurately even relatively small concentration changes during the reaction. Absorption measurements in the visible region have also proved useful (*e.g.* in the reactions of the colorless hexacarbonylmetals, which generally lead to colored substitution products). In some cases the rate of evolution of CO was also followed by gas-volumetric measurements; small quantities of CO, however, are difficult to detect. With labeled donors L (*e.g.* ^{14}CO or $^{14}C_6H_6$), the substitution can be followed in the gas phase or in solution by the decrease in activity. Rate equations can be obtained from these investigations with the aid of *McKay*'s equations[7].

4. Results of Kinetic Studies

4.1. Carbonylmetals

Among the compounds $M(CO)_x$, those most extensively used in kinetic studies are the hexacarbonyls of chromium, molybdenum, and tungsten, owing to their chemical properties. Unlike other carbonylmetals, such as $Fe(CO)_5$, $Co_2(CO)_8$, and $Mn_2(CO)_{10}$, they never undergo disproportionation on reaction with n donors, but are always substituted. Extensive investigations by various research groups have shown that both the exchange reactions of $M(CO)_6$ *(1)* with ^{14}CO in the gas phase[8–10] and in solution[11] and the reactions with unidentate and multidentate n and π donors[12–16] proceed by an S_N1 mechanism ($k_2 > k_1$) over a wide concentration range.



(6)

The structures discussed for the intermediates *(2)* formed in the rate-determining step are the tetragonal pyramid and the trigonal bipyramid. The molecules $M(CO)_5$ formed on irradiation of *(1)* at −180 °C in a matrix have symmetry C_{4v} according to their IR spectra[17].

In the presence of a large excess of phosphine, the rate of formation of pentacarbonylphosphinemetals $M(CO)_5PR_3$ *(4)* from *(1)* satisfies the equation

$$\frac{d[(4)]}{dt} = k[(1)] + k'[(1)]\,[PR_3] \qquad (7)$$

The second order term, the importance of which increases with the size of the central atom[18,19], can be

[5] *C. K. Ingold*: Structure and Mechanism in Organic Chemistry. 1st Edit., Cornell University Press, Ithaca 1953, Chapters 5 and 7.

[6] *C. H. Langford* and *H. B. Gray*: Ligand Substitution Processes. 1st Edit., W. A. Benjamin, Inc., New York 1965, Chapter 1.

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[10] *G. Cetini* and *O. Gambino*, Atti Accad. Sci. Torino, I, Cl. Sci. fisiche, mat. natur *97*, 1197 (1963).

[11] *G. Cetini*, *O. Gambino*, *G. A. Vaglio*, and *M. Valle*, private communication.

[12] *H. Werner* and *R. Prinz*, Angew. Chem. *77*, 1041 (1965); Angew. Chem. internat. Edit. *4*, 994 (1965).

[13] *D. A. Brown*, *N. J. Gogan*, and *H. Sloan*, J. chem. Soc. (London) *1965*, 6873.

[14] *H. Werner* and *R. Prinz*, J. organometallic Chem. *5*, 79 (1966).

[15] *H. Werner*, J. organometallic Chem. *5*, 100 (1966).

[16] *H. Werner* and *R. Prinz*, Chem. Ber. *99*, 3582 (1966).

[17] *I. W. Stolz*, *G. R. Dobson*, and *R. K. Sheline*, J. Amer. chem. Soc. *85*, 1014 (1963).

[18] *R. J. Angelici* and *J. R. Graham*, J. Amer. chem. Soc. *88*, 3658 (1966).

[19] *J. R. Graham* and *R. J. Angelici*, Inorg. Chem. *6*, 2082 (1967).

explained by a direct attack of the phosphine on the metal atom or on the C atom of a CO group.

In the reactions of hexacarbonylmetals *(1)* with multidentate donors L, the compounds *(3)* are formed as intermediates. The rate of further intramolecular substitution

$$(3) \xrightarrow[-CO]{k_3} M(CO)_4L \quad \text{(L bidentate)} \tag{8}$$

$$(3) \xrightarrow[-CO]{k_3} M(CO)_4L \xrightarrow[-CO]{k_4} M(CO)_3L \quad \text{(L terdentate)} \tag{9}$$

$$(3) \xrightarrow[-CO]{k_3} M(CO)_4L \xrightarrow[-CO]{k_4} M(CO)_3L \xrightarrow[-CO]{k_5} M(CO)_2L \quad \text{(L quaterdentate)} \tag{10}$$

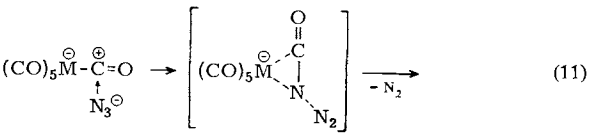
is strongly dependent on the nature of L[16]. For example, if L is a diamine, $k_3 > k_1$; in this case there is no evidence of the existence of intermediates under the conditions used. If on the other hand L is a diphosphine, k_1 and k_3 are comparable in magnitude[20]. With $L = C_2H_4[P(C_6H_5)_2]_2$, it is possible in the case of M = Mo to isolate a compound *(3)* in which only one of the two phosphorus atoms of the diphosphine is coordinately bound to the metal atom[21]; the formation of the chelate complex $M(CO)_4L$, as expected, proceeds with first order kinetics in this case.

The activation energies of the substitution reactions of the hexacarbonylmetals increase in the order Mo < Cr < W (see Table 1). This increase parallels the increase in the force constants for the M–C stretching vibration of the compounds $M(CO)_6$, which are 1.81, 2.03, and 2.15 mdyn/Å for M = Mo, Cr, and W respectively[22]. The kinetic measurements thus confirm numerically the experimentally observed higher reactivity of $Mo(CO)_6$ as compared with $Cr(CO)_6$ and $W(CO)_6$, and so confirm the general experience that complexes of elements of the second transition series are very often more reactive than the corresponding compounds of elements of the first and third transition series.

Table 1. Activation energies E_a of substitution reactions of the hexacarbonylmetals (kcal/mole).

	Cr	Mo	W	Ref.
$M(CO)_6$ + ^{14}CO (Vapor)	39.3	30.8	40.4	[8–10]
$M(CO)_6$ + ^{14}CO (Decalin)	39.0	31.6	40.6	[11]
$M(CO)_6$ + $P(C_4H_9)_3$ (Decalin)	40.8	32.3	40.5	[19]
$M(CO)_6$ + $P(C_6H_5)_3$ (*n*-Decane)	38.7	30.8	39.6	[16]
$M(CO)_6$ + C_7H_8 (*n*-Decane)	39.0	30.0		[14, 23]

$Cr(CO)_6$ and $W(CO)_6$ react with N_3^- without elimination of CO to form the anions $[M(CO)_5NCO]^-$ (M=Cr, W). Some recent investigations[24] have shown that the rate-determining step is bimolecular, and is probably a direct nucleophilic attack of the azide ion on the C atom of a CO group. The subsequent steps, *i.e.* removal of N_2 and formation of the M–N bond, appear to be synchronous as is assumed in the Curtius azide degradation.



$$[(CO)_5M\text{-}N{=}C{=}O]^-$$

A similar primary step must also be assumed for the reactions of *(1)* with carbanions[25], and the Hieber base reaction probably also begins with a nucleophilic attack of an OH^- ion on the CO group of the carbonylmetal[26].

$Fe(CO)_5$ is practically inert to labeled carbon monoxide[27,28] and phosphines[29] below its decomposition point (90 °C). In the presence of CF_3COOH, however, rapid exchange occurs with ^{14}CO even at −20 °C[30], with preferential substitution of the axial CO ligands. Since the exchange rate is independent of the ^{14}CO concentration, the rate-determining step must be assumed to be the removal of one CO from the protonated intermediate complex. The reactions of $Fe(CO)_5$ with nitrogen donors, such as *n*-butylamine or pyrrolidine, probably proceed by primary attack of the donor on the C atom of a CO group[31].

In contrast to $M(CO)_6$ and $Fe(CO)_5$, $Ni(CO)_4$ *(5)* reacts with ^{14}CO[28] and $P(C_6H_5)_3$[32] even at 0 °C in toluene. Both reactions are first order with respect to the $Ni(CO)_4$ concentration and zeroth order with respect to the ligand concentration. Nevertheless, the mechanisms of these reactions do not appear to be the same, since the activation parameters are quite different[33] (*(5)* + ^{14}CO in toluene: $\Delta H^{\neq} = 12$ kcal/mole, $\Delta S^{\neq} = -26$ cal/mole·deg; *(5)* + $P(C_6H_5)_3$ in toluene: $\Delta H^{\neq} = 21$ kcal/mole, $\Delta S^{\neq} = +2$ cal/mole·deg). The strongly negative activation entropy for the CO exchange is particularly surprising, and, according to general experience, is evidence against a "normal" S_N1 mechanism. The first step in this case may be, not a dissociation process, but a rearrangement of the tetrahedral $Ni(CO)_4$ to the square planar structure[34,34a].

[20] *H. Werner* and *R. Prinz*, Proc. int. Conf. Coordinat. Chem. *1966*, 9.

[21] *H. Werner* and *W. D. Fleischmann*, unpublished, see [1].

[22] *L. H. Jones* in *B. Jezowska-Trzebiatowska*: Theory and Structure of Complex Compounds. Pergamon Press, London 1964, p. 45.

[23] *H. Werner* and *R. Prinz*, unpublished.

[24] *W. Beck, H. Werner, H. Engelmann*, and *H. S. Smedal*, Chem. Ber. *101*, 2143 (1968).

[25] *E. O. Fischer* and *A. Maasböl*, Chem. Ber. *100*, 2445 (1967).

[26] *T. Kruck, M. Höfler*, and *M. Noack*, Chem. Ber. *99*, 1153 (1966).

[27] *D. F. Keeley* and *R. E. Johnson*, J. inorg. nuclear Chem. *11*, 33 (1959).

[28] *F. Basolo* and *A. W. Wojcicki*, J. Amer. chem. Soc. *83*, 520 (1961).

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[30] *F. Basolo, A. T. Brault*, and *A. J. Poe*, J. chem. Soc. (London) *1964*, 676.

[31] *W. F. Edgell* and *B. J. Bulkin*, J. Amer. chem. Soc. *88*, 4839 (1966).

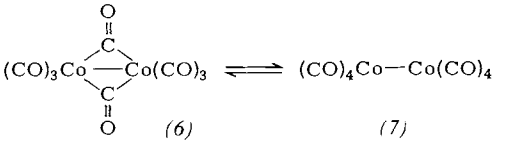
[32] *R. F. Heck*, J. Amer. chem. Soc. *85*, 657 (1963).

[33] *L. R. Kangas, R. F. Heck, P. M. Henry, S. Breitschaft, E. M. Thorsteinson*, and *F. Basolo*, J. Amer. chem. Soc. *88*, 2334 (1966).

[34] *S. Breitschaft* and *F. Basolo*, J. Amer. chem. Soc. *88*, 2702 (1966).

[34a] Note added in proof: For an explanation of the contradictory data, see *J. P. Day, F. Basolo, R. G. Pearson, L. F. Kangas*, and *P. M. Henry*, J. Amer. chem. Soc. *90*, 1925 (1968).

The reactions of $Co_2(CO)_8$ with labeled carbon monoxide [28, 34] and alkynes [35] is also thought to start with rearrangement of the complex, in this case with cleavage of one of the CO bridge bonds of *(6)*. This is supported by the results of IR measurements, which indicate that *(6)* and *(7)* exist in equilibrium in solution [36].



(6) *(7)*

$Co_2(CO)_8$ reacts much more rapidly with triphenylphosphine than with ^{14}CO or alkynes. The reaction rate is independent of the phosphine concentration at a molar ratio $Co_2(CO)_8:P(C_6H_5)_3 \leqslant 1:2$, but is directly proportional to this concentration at molar ratios $> 1:2$ [32]. The substitution could proceed *via* a primary 1:1 adduct, the decomposition of which, with liberation of CO, is rate-determining (k_1 and $k_3 > k_2$).

$$Co_2(CO)_8 + P(C_6H_5)_3 \xrightarrow{k_1} Co_2(CO)_8P(C_6H_5)_3 \xrightarrow[-CO]{k_2}$$

$$Co_2(CO)_7P(C_6H_5)_3 \xrightarrow[+P(C_6H_5)_3]{k_3} [Co(CO)_3[P(C_6H_5)_3]_2]^{\oplus}[Co(CO)_4]^{\ominus} \quad (12)$$

Different authors have different views on the mechanism of the reaction of $Mn_2(CO)_{10}$ with triphenylphosphine, which proceeds in accordance with a first order rate equation. Whereas *Wawersik* and *Basolo* [37] explain the formation of the substituted compounds by a reaction sequence:

$$Mn_2(CO)_{10} \underset{-CO}{\xrightarrow{k_1}} Mn_2(CO)_9 \xrightarrow[+P(C_6H_5)_3]{k_2}$$

$$Mn_2(CO)_9P(C_6H_5)_3 \underset{-CO}{\xrightarrow{k_3}} Mn_2(CO)_8P(C_6H_5)_3$$

$$\xrightarrow[+P(C_6H_5)_3]{k_4} Mn_2(CO)_8[P(C_6H_5)_3]_2 \quad (13)$$

($k_1 < k_2$), *Hopgood* and *Poe* [38] believe that the first step is homolysis of the Mn–Mn bond to give $Mn(CO)_5$ radicals, which can either recombine, decompose after diffusion out of the solvent cage, or react with the phosphine.

$$Mn_2(CO)_{10} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [2 \cdot Mn(CO)_5]$$

$$[2 \cdot Mn(CO)_5] \xrightarrow{k_2} 2 \cdot Mn(CO)_5 \xrightarrow{\text{fast}} 2\,Mn + 10\,CO$$

$$[2 \cdot Mn(CO)_5] + P(C_6H_5)_3 \xrightarrow{k_3} \text{products} \quad (14)$$

The activation energy of 37 kcal/mole, which is considerably higher than the dissociation energy found for the Mn–Mn bond by mass spectrometry (19 kcal/mole), favors the first of the above suggestions. In the reactions of $Mn_2(CO)_{10}$ with amines, which lead *via* $[Mn(CO)_5L]^-[Mn(CO)_5]^-$ to the series of compounds $[MnL_6]^{2+}[Mn(CO)_5]_2^-$ (L = amine) [39], the first step in polar solvents is assumed to be amine-assisted heterolysis of the Mn–Mn bond [40].

In the dodecacarbonyls of iron, ruthenium, and osmium, all the CO groups are exchangeable with ^{14}CO; the exchange rate is independent of the ^{14}CO concentration [41, 42]. In the case of $Fe_3(CO)_{12}$, which contains both terminal and bridge CO ligands, a continuous rapid interconversion of the Fe–CO bonds is postulated to explain the kinetic data.

4.2. Carbonylnitrosylmetals

In contrast to the substitution reactions of $Ni(CO)_4$ *(5)*, the reactions of the "pseudo-tetracarbonylnickels" $Co(CO)_3NO$ *(8)*, $Fe(CO)_2(NO)_2$ *(9)*, and $Mn(CO)(NO)_3$ *(10)* (which also have tetrahedral configurations) with n donors L proceed by an S_N2 mechanism [32, 43–45]. A trigonal-bipyramidal arrangement of the ligands is conceivable in the transition state.

$$(8) + L \rightarrow Co(CO)_2(NO)L + CO \quad (15)$$

$$(9) + L \rightarrow Fe(CO)(NO)_2L + CO \quad (16)$$

$$(10) + L \rightarrow Mn(NO)_3L + CO \quad (17)$$

The reactions corresponding to equations (15) to (17) are particularly fast when L is readily polarizable; this means that the metal atoms in the carbonylnitrosylmetals may be regarded as typical "soft" acids [46]. In the reactions of *(8)* with $L = PR_3$, there is an almost linear relation between the second order rate constants and the polarizability of the phosphine [43].

(8) and *(9)* react with 1,2-bis(diphenylphosphino)-ethane (P–P) in tetrahydrofuran or toluene at 25 °C to form first the intermediates *(11)* and *(13)*, which can be detected by IR spectroscopy, and which lose CO at somewhat higher temperatures to form the chelate complexes *(12)* and *(14)* [44]. The rate of the monosubstitution (k_1 or k_1') is first order with respect to the diphosphine concentration, while the rate of the second (k_2 or k_2') is independent of this concentration.

[35] *M. R. Tirpark, J. H. Wotiz*, and *C. A. Hollingworth*, J. Amer. chem. Soc. *80*, 4265 (1958).

[36] *K. Noack*, Spectrochim. Acta *19*, 1925 (1963); Helv. chim. Acta *47*, 1064 (1964).

[37] *H. Wawersik* and *F. Basolo*, personal communication; see also *H. Wawersik*, Dissertation, Technische Hochschule München, 1967.

[38] *D. Hopgood* and *A. J. Poe*, Chem. Commun. *1966*, 831.

[39] *W. Hieber, W. Beck*, and *G. Zeitler*, Angew. Chem. *73*, 364 (1961).

[40] *H. Werner* and *E. Deckelmann*, unpublished.

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[43] *E. M. Thorsteinson* and *F. Basolo*, J. Amer. chem. Soc. *88*, 3929 (1966).

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[45] *H. Wawersik* and *F. Basolo*, J. Amer. chem. Soc. *89*, 4626 (1967).

[46] For the concept of "hard and soft acids and bases", see *R. G. Pearson*, J. Amer. chem. Soc. *85*, 3533 (1963); Science (Washington) *151*, 172 (1966); *R. G. Pearson* and *J. Songstad*, J. Amer. chem. Soc. *89*, 1827 (1967); *H. Werner*, Chemie in unserer Zeit *1*, 135 (1967); *B. Saville*, Angew. Chem. *79*, 966 (1967); Angew. Chem. internat. Edit. *6*, 928 (1967).

$$(8) + \text{P–P} \xrightarrow[-CO]{k_1} \underset{(11)}{Co(CO)_2(NO)P\text{–}P} \xrightarrow[-CO]{k_2} \underset{(12)}{Co(CO)(NO)P\text{–}P} \quad (18)$$

$$(9) + \text{P–P} \xrightarrow[-CO]{k_1'} \underset{(13)}{Fe(CO)(NO)_2P\text{–}P} \xrightarrow[-CO]{k_2'} \underset{(14)}{Fe(NO)_2P\text{–}P} \quad (19)$$

The reactions of the bridge complexes $P\text{–}P[Co(CO)_2NO]_2$ and $P\text{–}P[Fe(CO)(NO)_2]_2$ with P–P to form *(12)* and *(14)* follow a second order rate equation [44]. This is also true of the exchange reaction:

$$Co(CO)_2(NO)L + L' \rightarrow Co(CO)_2(NO)L' + L \quad (20)$$

The reaction rate in this case is determined mainly by the nature of the ligand L, and increases in the order $P(C_6H_5)_3 < P(OCH_3)_3 < P(OC_6H_5)_3 < As(C_6H_5)_3 \approx P(OCH_2)_3CCH_3 < CNC_6H_{11}$ for a given L'. For the same complex $Co(CO)_2(NO)L$, the reactivity of L' increases in the order $P(OC_6H_5)_3 < P(C_6H_5)_3 < P(C_6H_5)_2C_2H_5 < P(n\text{-}C_4H_9)_3$ [47]. The substitution of a second CO group (eq. (21)) proceeds more slowly in every case than the ligand exchange (20).

$$Co(CO)_2(NO)L + L' \rightarrow Co(CO)(NO)LL' + CO \quad (21)$$

The difference in the reaction behavior of carbonylmetals and carbonylnitrosylmetals can be seen not only on comparison of $Ni(CO)_4$ with $Co(CO)_3NO$ but also on comparison of $Fe(CO)_5$ with $Mn(CO)_4NO$ *(15)*. The compound *(15)*, which is the first in the series of "pseudo-pentacarbonylirons", reacts with phosphines, phosphites, and arsines at $\approx$ 50–70 °C by an S_N2 mechanism [45].

$$\underset{(15)}{Mn(CO)_4NO} \xrightarrow{+L} Mn(CO)_4(NO)L \xrightarrow[-CO]{} Mn(CO)_3(NO)L \quad (22)$$

The relatively low activation energy (*(15)* + $P(C_6H_5)_3$ in *p*-xylene: E_a = 20 kcal/mole), as in the case of $Co(CO)_3NO$ (*(8)* + $P(C_6H_5)_3$ in toluene: E_a = 15 kcal/mole), indicates that in these reactions the addition of a ligand L to the original complex is favored over the dissociation of an M–CO bond. This is probably because the metal atoms in the carbonylnitrosylmetals carry a formal negative charge as indicated in resonance formula *(16)*, with the result that M–CO backbonding is strengthened and dissociation therefore becomes more difficult. This argument is supported by the values of the force constants of the M–C stretching vibrations of $Ni(CO)_4$ (2.1 mdyn/Å) and $Co(CO)_3NO$ (2.92 mdyn/Å) [48,49].

$$\underset{(16)}{\overset{\ominus}{M}=\overset{\oplus}{N}=O} \leftrightarrow \underset{(17)}{M\text{–}\ddot{N}=O}$$

The resonance formula *(17)*, which makes little contribution to the ground state of the carbonylnitrosylmetals, could be more important in the transition state of a bimolecular reaction step. In *(17)*, the metal has a free low-energy orbital, which could explain why the addition of a donor ligand is favored.

4.3. Carbonylmetal Hydrides

The carbonylmetal hydrides $HMn(CO)_5$ and $HCo(CO)_4$ undergo substitution reactions much more readily than the corresponding metal carbonyls $Mn_2(CO)_{10}$ and $Co_2(CO)_8$. The rate of the exchange is independent

$$HMn(CO)_5 + 5\,{}^{14}CO \rightarrow HMn({}^{14}CO)_5 + 5\,CO \quad (23)$$

of the ^{14}CO concentration [30], and is much lower than the rate of reaction of the isoelectronic $[HFe(CO)_5]^+$ cation with labeled carbon monoxide, indicating a higher M=CO double bond character in the uncharged pentacarbonylhydridomanganese. The reactions

$$HCo(CO)_4 + P(C_6H_5)_3 \rightarrow HCo(CO)_3P(C_6H_5)_3 + CO \quad (24)$$

$$HCo(CO)_3L + L \rightarrow HCo(CO)_2L_2 + CO \quad (L = PO_3C_6H_{11}) \quad (25)$$

probably also follow an S_N1 mechanism [32, 50]. The formation of an intermediate $HCo(CO)_3$ by loss of CO from $HCo(CO)_4$ was assumed earlier in connection with studies on the mechanism of hydroformylation (oxo synthesis) [51].

4.4. Carbonylmetal Halides

The carbonylmetal halides used so far in kinetic studies nearly all have octahedral structures. It is therefore not surprising that their substitutions proceed mainly by an S_N1 mechanism.

The following reactions of pentacarbonylmanganese and pentacarbonylrhenium halides have recently been particularly extensively studied.

$$\begin{array}{ccc} M({}^{14}CO)_5X & & M(CO)_3LL'X \\ {\scriptstyle +\,{}^{14}CO}\uparrow{\scriptstyle (b)} & & {\scriptstyle +\,L'}\uparrow{\scriptstyle (e)} \\ M(CO)_5X & \xrightarrow[(a)]{+L} & M(CO)_4LX \\ {\scriptstyle (c)}\searrow & & \nearrow{\scriptstyle +\,L\ (d)} \\ & [M(CO)_4X]_2 & \end{array} \quad (26)$$

The rate of the monosubstitution (26a) is independent of the ligand concentration [L], but depends on X; at a given temperature it increases in the order X = I <

[47] *E. M. Thorsteinson* and *F. Basolo*, Inorg. Chem. *5*, 1691 (1966).

[48] *L. H. Jones*, J. chem. Physics *28*, 1215 (1958).

[49] *R. S. McDowell, W. H. Horrocks jr.*, and *J. T. Yates*, J. chem. Physics *34*, 530 (1961).

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Br < Cl [52-54, 54a]. This variation of the reactivity is probably due to the differences in the electronegativities of the halogens; the greater the electronegativity, the smaller is the degree of M–CO back-bonding and hence the strength of the M–CO bond. There is as yet no satisfactory explanation for the contrary trends shown by the activation energies of the first step

$$M(CO)_5X \rightarrow M(CO)_4X + CO \qquad (27)$$

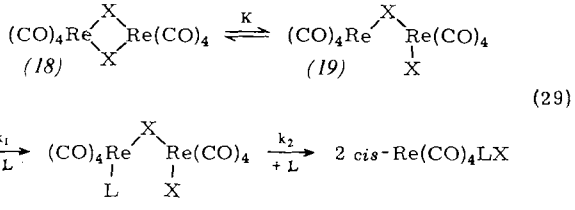
postulated for the substitution. For M – Mn, the E_a values increase with increasing atomic weight of the halogen [53], while for M = Re they decrease [54]. The pentacarbonylmanganese halides react appreciably faster than the corresponding rhenium compounds at the same temperature. In the exchange reaction of $Mn(CO)_5X$ with ^{14}CO in accordance with equation (26b), it appears, contrary to earlier findings [52], that the exchange rate for the four equatorial CO groups differs only slightly from that for the axial CO group [55].

The formation of the dinuclear complexes $[M(CO)_4X]_2$ (26c), like the substitution (26a), probably proceeds *via* an $M(CO)_4X$ intermediate [54]. The rate of the dimerization surprisingly changes with the concentration of the $M(CO)_5X$ solutions, just as is found in the reactions of hexacarbonylmetals with aromatic π donors [14]. The existence of equilibria is probably the deciding factor in both cases.

The reactions of the dimeric tetracarbonylrhenium halides *(18)* with $P(C_6H_5)_3$ and with pyridine and pyridine derivatives (eq. (26d)) obey a second order rate equation [56].

$$\frac{d[Re(CO)_4LX]}{dt} = k[(Re(CO)_4X)_2][L] \qquad (28)$$

The rate constant k is found to be approximately a function of the basicity of the substituent L. It is thought that either the first step is the formation of an intermediate with a 7-coordinate metal atom, or the bimolecular rate-determining step (k_1) is preceded by a rapid equilibrium between *(18)* and *(19)* [56] ($k_2 > k_1$).



(29)

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[53] *R. J. Angelici* and *F. Basolo*, J. Amer. chem. Soc. *84*, 2495 (1962).

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The fact that only *cis*-$Re(CO)_4LX$ is formed is plausibly explained by the reaction sequence indicated.

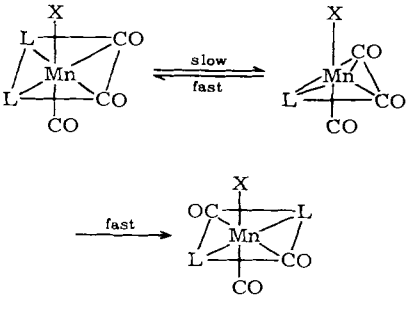
$$[Mn(CO)_4X]_2 + 4\,L \rightarrow \underset{(20)}{2\,Mn(CO)_3L_2X} + 2\,CO \qquad (30)$$

The reaction (30) (L = pyridine, γ-picoline, 3-chloropyridine) gives an additive rate equation [57]:

$$\frac{d[(20)]}{dt} = k'[(Mn(CO)_4X)_2] + k''[(Mn(CO)_4X)_2][L] \qquad (31)$$

The simultaneous occurrence of dissociation (k') and addition (k'') in this case could be explained by the fact that the Mn–X bond is weaker than the Re–X bond.

Like the monosubstitution (26a), the disubstitution (26e) proceeds under relatively mild conditions. The rate is again independent of the nature and concentration of L′, and increases in the order X = I to Cl [58, 59]. It is also strongly dependent on L; the bulkier and the "harder" this ligand is, the more strongly is the dissociation favored. For example, $Mn(CO)_4P(C_6H_5)_3Br$ in tetrachloroethane at 40 °C reacts about seven times as fast as $Mn(CO)_4P(n\text{-}C_4H_9)_3Br$ (phenyl is larger than *n*-butyl), and $Re(CO)_4(C_5H_5N)Br$ in CCl_4 at 60 °C reacts about six times as fast as $Re(CO)_4P(C_6H_5)_3Br$ (pyridine is "harder" than triphenylphosphine). The compounds $Mn(CO)_3LL'X$ (or $Mn(CO)_3L_2X$) formed in accordance with equation (26e) for M = Mn initially have the *cis* configuration, but rearrange slowly in solution to give the *trans* form [60]. The isomerization is probably intermolecular and begins with the removal of L.



(32)

A mechanism proposed by *Cohen* and *Basolo* [61] for the substitution reactions of tetracarbonyliron dihalides with n donors L (L = ^{14}CO, $P(C_6H_5)_3$, $P(OC_6H_5)_3$, $As(C_6H_5)_3$, $Sb(C_6H_5)_3$) should be viewed with caution.

When L is present in excess, the rate of formation of *(21)* is independent of the donor concentration; it is influenced by light and by free halogen. The obvious

[57] *F. Zingales* and *U. Sartorelli*, Inorg. Chem. *6*, 1243 (1967).

[58] *R. J. Angelici* and *F. Basolo*, Inorg. Chem. *2*, 728 (1963).

[59] *F. Zingales, U. Sartorelli*, and *A. Trovati*, Inorg. Chem. *6*, 1246 (1967).

[60] *R. J. Angelici, F. Basolo*, and *A. J. Poe*, J. Amer. chem. Soc. *85*, 2215 (1963).

[61] *I. A. Cohen* and *F. Basolo*, J. inorg. nuclear Chem. *28*, 511 (1966).

$$Fe(CO)_4X_2 + L \rightleftharpoons (CO)_4Fe\begin{matrix}X\\ \diagup\\ \diagdown\\ X\end{matrix}L$$

$$Fe(CO)_4X_2L \rightleftharpoons Fe(CO)_4 + LX_2$$
$$Fe(CO)_4 + L \rightarrow Fe(CO)_4L \qquad (33)$$
$$Fe(CO)_4L + LX_2 \rightarrow Fe(CO)_3LX_2 + L + CO$$
(21)

assumption suggested by the kinetic data, *i.e.* that the first step is loss of CO, is dismissed by the authors because of the low activation energy of 6.2 kcal/mole. However, their argument for the relationship between the E_a values and the position of the ν_{CO} absorptions should be critically checked.

The halogen exchange on $Fe(CO)_4X_2$ proceeds as follows

$$Fe(CO)_4X_2 + X_2^* \rightleftharpoons Fe(CO)_4X_2^* + X_2 \qquad (33a)$$

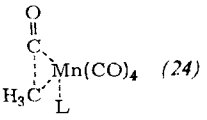
by an S_N1 mechanism [61a]. The activation energy is 28 kcal/mole when X = Br and 14 kcal/mole when X = I. Of the monocarbonylbis(triphenylphosphine) rhodium chlorides, the rhodium(III) compound $Rh(CO)[P(C_6H_5)_3]_2Cl_3$ reacts with ^{14}CO by an S_N1 mechanism [62], and the rhodium(I) compound $Rh(CO)[P(C_6H_5)_3]_2Cl$ by an S_N2 mechanism [63]. In general, a direct attack of the substituting ligand on the central atom appears to be favored in square planar neutral complexes.

4.5. Carbonylalkylmetals and Carbonylacylmetals

Unlike the halogen compounds $Mn(CO)_5X$ (X = Cl, Br, I), pentacarbonylmethylmanganese reacts with various n donors without elimination of CO to give acetylmanganese complexes.

$$CH_3Mn(CO)_5 + L \rightarrow CH_3COMn(CO)_4L \qquad (34)$$
(22) *(23)*

When L = ^{14}CO, the activity is found not in the keto group formed but quantitatively in the CO ligands attached to the metal [64,65]. In agreement with this, stereochemical studies show that *(23)* is formed not by direct insertion of CO into the H_3C-Mn bond but very probably by migration of the methyl group onto one of the *cis* CO ligands [65,66]. The fact that this migration is decisively assisted by the substituent L suggests a transition state *(24)* [67].


(24)

This agrees with the fact that for L = $C_6H_{11}NH_2$, the rate of the reaction (34) in apolar solvents such as *n*-hexane exhibits a first-order dependence on the concentrations of both reactants [68]. In polar solvents, the solvent evidently takes over the role of L; the course of the reaction can then be formulated as follows (S = solvent):

$$(22) + S \rightleftharpoons CH_3COMn(CO)_4S \underset{-S}{\overset{+L}{\longrightarrow}} CH_3COMn(CO)_4L \qquad (35)$$

The rate is independent of [L], since the first step is very much slower than the subsequent displacement of S by L [68,69]. It has been shown that the reaction of $CH_2FMn(CO)_5$ with the strongly nucleophilic iodide ion to form $[CH_2FCOMn(CO)_4I]^-$ is an S_N2 reaction in the presence of an excess of I^-, even in 2,2′-diethoxydiethyl ether [70].

Acylpentacarbonylmanganese compounds react with $P(C_6H_5)_3$ or I^- in accordance with a first order rate equation [69,70].

$$RCOMn(CO)_5 + L \xrightarrow{k} RCOMn(CO)_4L + CO \qquad (36)$$
(25) *(26)*

When R = $C_6H_5CH_2CH(CH_3)$, *i.e.* the manganese compound *(25)* is optically active, the direction of rotation is unchanged in the reaction product *(26)* [70]. For R = CH_3, the rate constant *k*, as expected, agrees with that (*k*′) of the decarbonylation

$$CH_3COMn(CO)_5 \xrightarrow{k'} (22) + CO \qquad (37)$$

In this case the dissociation of an Mn–CO bond is probably followed by fast migration of the CH_3 group onto the manganese atom.

The reactions of acyltetracarbonylcobalt compounds with $P(C_6H_5)_3$ or ^{14}CO, like the reactions of *(25)*, proceed by an S_N1 mechanism [34,71]. $CH_3COCo(CO)_4$ dissociates about 2250 times as rapidly as $CH_3COMn(CO)_5$ in ether at 25 °C. Comparison of $(C_6H_5)_3PAuCo(CO)_4$ with $(C_6H_5)_3PAuMn(CO)_5$ shows that the cobalt compound is much more reactive toward ^{14}CO than the manganese complex [34]. This confirms the observation made earlier on the unsubstituted carbonylmetals that the dissociation of an M–CO bond within a class of compounds becomes less favored with increasing coordination number of the metal atom.

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[64] *T. H. Coffield, J. Kozikowski*, and *R. D. Closson*, unpublished; see: *C. W. Bird*, Chem. Reviews *62*, 283 (1962).
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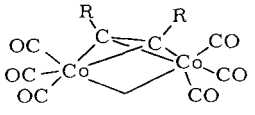
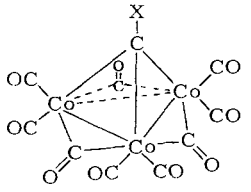
[71] *R. F. Heck*, J. Amer. chem. Soc. *85*, 651 (1963).

Two carbonylcobalt complexes having remarkable structures *(27)* and *(28)*, which, like the carbonylalkylcobalts and carbonylacylcobalts, contain Co–C σ bonds, readily undergo CO exchange reactions with ^{14}CO. The exchange rate always exhibits first-order dependence on the concentration of the complex, and is independent of the concentration of labeled carbon monoxide [27, 72, 73].



(27)



(28)

It has been suggested that the first step in the reactions of *(27)* is an intramolecular rearrangement introduced by the cleavage of a Co–C σ bond [73]. On variation of the substituents on the acetylenic C atoms, the first order rate constants decrease in the order $C_2(CH_3)_2 > C_2(C_6H_5)_2 > C_2H_2 > C_2(CH_2Cl)_2 > C_2(COOCH_3)_2 > C_2(CF_3)_2$. This sequence could reflect the difference in the strengths of the Co-alkyne bonds.

4.6. Amine-, Phosphine-, Arsine-, Stibine-, Isocyanide-, and Olefincarbonylmetals

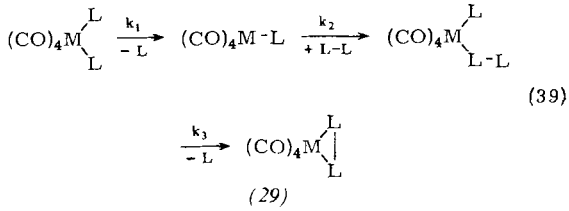
Substitution reactions of the amine-, phosphine-, arsine-, stibine-, isocyanide-, and olefincarbonylmetals $M(CO)_{n-m}L_m$ (which are mostly readily obtainable from carbonylmetals $M(CO)_n$) with n or π donors L′ can lead to displacement of CO, of L, or of CO and L. The principal factors affecting the course of the reaction, apart from the nature of the donor L′, are the number and nature of the ligands L. The effects of these factors are clear from the reactions of substituted carbonylmetals of chromium, molybdenum, and tungsten.

(a) The reactions of the compounds $M(CO)_5L$ (L = RNH_2, PR_3, CNR) with unidentate donors L′ lead predominantly to substitution of CO.

$$M(CO)_5L + L' \rightarrow M(CO)_4LL' + CO \qquad (38)$$

For M = Mo and L′ = $P(C_6H_5)_3$, the reaction rate in *n*-decane at 97.8 °C varies with L in the order $P(C_6H_5)_3 > P(OC_2H_5)_3 > CNC_6H_{11}$. The formation of $Mo(CO)_4[P(C_6H_5)_3]_2$ from $Mo(CO)_5P(C_6H_5)_3$ under these conditions takes place largely by an S_N1 mechanism [74]. A dissociation step (in this case the cleavage of an M–P bond) is also rate-determining in the reactions of the dinuclear complex $[M(CO)_5]_2L–L$ (M = Cr, Mo, W; L–L = $C_2H_4[P(C_6H_5)_2]_2$) with chelating groups L′–L′ [21, 75].

(b) The disubstitution products $M(CO)_4L_2$ readily undergo ligand exchange with bidentate donors L–L (L–L = $C_2H_4[P(C_6H_5)_2]_2$, dipy [*]), the exchange rate being independent of the concentration of L–L [76, 77]. The following reaction course therefore seems plausible (k_2 and $k_3 > k_1$):

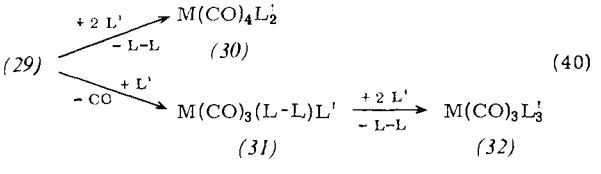


(39)

(29)

For M = Mo and L–L = dipy, the rate constant k_1 increases with changing L in the order $Sb(C_6H_5)_3 < PC_6H_5Cl_2 < P(C_6H_5)_3 < As(C_6H_5)_3 \ll$ pyridine $\ll PCl_3$ [77]. For M = Mo and L–L = $C_2H_4[P(C_6H_5)_2]_2$, the rate constant increases in the order $P(OC_6H_5)_3 \ll P(C_6H_5)_3$ and $PC_6H_5Cl_2 \ll PCl_3$ [76]. The reaction of *cis*-$Mo(CO)_4[P(C_6H_5)_3]_2$ with dipy is much faster than that of *trans*-$Mo(CO)_4[P(C_6H_5)_3]_2$, *i.e.* the dissociation of the Mo–P bond is facilitated, probably on steric grounds, by an adjacent $P(C_6H_5)_3$ ligand.

(c) The chelate complexes *(29)* with M = Cr and L–L = dipy, *o*-phenanthroline, or 1,2-diamino-2-methylpropane react with phosphines and phosphites L′ with exclusive substitution of CO. The reaction rate exhibits first-order dependence on [*(29)*] and is independent of [L′], so that the first step may be assumed to be a dissociation [78, 79]. The reactions of the corresponding compounds of molybdenum and tungsten with L′(=PR_3 or $P(OR)_3$) lead to both CO substitution and ligand exchange (eq. (40)).



(40)

(29) *(30)* *(31)* *(32)*

The kinetic data, which formally agree with an additive rate equation

$$-\frac{d[(29)]}{dt} = k[(29)] + k'[(29)][L'] \qquad (41)$$

(M = Mo, W), have been interpreted as indicating that simultaneously with the primary dissociation (*k*), L′ also directly attacks the metal atom of the original complex (*k*′) [80, 81]. The dependence of the rate on [L′] could however also be explained by the reaction sequence (42).

[*] 2,2′-Bipyridine.

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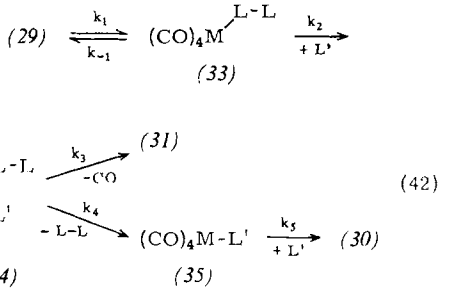
[80] *J. R. Graham* and *R. J. Angelici,* J. Amer. chem. Soc. *87*, 5590 (1965).

[81] *J. R. Graham* and *R. J. Angelici,* Inorg. Chem. *6*, 992 (1967).



The reactions of the tetracarbonylmetal-diene complexes *(29)* (L–L = norbornadiene, 1,5-cyclooctadiene) with n [23,76,82] and π donors [20,83] very probably proceed by a mechanism of this type. The first step is the partial cleavage of the diene-metal bond; the coordination vacancies in the resulting intermediate *(33)* can be filled either by recombination (k_{-1}) or by addition of L′ (k_2). For the reaction (43)

$$(29) + L_\pi \rightarrow \underset{(36)}{M(CO)_3L_\pi} + L\text{–}L + CO \qquad (43)$$

the application of the Bodenstein theorem to a reaction sequence analogous to (42) gives the equation

$$\frac{d[(36)]}{dt} = \frac{k_1k_2[(29)][L_\pi]}{k_{-1} + k_2[L_\pi]} \qquad (44)$$

which is exactly satisfied for M = Cr, L–L = norbornadiene, and L_π = mesitylene, hexamethylbenzene, or naphthalene [23,83].

(d) The reactions of the cycloheptatrienetricarbonylmetals $C_7H_8M(CO)_3$ (M = Cr, Mo, W) with trimethyl phosphite lead even under very mild conditions to substitution of the triene and formation of $M(CO)_3[P(OCH_3)_3]_3$. Kinetic studies show that these reactions follow an S_N2 mechanism [84]. The activation energy increases in the order M = Mo (9.8) < W (11.3) < Cr (16.5 kcal/mole); the E_a values are about 10–15 kcal/mole lower than those of the reactions of the diene-tetracarbonylmetals with n and π donors.

The exchange reaction

$$\underset{(37)}{C_7H_8Cr(CO)_3} + {}^{14}C_7H_8 \rightarrow \underset{(38)}{{}^{14}C_7H_8Cr(CO)_3} + C_7H_8 \qquad (45)$$

gives an additive rate law [85]:

$$\frac{d[(38)]}{dt} = k[(37)] + k'[(37)][{}^{14}C_7H_8] \qquad (46)$$

The course of the substitution reactions of the compounds $M(CO)_{6-n}L_n$ (M = Cr, Mo, W) can be summarized as follows. If L is a phosphine, isocyanide [86], or olefin, *i.e.* a "soft" base, the ligand exchange evidently predominates over the CO substitution with increasing *n*; similarly, if the steric conditions remain approximately the same, nucleophilic attack of the donor L′ on the original complex is favored. If on the other hand L is an amine, *i.e.* a "hard" base, the tendency toward ligand exchange or CO substitution becomes less distinct. The reaction behavior appears to be determined by the interplay of the donor and acceptor character of the ligands L and CO.

The substitution and ligand exchange reactions of the carbonylphosphine complexes of iron and nickel proceed almost exclusively by an S_N1 mechanism. The activation energy for the removal of a CO group from *(39)*

$$\underset{(39)}{Fe(CO)_4P(C_6H_5)_3} \xrightarrow[-CO]{k_1} Fe(CO)_3P(C_6H_5)_3 \xrightarrow[+P(C_6H_5)_3]{k_2} Fe(CO)_3[P(C_6H_5)_3]_2 \qquad (47)$$

($k_2 > k_1$) (E_a = 43.5 kcal/mole) is remarkably high [29], and is comparable with that of the reaction of $Cr(CO)_5P(C_6H_5)_3$ with $P(C_6H_5)_3$ [74]. In the presence of CF_3COOH in 1,2-dichloroethane, three of the four CO groups in *(39)* are extremely labile and undergo rapid exchange with ^{14}CO even at −30 °C [30].

The CO exchange of the compounds $Ni(CO)_3P(C_6H_5)_3$ *(40)* and $Ni(CO)_2[P(C_6H_5)_3]_2$ *(41)* is much slower than that of $Ni(CO)_4$ *(5)*. The first order rate constants of the reactions of *(5)*, *(40)*, and *(41)* with ^{14}CO in toluene at 25 °C are related as 420:70:1 [28]. The rates of reactions (48), (49), and (50) are independent

$$Ni(CO)_3PR_3 + PR'_3 \rightarrow Ni(CO)_2(PR_3)PR'_3 + CO \qquad (48)$$

$$Ni(CO)_2(PR_3)_2 + PR'_3 \rightarrow Ni(CO)_2(PR_3)PR'_3 + PR_3 \qquad (49)$$

$$Ni(CO)_2(PR_3)PR'_3 + PR'_3 \rightarrow Ni(CO)_2(PR'_3)_2 + PR_3 \qquad (50)$$

of [PR′$_3$], but are strongly dependent on the nature of the coordinated phosphine; the variation of reactivity is found to be similar to that in reactions (38) and (39) [31].

4.7. Arenecarbonylmetals

In thermal substitution reactions of the arenetricarbonylmetals, the aromatic ligand is always displaced. According to *Strohmeier* [87–89], the ligand exchange

$$\underset{(42)}{C_6H_5XM(CO)_3} + {}^{14}C_6H_5X \rightarrow \underset{(43)}{{}^{14}C_6H_5XM(CO)_3} + C_6H_5X \qquad (51)$$

(M = Cr, Mo, W; X = H, Cl, CH_3) satisfies the rate equation

$$\frac{d[(43)]}{dt} = k[(42)]^2 + k'[(42)][{}^{14}C_6H_5X] \qquad (52)$$

The constants *k* and *k′*, which are functions of the Hammett σ parameter of X, increase in the order M = Cr < W < Mo at a given temperature. The first

[82] *F. Zingales, M. Graziani,* and *U. Belluco,* J. Amer. chem. Soc. *89*, 256 (1967).

[83] *H. Werner* and *R. Prinz,* Z. Naturforsch. *22b*, 260 (1967).

[84] *A. Pidcock* and *B. W. Taylor,* J. chem. Soc. (London) *A 1967*, 877.

[85] *W. Strohmeier* and *H. Mittnacht,* Z. physik. Chem. N.F. *34*, 82 (1962).

[86] For exchange reactions of $M(CO)_{6-n}(CNR)_n$ with ^{14}CO and ^{14}CNR, see *G. Cetini* and *O. Gambino,* Atti Accad. Sci. Torino I, Cl. Sci. fisiche, mat. natur *97*, 1189 (1963).

[87] *W. Strohmeier* and *H. Mittnacht,* Z. physik. Chem. N.F. *35*, 253 (1962).

[88] *W. Strohmeier* and *E. H. Staricco,* Z. physik. Chem. N.F. *38*, 315 (1963).

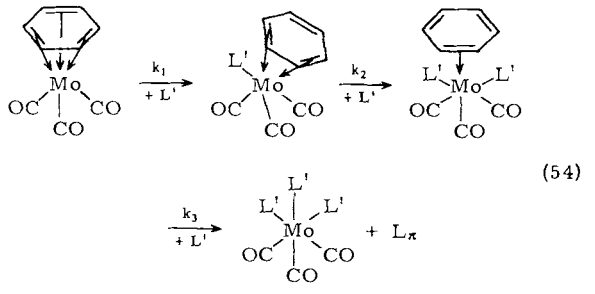
[89] *W. Strohmeier* and *R. Müller,* Z. physik. Chem. N.F. *40*, 85 (1964).

term in equation (52) is particularly interesting, and suggests the formation of an activated complex from two molecules of *(42)*. A rate equation analogous to (46) is found for the exchange reaction of $C_{10}H_8Cr(CO)_3$ with ^{14}C-labeled naphthalene.

The reactions of the arenetricarbonylmolybdenums *(44)* with phosphines [90] and phosphites [91] proceed by a "normal" S_N2 mechanism.

$$Mo(CO)_3L_\pi + 3\,L' \rightarrow Mo(CO)_3L'_3 + L_\pi \qquad (53)$$

Assuming an initial rate-determining attack of the substituent L′ on the metal atom followed by cleavage of the arene-molybdenum bond, the following reaction course is conceivable (k_2 and $k_3 > k_1$):



(54)

On substitution of the aromatic ring, the rate decreases as the number of methyl groups is increased, as is to be expected on the basis of bonding theory. Reversal of the reaction (54) is possible *e.g.* for L′ = $C_6H_5NH_2$ [92]; the formation of the compound *(44)* (L_π = mesitylene) in polar solvents such as dioxane or tetrahydrofuran then proceeds substantially by an S_N1 mechanism.

Kinetic studies [93–95] on substitution reactions on the cyclic ligands of arenetricarbonylchromiums such as

$$C_6H_5XCr(CO)_3 + OCH_3^\ominus \xrightarrow{(CH_3OH)} C_6H_5OCH_3Cr(CO)_3 + X^\ominus \qquad (55)$$
$$(X = F, Cl)$$

$$p\text{-}(m\text{-})XC_6H_4COOCH_3Cr(CO)_3 + OH^\ominus \xrightarrow{(Acetone/H_2O)} p\text{-}(m\text{-})XC_6H_4COOHCr(CO)_3 + OCH_3^\ominus \qquad (56)$$
$$(X = CH_3, Cl, NH_2, OCH_3, COOCH_3)$$

$$C_6H_5CH_2ClCr(CO)_3 + H_2O \xrightarrow{(Acetone/H_2O)} C_6H_5CH_2OHCr(CO)_3 + H^\oplus + Cl^\ominus \qquad (57)$$

clearly show that the reactivity of the coordinated aromatic ligand is always greater than that of the free benzene derivative. This means that in the nucleophilic substitution (55), the electron density on the electrophilic center of the ring is evidently decreased by complex formation, *i.e.* the $Cr(CO)_3$ group acts as an electron-attracting substituent, the influence of which is comparable to that of an NO_2 group in the *para* position [93].

4.8. π-Cyclopentadienylcarbonylmetals

Of the monomeric cyclopentadienylcarbonylmetals, the compounds $C_5H_5M(CO)_2$ (M = Co, Rh, Ir) react much more readily with n and π donors than the complexes $C_5H_5M(CO)_3$ (M = Mn, Tc, Re) and $C_5H_5V(CO)_4$. Reactions of the type

$$C_5H_5M(CO)_2 + L \rightarrow C_5H_5M(CO)L + CO \qquad (58)$$

(L = ^{14}CO, CNR, PR_3, $P(OR)_3$) are possible under relatively mild conditions, *e.g.* in toluene at 40 °C; they all proceed by an S_N2 mechanism [96,97,97a]. The reaction rate is a function not only of L but also of M; for L = $P(C_6H_5)_3$, the rate increases in the order Ir < Co ≪ Rh. Similar special behavior of the 4d metal was mentioned in connection with the hexacarbonylmetals (cf. Section 4.1.).

Replacement of the CO groups in $C_5H_5Mn(CO)_3$ by L has not so far been achieved by heating. On the other hand, CO is readily split off to form compounds of the type *(45)* on UV irradiation *e.g.* in *n*-hexane. If L is an olefin such as ethylene, propylene, cyclopentene, cycloheptene, or cyclooctene, ligand exchange takes place in the presence of L′ (= PR_3, $P(OR)_3$, or $S(C_6H_5)_2$)

$$C_5H_5Mn(CO)_2L + L' \rightarrow C_5H_5Mn(CO)_2L' + L \qquad (59)$$
(45)

The cleavage of the Mn–L bond is rate-determining in this reaction [98].

The CO exchange of $[C_5H_5Ni(CO)]_2$ depends on the concentration of labeled carbon monoxide [96]. In the reactions of the dicarbonylcyclopentadienyliron halides $C_5H_5Fe(CO)_2X$ with ^{14}CO, the rate is determined by the nature of the halogen, and increases under the same conditions in the ratio 1:25:500 for X = I, Br, Cl [52].

4.9. π-Allylcarbonylmetals

Like the π-cyclopentadienyl residue, the π-allyl residue may be formally regarded as an anionic delocalized π-electron system. The π-C_3H_5–M bond is generally very stable, and is not broken in reactions with Lewis bases. Of the π-allylcarbonylmetals prepared so far, the cobalt compounds *(46)* react by an S_N1 mechanism, while the isoelectronic iron complexes

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[91] *A. Pidcock, J. D. Smith*, and *B. W. Taylor*, J. chem. Soc. (London) *A 1967*, 872.

[92] *H. Werner* and *R. Prinz*, Chem. Ber. *100*, 265 (1967).

[93] *D. A. Brown* and *J. R. Raju*, J. chem. Soc. (London) *A 1966*, 40.

[94] *G. Klopman* and *F. Calderazzo*, Inorg. Chem. *6*, 977 (1967).

[95] *J. D. Holmes, D. A. K. Jones*, and *R. Pettit*, J. organometallic Chem. *4*, 324 (1965).

[96] *A. Wojcicki* and *F. Basolo*, J. inorg. nuclear Chem. *17*, 77 (1961).

[97] *H. G. Schuster-Woldan* and *F. Basolo*, J. Amer. chem. Soc. *88*, 1657 (1966).

[97a] Note added in proof: An S_N2 reaction can also be assumed for the reaction of $C_5H_5V(CO)_4$ with $P(C_6H_5)_3$: see *W. Strohmeier* and *H. Blumenthal*, Z. Naturforsch. *22b*, 1351 (1967).

[98] *R. J. Angelici* and *W. Loewen*, Inorg. Chem. *6*, 682 (1967).

(47) (though the metal here has a higher coordination number than in *(46)*) react by an S_N2 mechanism [50,99,100] (R = H, CH_3, C_6H_5, Cl, Br, $COOCH_3$; L = $P(C_6H_5)_3$, $PO_3C_6H_{11}$).

$$\underset{(46)}{\pi\text{-}C_3H_4RCo(CO)_3} + L \rightarrow \pi\text{-}C_3H_4RCo(CO)_2L + CO \quad (60)$$

$$\underset{(47)}{\pi\text{-}C_3H_5Fe(CO)_3X} + L \rightarrow \pi\text{-}C_3H_5Fe(CO)_2(L)X + CO \quad (61)$$

The substituent R has relatively little influence on the rate of the reaction (60). The reactivity of *(47)* depends on X in the same manner as in the π-cyclopentadienyl compounds $C_5H_5Fe(CO)_2X$.

4.10. Carbene-Carbonylmetal Complexes

The compounds $M(CO)_5C(OCH_3)R$ [101] having a carbene residue as a ligand exhibit surprising reactivity toward nucleophiles. They react as analogs of the hexacarbonylmetals with tertiary phosphines, *i.e.* with substitution of a CO group.

$$\underset{(48)}{M(CO)_5C(OCH_3)R} + PR'_3 \rightarrow \underset{}{cis\text{-}M(CO)_4(PR'_3)C(OCH_3)R} + CO \quad (62)$$

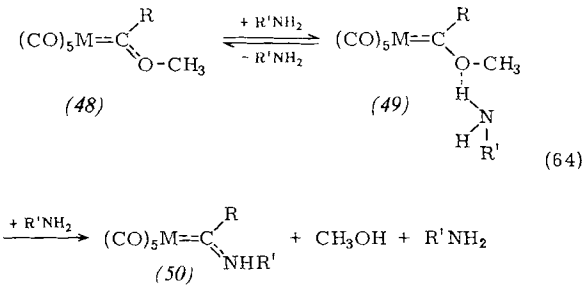
(M = Cr, Mo, W; R = CH_3, C_6H_5; R′ = C_2H_5, *n*-C_4H_9, C_6H_{11}, C_6H_5, *p*-$CH_3C_6H_4$). The dominating rate-determining step must be assumed to be the cleavage of an M–CO bond [102,103]. The activation energies for the CO substitution (M = Cr and R = CH_3: E_a = 28.2 kcal/mole; M = Cr and R = C_6H_5: E_a = 27.4 kcal/mole), which are relatively low in relation to those of the reactions of the hexacarbonylmetals, suggest that the carbene ligand can contribute considerably to the stabilization of the transition state involved in the dissociation. The reaction of tertiary aliphatic phosphines with *(48)* also leads to cleavage of the metal-carbene bond [103].

The kinetics of the "ester-like" reaction of (48) with primary amines $R'NH_2$ has also been studied [104]. For M = Cr, R = C_6H_5 and R′ = C_6H_{11}, *n*-C_4H_9, $CH_2C_6H_5$, the reaction in dioxane follows a third order rate equation

$$-\frac{d[(50)]}{dt} = k[(48)][R'NH_2]^2 \quad (63)$$

which suggests that the aminocarbene complex *(50)* is formed by a multi-step mechanism.

The existence of hydrogen bonds in the primary adduct *(49)* can be shown by NMR measurements.



(64)

5. Summary and Outlook

The results of the investigations described above show that the course of substitution reactions of carbonylmetal complexes is determined mainly by steric and electronic factors. Complexes having a relatively small central atom that is substantially screened by the surrounding ligands are not readily accessible to direct attack by a donor L, and so react preferentially by an S_N1 mechanism. An S_N2 mechanism is favored when the metal atom is large or when it is coordinated to ligands other than CO, such as NO, π-C_5H_5, or C_6H_6, which are capable of strong π back-bonding.

Generalizations of this type must for the present be treated with caution, since development is still in progress and the end is not yet in sight. Despite this limitation, however, the value of the kinetic studies is obvious; they provide an insight into the reaction mechanism, and so offer the possibility of controlling a given reaction by alteration of the conditions. The importance of the present results, however, goes much farther. They have excited new interest in the phenomenon of the bonding in carbonylmetals, and thrown doubt on several established ideas. As examples we may again consider the compounds $M(CO)_{n-m}L_m$ discussed in Section 4.6. It is generally argued that the ligands L, the majority of which are stronger donors than acceptors, cause an increase in the electron density on the metal atom; this leads to stronger back-bonding and hence to an increase in the M–CO bond strength. Application of this bonding concept to the reaction behavior suggests that the dissociation of an M–CO bond should be more difficult in the complexes $M(CO)_{n-m}L_m$ than in unsubstituted carbonylmetals $M(CO)_n$. This is so if L is a phosphine or phosphite, but not when L is an amine. To explain this, reference is often made to the HSAB concept [46]. Amines are "hard" bases, whereas phosphines are "soft", and form stronger bonds with "soft" acids (metal atoms having low oxidation numbers). However, this classification has little bearing on the difference in the strength of the M–CO bonds that is reflected in the substitution reactions of amine- and phosphinecarbonylmetals. The HSAB concept (which is based on thermodynamic considerations) appears to be overrated in this case.

Another point must be emphasized in a comparison of bond character and reactivity. The resonance formulas *(51)* and *(52)* considered in the description

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[100] *R. F. Heck* and *C. R. Boss*, J. Amer. chem. Soc. *86*, 2580 (1964).

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[103] *H. Werner* and *H. Rascher*, Helv. chim. Acta *51*, 1765 (1968).

[104] *B. Heckl*, *H. Werner*, and *E. O. Fischer*, Angew. Chem. *80*, 847 (1968); Angew. Chem. internat. Edit. *7*, 817 (1968); see *B. Heckl*, Diplomarbeit, Technische Hochschule München, 1967.

$$M{=}C{=}\ddot{O} \;\leftrightarrow\; :\overset{\ominus}{M}{-}C{\equiv}\overset{\oplus}{O}:$$

(51) *(52)*

of the M–CO bond relate only to the ground state; however, the reaction behavior is determined by the energy of the transition state. It is possible that ligands such as amines contribute to the stabilization of the transition state, though the reason for this is still unclear. A fuller knowledge of the electronic structure of the excited states of carbonylmetals would be very useful.

Finally, it should be mentioned that the kinetic studies have also led to preparative successes. Thus the study of the mechanism of substitution reactions of hexacarbonylmetals and the application of the knowledge gained led to the preparation of the first hexamethylborazine–transition metal complex $B_3N_3(CH_3)_6$-$Cr(CO)_3$ [105], and other complexes of this type are now also known [106]. It is not difficult to predict that a combination of kinetic and preparative work in this field will continue to be fruitful in the future.

The work described here was carried out with the assistance in particular of Dr. R. Prinz, as well as of Dipl.-Chem. Edith Deckelmann, Dipl.-Chem. K. Deckelmann, Dipl.-Chem. B. Heckl, Renate Koneberg, and Hermine Rascher, to all of whom I am very grateful. The work was supported by grants from the Deutsche Forschungsgemeinschaft and the Verband der Chemischen Industrie. Thanks are also due to Prof. Dr. E. O. Fischer for his support of our investigations.

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[106] *H. Werner*, *R. Prinz*, and *E. Deckelmann*, Chem. Ber., in press.

COMMUNICATIONS

A New Synthesis of Isocyanates and Isothiocyanates

By *G. Greber* and *H. R. Kricheldorf* [*]

Dedicated to Professor E. Husemann on the occasion of her 60th birthday

Thermal cleavage of carbamoyl chloride and carbamic esters (urethanes) usually gives only poor yields of isocyanates because the high cleavage temperatures (200–300 °C) favor side reactions and the decomposition products undergo reverse reaction at slightly lower temperatures.

We have found that chlorides, anhydrides, and esters *(1)* of carbamic acids, when *N*-silylated to *(2)* [*e.g.*, by chlorotrimethylsilane/triethylamine or mono- or bis-(trimethylsilyl)-acetamide], decompose to isocyanate *(3)* and a silicon compound *(4)* even between −20 and +120 °C.

$$R^1\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}X \xrightarrow{+\,R^2Si(CH_3)_3} R^1\text{-}N(Si(CH_3)_3)\text{-}\overset{\overset{O}{\|}}{C}\text{-}X \xrightarrow{\Delta}$$

(1) *(2)*

$$R^1\text{-}N{=}\overset{\overset{O}{\|}}{C} + X\text{-}Si(CH_3)_3$$

(3) *(4)*

X = Cl, $OCOR^3$, OR^3; R^1, R^3 = alkyl, aryl, or cycloalkyl
R^2 = Cl, CH_3CON–, $CH_3CONSi(CH_3)_2$–

Since the products *(4)* and *(3)* undergo neither back-reaction nor, to an appreciable extent, side reactions, even sensitive or very reactive isocyanates can be obtained in yields of between 70 and 95%. For urethanes R^1–NH–$COOR^3$ the temperature for fission depends on the nature of R^3 if R^1 remains the same; it decreases rapidly with increasing stability of the anion R^3–$O^{\ominus}$ (examples: $R^1 = C_6H_5$; $R^3 = C_2H_5$, C_6H_5, *p*-Cl–C_6H_4, or *p*-NO_2–C_6H_4; fission at 80–110 °C, 50 to 70 °C, 10–30 °C, or −20–0 °C, respectively).

Preparative work starts with an amine, which is first acylated by a chloroformic or carbonic ester to the urethane and then silylated; for fission the reaction mixture is warmed. Instead of chlorotrimethylsilane, other chlorosilanes such as chlorotrialkyloxysilanes, and even $SiCl_4$ can be used. This method can also be used for amino alcohols and amino thiols which become disilylated on N and O or N and S. Cleavage of these compounds gives isocyanates of a new type, containing protected hydroxy or mercapto groups. For instance, from 2-aminoethanol we prepared (2-isocyanatoethoxy)trimethylsilane (b.p. 55–56 °C/14 torr) for the first time, the yield being about 70%.

Like urethanes, *S*-alkyl(aryl) thiocarbamate or *O*-alkyl(aryl) thiocarbamate can also be cleaved, after *N*-silylation, in good yield to isocyanates or isothiocyanates and a silicon-containing component.

Preparation of isocyanates from urethanes:

The urethane (1 mole) is heated to the b.p. with triethylamine (1.2 moles) in toluene (*ca.* 1 l), chlorotrimethylsilane (1.2 moles) is added, and the whole is heated for a further 2 h under reflux with stirring. After cooling, the precipitated triethylammonium chloride is filtered off and the filtrate is fractionated for isolation of the isocyanate.

Preparation of isocyanates from carbamoyl chlorides:

A solution of carbamoyl chloride (1 mole) in CCl_4 (*ca.* 1 l) is treated at −20 to 0 °C with a solution of trimethylsilylacetamide (1 mole) in CCl_4 (0.5 l) and kept at the reaction temperature for another hour. The mixture is then filtered from the precipitated acetamide, freed from solvent, and fractionated for isolation of the isocyanate.

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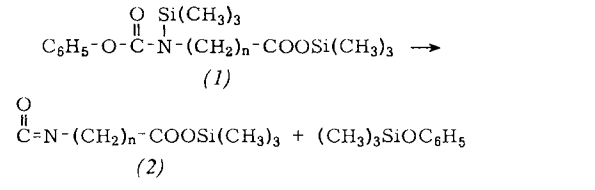
Preparation of Silyl Esters of Isocyanato Carboxylic Acids

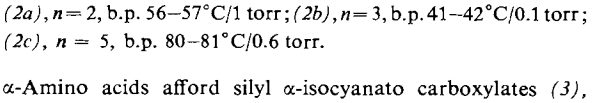
By *G. Greber* and *H. R. Kricheldorf*[*]

Dedicated to Professor E. Husemann on the occasion of her 60th birthday

On thermal fission of trimethylsilyl *N*-(phenoxycarbonyl)-*N*-(trimethylsilyl)amino carboxylates *(1)*[1] derived from β-, γ-, or ε-amino acids we obtained stable, distillable silyl β-, γ-, and ε-isocyanato carboxylates *(2)*.



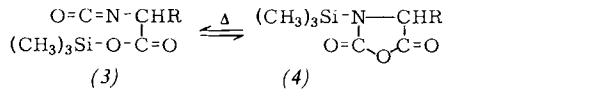
(1)



(2)

(2a), $n = 2$, b.p. 56–57°C/1 torr; *(2b)*, $n = 3$, b.p. 41–42°C/0.1 torr; *(2c)*, $n = 5$, b.p. 80–81°C/0.6 torr.

α-Amino acids afford silyl α-isocyanato carboxylates *(3)*, which however exist in equilibrium with the *N*-carboxy-*N*-(trimethylsilyl)amino acid anhydrides *(4)*; rise in temperature shifts the equilibrium in favor of *(3)*.



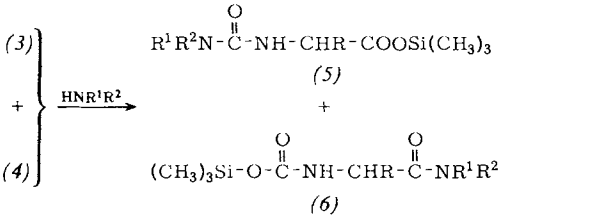
(3) *(4)*

R = H, CH_2–O–$Si(CH_3)_3$, CH_2–C_6H_5, or CH_2–C_6H_4–O–$Si(CH_3)_3$.

Silylation of α-*N*-carboxyamino acid anhydrides affords the same mixture.

Treating the mixture of *(3)* and *(4)* with primary or secondary amines affords the urea derivatives *(5)* and the carbamic acid derivatives *(6)*, which can be hydrolyzed to the substituted hydantoic acids or α-amino amides, respectively; these products can be separated readily and quantitatively. At high temperatures good yields (up to 90%) of the hydantoic acid derivatives, and at low temperature good yields (up to 90%) of α-amino amides, result.

Mixtures of *(3)* and *(4)* are stable over several hours only in dilute solution below 25 °C. It is interesting that, like one of these silyl esters of α-isocyanato carboxylic acids, trimethylsilyl *o*-isocyanatobenzoate exists in temperature-dependent equilibrium with *N*-carboxy-*N*-(trimethylsilyl)anthranilic anhydride.



(5) + *(6)*

R^1 = H, alkyl, aryl, or cycloalkyl

R^2 = alkyl, aryl, or cycloalkyl.

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[1] *G. Greber* and *H. R. Kricheldorf*, Angew. Chem. *80*, 1028 (1968); Angew. Chem. internat. Edit. *7*, 941 (1968).

Asymmetric Catalytic Hydrogenation with an Optically Active Phosphinerhodium Complex in Homogeneous Solution[1]

By *L. Horner, H. Siegel,* and *H. Büthe*[*]

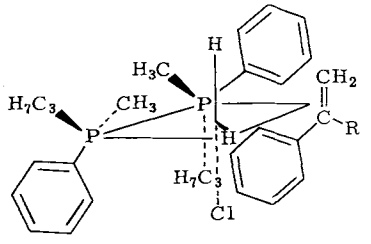
Dedicated to Professor Werner Schultheis on the occasion of his 65th birthday

In a recent publication[2] we pointed out that, with the use of optically active tertiary phosphines as ligands in complexes of univalent rhodium, an asymmetric hydrogenation of unsymmetrically substituted C–C double bonds should be possible.

Knowles and *Sabacky*[3] have used this method and optically active methylphenyl-*n*-propylphosphine[4] to prepare optically active hydratropic acid (15% optical yield) from atropic acid and methylsuccinic acid (3% optical yield) from itaconic acid.

We have found that α-ethylstyrene and α-methoxystyrene can be hydrogenated to (*S*)–(+)-2-phenylbutane *(1)* (7–8% optical yield) and (*R*)–(+)-1-methoxy-1-phenylethane *(2)* (3–4% optical yield) respectively, by use of a phosphinerhodium complex formed *in situ* from [Rh(1,5-hexadiene)Cl]$_2$ and (*S*)–(+)-methyl-phenyl-*n*-propylphosphine in benzene at normal pressure and room temperature.

Assuming an a-chloro-ef-dihydrido-d-olefin-bc-bisphosphinerhodium complex *(3)*[**] one finds from conformative reasoning (methyl and *n*-propyl groups of both phosphines in skew positions) that the olefin will be fixed to the complex in such a way that the *cis*-addition of hydrogen preferentially yields (*S*)–(+)-*(1)* from α-ethylstyrene and (*R*)–(+)-*(2)* from α-methoxystyrene. The preferential formation of (*S*)–(+)-hydratropic acid from atropic acid[3] agrees with this model.



(3)

Procedures:

$2.2 \cdot 10^{-4}$ moles of (*S*)–(+)-methylphenyl-*n*-propylphosphine are added to a solution of $0.5 \cdot 10^{-4}$ moles of [Rh-(1,5-hexadiene)Cl]$_2$[5] in 20 ml benzene under hydrogen in a shaking flask. 10^{-2} moles of olefin are then injected into the homogeneous yellow-orange solution. The reaction which takes 6–8 hours is checked by gas-chromatography. The hydrogenation products are separated from the rhodium complex by chromatography on Al_2O_3 (Woelm), fractionally distilled, and identified by NMR spectroscopy. Their configurations are determined through ORD measurements.

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[1] Communication 22 on "Studien zum Vorgang der Wasserstoffübertragung" (Studies on the Process of Hydrogen Transfer). – Communication 21: *L. Horner* and *D. Degner*, Tetrahedron Letters *1968*, 5889.

[2] *L. Horner, H. Büthe,* and *H. Siegel*, Tetrahedron Letters *1968*, 4023.

[**] The Rh atom at the center of the octahedron is not shown because of lack of space.

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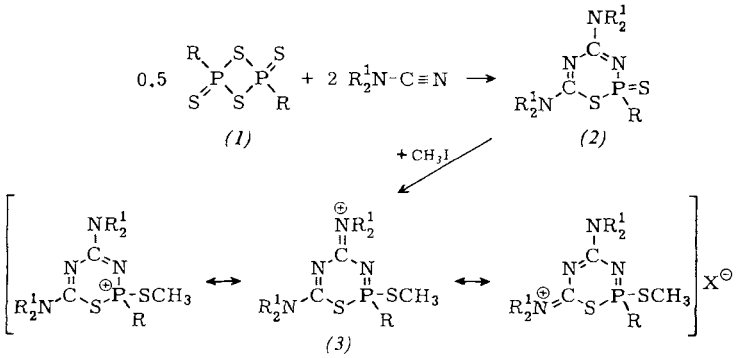
Synthesis of 2*H*-1,3,5,2-P^V-Thiadiazaphosphorine Derivatives[1]

By *A. Schmidpeter* and *N. Schindler* [*]

Owing to their high reactivity toward nucleophiles, dimeric thiophosphonic anhydrides *(1)* are suitable for use in the synthesis of phosphorus-nitrogen heterocycles both by cyclocondensation[2] and – as here – by cycloaddition. In the reaction of *(1)* with an excess of dialkylcyanamides we obtained quantitative yields of derivatives of a new ring system, 4,6-diamino-2*H*-1,3,5,2-P^V-thiadiazophosphorine-2-thiones *(2)*. The reaction probably begins with nucleophilic ring opening in *(1)*[3] by the cyanide nitrogen; it resembles the reaction of $[SO_3]$, which is isoelectronic with $[RPS_2]$, with nitriles[4].

The compounds *(2)* are colorless, crystalline, and stable to water and ammonia. Their structure is confirmed by their analytical composition, their molecular weight, the nonequivalence of the residues R^1 in the ^1H–NMR spectrum, the intensity ratio of the ^1H–NMR signals, and the uniformity of the ^{31}P signal. They react in molar proportions with methyl iodide to form *(3)*, X = I. These salts can be recrystallized from water, hydrolyze only very slowly with loss of methylthiol, and can be converted *e.g.* into *(3)*, X = $B(C_6H_5)_4$ by precipitation from aqueous solution.



(1) *(2)* *(3)*

R	R^1	m.p. (°C)	$\delta^{31}P$ [a]	δ^1H [a] ($R^1\alpha$)	($R^1\beta$)
	(2)				
C_2H_5	C_2H_5	121–123	−68.5	−3.60; −3.53	−1.18
C_2H_5	C_6H_{11}	184–185	−65.0	−3.60	
p-$CH_3OC_6H_4$	C_2H_5	178–179	−56.5	−3.55; −3.50	−1.16
p-$CH_3OC_6H_4$	$^1/_2$–$(CH_2)_5^-$	108–111	−57.5	−3.67	−1.51
C_6H_5S	C_2H_5	145–147	−61.0	−3.48	−1.15
	(3), X = I				
C_2H_5	C_2H_5		−63.0	−3.80; −3.78	−1.32; −1.25
C_2H_5	C_6H_{11}	168–170 (decomp.)	−58.8	−3.79	
p-$CH_3OC_6H_4$	C_2H_5	124–126 (decomp.)	−50.0	−3.91; −3.84	−1.36; −1.33
p-$CH_3OC_6H_4$	$^1/_2$–$(CH_2)_5^-$	135–137 (decomp.)	−51.7	−3.90	−1.77
C_6H_5S	C_2H_5	112–114 (decomp.)	−66.0	−3.62	−1.25; −1.16

[a] The chemical shifts for ^{31}P and ^1H signals were measured in CH_2Cl_2 against H_3PO_4 and TMS respectively in ppm; the negative sign indicates downfield shifts.

The methylation of the thiono sulfur of *(2)* results in a distinct decrease in the shielding of all the protons of the dialkylamino groups. This shows the distribution of the positive charge and the increased participation of phosphazene bond structures in *(3)*. The strengthening of the phosphazene ring bond, as expected[5], is generally accompanied by an upfield shift of the ^{31}P signal.

Procedure:

About 4 moles of a liquid dialkylcyanamide are added to 1 mole of *(1)*, which dissolves with strong evolution of heat. The solution is heated for a few minutes at 100–130 °C, and solidifies on cooling to give a crystal slurry. The product *(2)* is filtered off and recrystallized from a little benzene. The reaction of the solid dicyclohexylcyanamide is carried out in the stoichiometric quantity with dioxane as the solvent.

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Unusual Formation of the Unusual 1,2,8,9-Tetraaza-1,8-cyclotetradecadiene-3,10-diol System and its 5,12-Dioxa Analog[1,2]

By *S. Hünig* and *J. Cramer* [*]

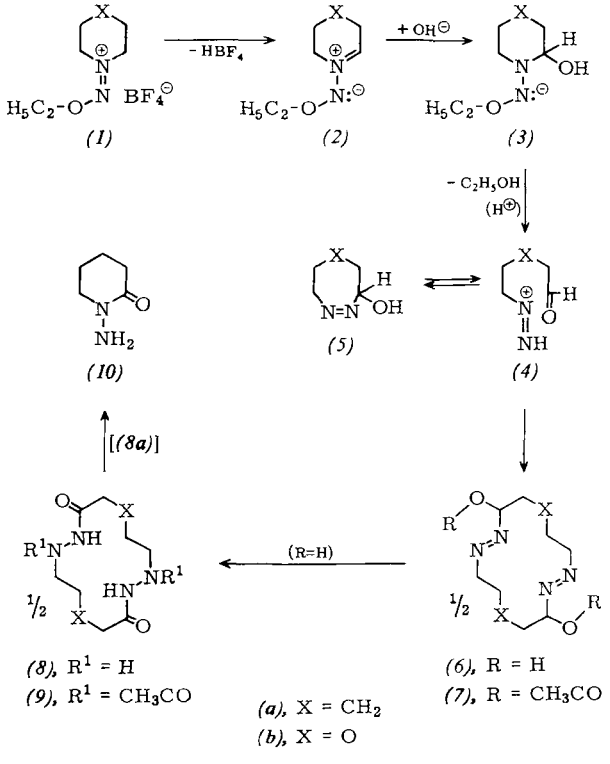
1,1-Pentamethylene-2-ethoxy-diazenium tetrafluoroborate (30.0 g)[3,4] is transformed into an ether extractable base [*ca.* 20% yield, m.p. 120 °C (decomp.)] when added to aqueous sodium carbonate solution (200 ml H_2O, 20 g Na_2CO_3, and 70 g NaCl) at −10 °C. This base has been characterized as 1,2,8,9-tetraaza-1,8-cyclotetradecadiene-3,10-diol *(6a)* on the basis of the following properties and an X-ray structure analysis[5]. Thus a six-membered ring is converted into a fourteen-membered ring that contains, in two positions, the hitherto rare combination[6,7] of an azo and an α-hydroxylalkyl group.

In confirmation of previous findings[3], *(6a)* has λ_{max} = 360 nm (CH_3OH) with ε = 27, as expected for aliphatic *trans*-azo compounds[8]. The fact that the IR spectrum is

clear between 1570 and 1500 cm^{-1} also excludes the presence of a *cis*-azo compound[9]. The sharp band at 3410 cm^{-1} (C_2Cl_4), independent of concentration, is assigned to an intramolecular bridging OH group: it disappears on acetylation of *(6a)* (by pyridine/acetic anhydride). The resulting *(7a)* now shows the ester-carbonyl band at 1750 cm^{-1} and unchanged UV absorption. The complicated NMR spectra[2] are also in accord with structures *(6a)* and *(7a)*. The largest masses found in the spectrometer are 210 ($M - H_2O$) for *(6a)* and 284 ($M - N_2$) for *(7a)*[10]. The molecular weight found for *(7a)* osmometrically in benzene was 319 (calc. 312).

Dilute HCl isomerizes *(6a)* to the very sparingly soluble *(8a)* (m.p. 261 °C), whose structure can be derived from the following results. Reduction of ammoniacal silver salt solution and absence of reaction with *p*-nitrobenzaldehyde indicate a secondary hydrazide[3]. This is supported by absence of UV absorption below 210 nm, and appearance of two NH bands at 3290 and 3250 cm^{-1} (KBr) and a low-frequency CO band (1630 cm^{-1}). Presence of the amide-II band at 1560 cm^{-1} requires a more than ten-membered ring since the amide group can be *transoid* only in large rings[11]. The mass spectrum[10] gives the required molecular weight of 228, which is increased to 232 on treatment with D_2O. Acetylation of *(8a)* affords a compound *(9a)* (m.p. 296 °C), isomeric with *(7a)* and giving one NH band (3170 cm^{-1}) and two CO bands (1695 and 1630 cm^{-1}), as well as the required molecular weight of 312. Concentrated HCl "halves" *(8a)* with renewed ring closure to the piperidine derivative *(10)*, which was identical with authentic material[3].

The transformations *(1)* → *(6)* → *(8)* occur also with the morpholine derivative *(1b)* (m.p. 97–98 °C): 1,8-dioxa-4,5,11,12-tetraaza-4,11-cyclotetradecadiene-3,10-diol *(6b)*, m.p. 150 °C (decomp.); *(7b)*, m.p. 218 °C (decomp.); *(8b)*,



m.p. 227 °C. These more readily soluble transformation products have the expected properties. The sequence *(1)* →→ *(6)*, as drawn, illustrates the reaction route that is at present the most probable[12]: deprotonation affords first the mesomeric zwitterion *(2)* and this readily adds nucleophiles at the α-carbon atom[1,3]; the OH adduct *(3)* loses ethanol, yielding, presumably by way of *(4)*, the "monomeric" intermediate *(5)*[13], that was earlier formulated in place of *(6)*[3]. Reaction of *(1)* with bases leads first to an absorption maximum at 375 nm with a higher extinction coefficient, indicating the presence of a *cis*-azo-compound[8]. The rate of transformation of *(5a)* into *(6a)* (356 nm in H_2O) decreases with increasing dilution, as expected for a dimerization.

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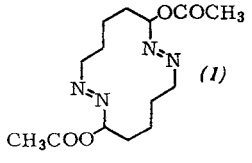
Crystal Structure of 1,2,8,9-Tetraaza-1,8-cyclotetradecadien-3,10-ylene Diacetate

By *R. Allmann* and *I. Kawada*[*]

A series of findings has led to ascription of a structure containing a fourteen-membered ring to the compound *(1)* that was prepared by *Hünig* and *Cramer*[1]. The X-ray structure analysis recorded below confirms this.

Well-formed colorless crystals of the diacetate *(1)* were available for the investigation. Boundary faces were {100}, {010,} {011}, and {11$\bar{1}$}. The short prismatic crystals used for measurement were of about 0.5 mm diameter. The following data were determined: Space group $P2_1/c$; $a = 8.18 \pm 1$, $b = 14.84 \pm 2$, $c = 7.50 \pm 1$ Å; $\beta = 116.1° \pm 1°$; $V = 817 \pm 3$ Å^3; $d_{py} = 1.265 \pm 2$, $d_{X\text{-ray}} = 1.270 \pm 4$ g·cm^{-3}; $Z = 2$; F_{000} (electrons/cell) = 336.



(1)

Using Cu–K_α radiation, 1448 independent reflections were measured with an automatic scintillation-counter diffractometer; of these, 77 lay below the limit of observation. Phase-determination of the 248 strongest reflections ($E > 1.4$) was achieved by the symbolic addition method[2]. A Fourier synthesis calculated with these values gave the positions of all eleven independent atoms except H [because of the centrosymmetry of *(1)*, only the atomic positions in one half of the molecule need to be determined]. After three cycles of refine-

ment of the coordinates by the method of least squares the R value fell to 16.8%. Then the ideal positions of the nine independent hydrogen atoms of the fourteen-membered ring were calculated and these were included in the subsequent calculations. In two further cycles of refinement, using isotropic temperature factors, the R value was lowered from 15.6 to 14.9%. The positions of the hydrogen atoms of the methyl groups have not yet been found. Figure 1 shows the projection of the nolecule on the x,y plane, with the calculated atomic distances and bond angles. The standard deviations of these values are somewhat less than 0.01 Å and 0.5 °, respectively.

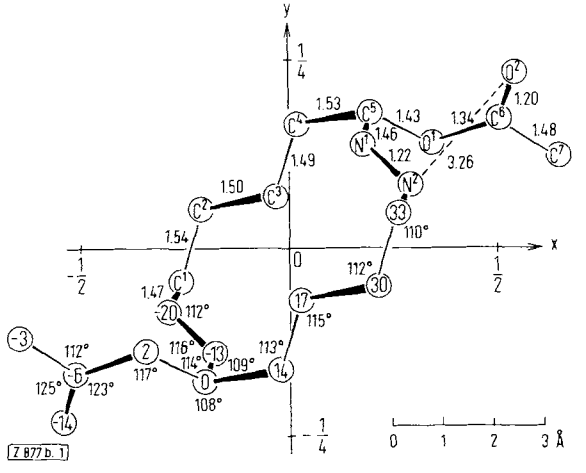


Fig. 1. x,y Projection of a molecule of 1,2,8,9-tetraaza-1,8-cyclodecadien-3,10-ylene diacetate *(1)*, with atomic distances and bond angles. Numbering of the atoms is shown in circles for one half of the molecule, and the heights (in 1/10 Å) above the plane of projection are shown in circles in the other half. The C—N bonds lie approximately in the direction of projection.

Each of the two sets of five carbon atoms (C^1—C^5) in the fourteen-membered ring forms a stretched zigzag chain (mean C—C distance 1.52 Å), these chains being joined by the two *trans*-azo groups (distances: C—N = 1.47; N=N = 1.22 Å). The acetoxy groups are approximately perpendicular to the plane of the ring with the carbonyl-oxygen atom approaching the azo group (separation: $O^2 \cdots N^2$ = 3.26 Å). The separations and angles are all normal, except for the short C—O bond in the acetoxy group (1.34 Å instead of 1.40 Å for a single bond $C(sp^2)$—O). The "hole" in the ring is completely filled by two hydrogen atoms (on C^3 and $C^{3'}$).

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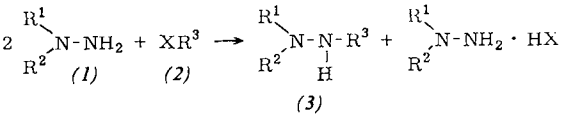
New Hydrazyls of Low Molecular Weight and Polymeric Hydrazyls[**]

By *D. Braun* and *G. Peschk*[*]

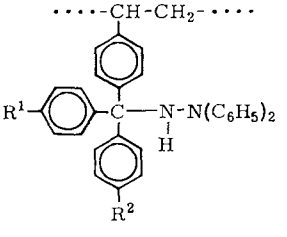
Almost all the stable hydrazyls known so far contain nitro groups[1]; the use of hydrazyls as radical traps in kinetic studies of polymerizations thus lead to uncontrollable side reactions. The only hydrazyl free from nitro groups known hitherto was 2,2-diphenyl-1-[2,4,6-tris(methoxycarbonyl phenyl]hydrazyl[2][***]. We have now prepared the hydrazines *(3a)*–*(3e)*, which contain no nitro group, by reaction of a hydrazine derivative *(1)* with a halogen compound *(2)* in the molar ratio 2:1 in ether or tetrahydrofuran. The hydrazines *(3a)*–*(3d)* can be oxidized by active PbO_2 to the hydrazyls, but these could not be isolated in solid form because they have, in general, a strong dehydrogenating action on the solvent.

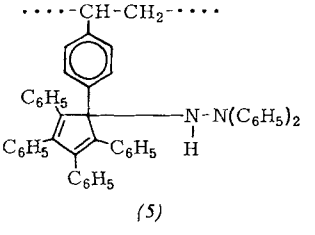


Cpd.	*(2)* X	*(3)*, name	*(3)*, M.p. (°C)	Hydrazyl $\tau_{1/2}$ [a]	Hydrazyl ESR lines
(a)	Cl	2,2-Diphenyl-1-[α-(4-biphenylyl)-benzhydrazyl]-hydrazine	85—86	≈ 3.5 h	7
(b)	Cl	2,2-Diphenyl-1-[α,α-bis(4-biphenylyl)-benzyl]hydrazine	124—126	≈ 3.5 h	7
(c)	Cl	9-[(Triphenylmethyl)-amino]carbazole	239—241	≈ 2.5 h	3
(d)	Br	9-[(Pentaphenylcyclo-pentadienyl)amino]-carbazole	218—219	45 min	3
(e)	F	9-[(2,4,6-Tricyano-phenyl)amino]-carbazole	157—159	—	—
(f)	Cl	Dodecahydro-9-(picrylamino)-carbazole	161—162	3.5 h	8

[a] Half-life determined by ESR measurements in benzene solution.

Dodecahydro-9-(picrylamino)carbazole *(3f)* was also prepared, as model substance. It could be oxidized by active PbO_2 to a relatively unstable radical.





(5)

(4a), $R^1 = R^2 = H$
(4b), $R^1 = H$, $R^2 = C_6H_5$
(4c), $R^1 = R^2 = C_6H_5$

The polyhydrazines *(4a)*–*(4c)* and *(5)* were obtained by treating diaryl(polyvinylphenyl)methyl chlorides[3] or tetraphenyl(polyvinylphenyl)cyclopentadienyl chloride[4] in tetrahydrofuran with 1,1-diphenylhydrazine (molar ratio 1:2 calculated on the chlorine content of the polymers). These products can be oxidized in benzene solution by active PbO_2 to polyhydrazyls that can be precipitated by dry light petroleum. The yellow-brown polymeric hydrazyls are stable in the solid state and are paramagnetic. They are soluble in benzene and tetrahydrofuran.

N-[(Pentaphenylcyclopentadienyl)amino]carbazole (3d):

N-Aminocarbazole (18.4 g, 0.1 mole) and pentaphenylcyclopentadienyl bromide[5] (26 g, 0.05 mole) in absolute tetrahydrofuran (*ca.* 150 ml) are refluxed gently for 5 h. The mixture is allowed to cool and precipitated hydrobromide is filtered off. The solution is concentrated and the substance remaining is dissolved in hot benzene and treated with an equal volume of hot ethanol, whereupon the hydrazine gradually crystallizes out. Pale yellow crystals [m.p. 218 to 219 °C, yield 25–27 g (80–85%)] are obtained after two recrystallizations.

To form the radical by oxidation, the substance is shaken with a ten-fold excess of active PbO_2 in benzene for 10 min. On rapid removal of the solvent, the reddish-brown solution affords an impure, reddish-brown paramagnetic product.

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[**] These investigations were supported by the Deutsche Forschungsgemeinschaft.

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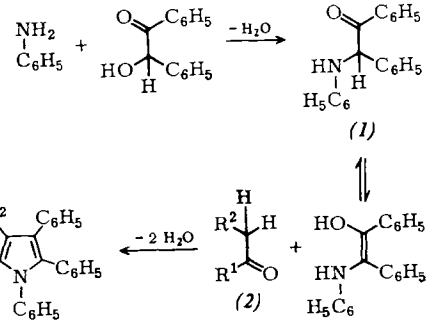
Simple Synthesis of Substituted 1,2,3-Triphenylpyrroles

By *H. J. Roth, H. George, F. Assadi*, and *H. J. Rimek* [*]

As simple as possible a synthesis of substituted 1,2,3-triphenylpyrroles was required in order that they might be precisely characterized when obtained photochemically [1]. For this purpose, benzoin was condensed with aniline under catalysis by traces of formic acid, yielding 2-anilino-2-phenylacetophenone (anilinodeoxybenzoin) *(1)* in almost quantitative yield. This was converted by reaction with CH-acidic



Cpd.	*(2)*	R^1	R^2	*(3)* Yield (%)	*(3)* M.p. (°C)
(a)	Acetophenone	C_6H_5	H	70	196
(b)	Phenylacetaldehyde	H	C_6H_5	75	175
(c)	Propiophenone	C_6H_5	CH_3	25	181
(d)	Phenylacetone	CH_3	C_6H_5	45	195–197
(e)	ω-Phenylacetophenone	C_6H_5	C_6H_5	20	277
(f)	Cyclopentanone	$-(CH_2)_3-$		30	188
(g)	Cyclohexanone	$-(CH_2)_4-$		53	174
(h)	Cycloheptanone	$-(CH_2)_5-$		35	158–160
(i)	Cyclooctanone	$-(CH_2)_6-$		24	144–148
(j)	1-Tetralone	$-o\text{-}C_6H_4-(CH_2)_2-$		35	208–210
(k)	2-Tetralone	$-o\text{-}(CH_2)_2-C_6H_4-$		28	209–210
(l)	1-Indanone	$-o\text{-}C_6H_4-CH_2-$		31	193–195

carbonyl compounds *(2)* into the pyrrole derivatives *(3)* in acceptable to good yields. The pyrroles *(3a)* [2], *(3b)* [3], and *(3c)* [4] have the properties recorded in the literature.

1,2,3-Triphenyl-4,5,6,7-tetrahydroindole (3 g):

2-Anilino-2-phenylacetone *(1)* (4 g) is refluxed with cyclohexanone (4 g) and 85% formic acid (200 g) for 3 h in a water separator (separating liquid: cyclohexanone/formic acid 30:1). The reaction mixture is allowed to cool and a 3–5-fold amount of methanol is added, whereupon white *(3 g)* crystallizes out after a few minutes; compound *(3 g)* can be recrystallized from *n*-butanol.

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$Pb(H_2PO_4)_4 \cdot (C_6H_5)_3PO$, Lead(IV) Tetrakis(dihydrogen phosphate) Stabilized by Triphenylphosphine Oxide

By *F. Huber* and *M. S. A. El-Meligy* [*]

Binary lead(IV) phosphates have been hitherto unknown. In our experience earlier attempts to prepare such compounds failed because of insufficient knowledge of conditions and gave only indefinite products with a considerable Pb(II) content [1] or complex lead(IV) phosphate(V) compounds [2] (the possible occurrence of complex phosphorus-containing lead(IV) derivatives had already been considered by *Bode* and *Voss* [3]). Our attempts to obtain lead(IV) phosphates by treatment of $Pb(OCOCH_3)_4$ or PbO_2 with phosphoric acid of various concentrations led finally to phosphatolead(IV) acids, *e.g.*, $H_2[Pb(H_2PO_4)_6]$, in which the central atom achieves the minimum coordination number 6 [4].

We then tried to stabilize lead(IV) phosphates by neutral electron-donors, such as $(C_6H_5)_3PO$, in two ways, namely, first by trapping binary lead(IV) phosphates by simultaneous complex formation with the donor at the moment of their formation in the above-mentioned reactions and, secondly, by anion-exchange of lead(IV) coordination compounds. We had no success with the first method, because complex formation with H_3PO_4 to very stable lead(IV) acids (formally $H_2[PbX_4(H_2PO_4)_2]$) associated *via* hydrogen bridges occurred immediately on dissolution of lead(IV) compounds in phosphoric acid and ligand exchange then occurred only subsequently in a slow reaction. The second method, however, was successful:

When $Pb(OCOCH_3)_4$ (11.1 g) was added to a solution of $(C_6H_5)_3PO$ (13 g) in anhydrous benzene (100 ml), a yellow precipitate was at once formed, which was slowly decolorized on addition of anhydrous phosphoric acid (9.3 g). After 3 hours' stirring at 50 °C the precipitate was filtered off under reduced pressure and dried. Elemental analysis accorded with the composition $Pb(H_2PO_4)_4 \cdot (C_6H_5)_3PO$ (oxidation value 99%).

This white crystalline product, which is slightly soluble in methanol but insoluble in other solvents, is astonishingly insensitive to moisture and is hydrolyzed only slowly in cold water although rapidly in hot water with separation of PbO_2; it decomposes in a vacuum above 140 °C. It was found thermogravimetrically that $(C_6H_5)_3PO$ is first split off quantitatively, and that the donor-free residue, presumably $Pb(H_2PO_4)_4$, then at once decomposes forming lead(II) phosphate.

The behavior on decomposition shows the importance of the donor for stabilization of the oxidation state +4 of the central atom; immediately after removal of the $(C_6H_5)_3PO$ the change of oxidation state $Pb^{IV} \rightarrow Pb^{II}$ occurs with loss of oxygen. The yellow precipitate that is formed on addition of

$(C_6H_5)_3PO$ to solutions of $Pb(OCOCH_3)_4$ in benzene decomposes when its isolation is attempted. From the analytically determined atomic ratio Pb:P = 1.00:0.93 and ligand exchange with H_3PO_4 to give $Pb(H_2PO_4)_4 \cdot (C_6H_5)_3PO$, however, it can be concluded that the yellow primary product is the 1:1 adduct $Pb(OCOCH_3)_4 \cdot (C_6H_5)_3PO$, which also had not previously been described.

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Structure of Molten Antimony[**]

By *H. U. Gruber* and *H. Krebs*[*]

The intensity distribution of Mo radiation scattered at a free surface of molten antimony has been measured with great accuracy by a Bragg-Brentano type camera followed by bent quartz crystal monochromator[1] and discriminator. The melt was placed in a quartz cuvette with a lustrous carbon window capable of being heated. The measured intensities were normalized by *Hosemann*'s empirical procedure[2].

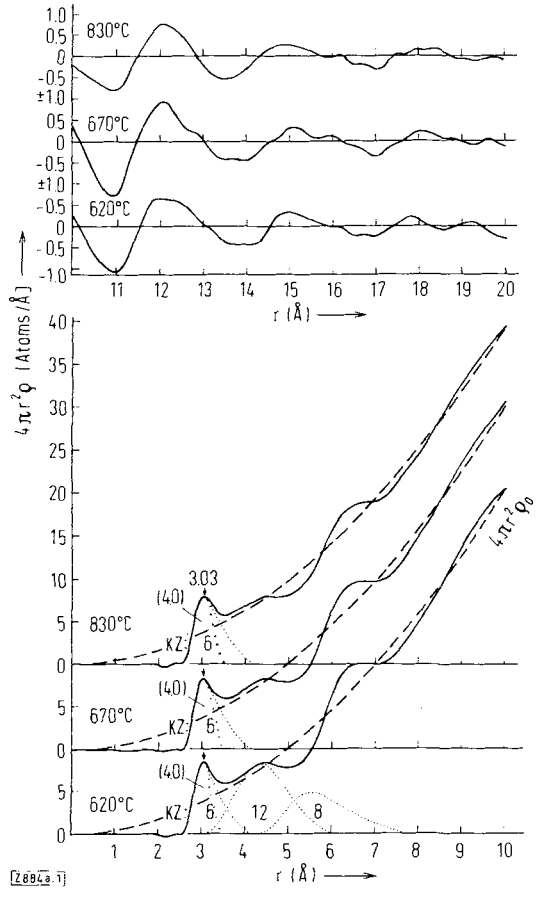

Fig. 1. Atom distribution curves for molten antimony. For r values > 10 Å only the deviation from the statistical distribution — the scale increased by a factor of 5 — is shown.

Figure 1 shows the atomic distribution curves at 620 (supercooled), 670, and 830 °C. Maxima can be recognized at $r \approx n \cdot 3.03$ Å where $n \approx 1, 2, 3, 4, 5$, and 6; there is also a well-developed maximum at $r \approx \sqrt{2} \cdot 3.03$ Å.

Hosemann[3] recently drew attention to the micellar structure of metallic melts. Accordingly antimony melts may be composed of double layers of limited extension as they can be cut out of a primitive cubic structure parallel to (100) (Fig. 2).

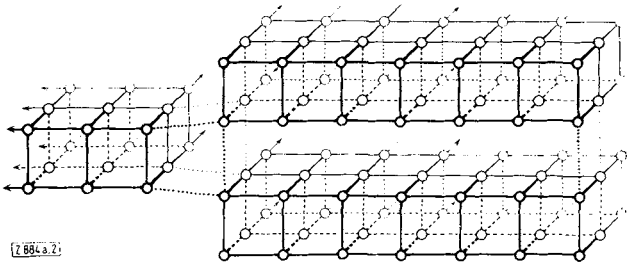

Fig. 2. Schematic representation of the atomic arrangement in molten antimony.

The atomatic distances are probably not equal within these double layers, but they alternate, as in the structures of black phosphorus or GeS[4]. The double layers may be arranged one on the other, as in GeS, since antimony has a strong tendency to take part in pσ bonds and sp hybridization is diminished[4]. In Figure 2 one possibility of lateral bonding of the double layers is indicated.

The great mobility of the atoms in the melt probably arises from the easy exchange between bilateral pσ bonding and unilateral sp hybrid bonding, so that a mesomeric bond is readily broken on one side and strengthened on the other[4].

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[**] Cf. *H. U. Gruber*, Dissertation, Universität Stuttgart 1968; *H. U. Gruber* and *H. Krebs*, Z. Naturforsch., in press.

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Electrical Conductivity and Formation of Chalcogenide Glasses in Ge–As–Se and Ge–Sb–Se Melts[**]

By *R. W. Haisty* and *H. Krebs*[*]

A high-polymeric glass can be formed from a melt only if a large portion of bivalent atoms (*e.g.*, O, S, Se, or Te) or atomic groups (*e.g.*, CH_2) with a bond angle $< 180°$ is present, allowing an irregular type of bonding[1,2] and thus, together with slight thermal dissociation, a certain mobility of the atoms in a viscous melt. If the starting material contains too many tervalent (*e.g.*, P, As, or Sb) and quadrivalent atoms (*e.g.*, Si or Ge), dissociation processes do not lead to sufficient mobility of the atoms to permit a molten liquid state. In this case the melting process must be connected with a complete change in the bonding system. As in molten germanium, the coordination number 6 should be approached, since then, as with germanium, mesomeric pσ bonding is possible. As a result metallic conductivity should occur and, in addition, the atoms then would be highly mobile, since by

local conversion into unilaterally binding sp hybrid quantum states bonds can be broken easily while others are strengthened [2, 3]. The high mobility of the electrons, and thus of the atoms themselves, should lead to great reactivity of the atoms and hence to crystallization of the melt.

These relations were verified experimentally for the systems Ge–Sb–Se and Ge–As–Se. The electrical conductivity could be measured up to high temperatures by a new, very rapid, electrodeless method [4].

Figure 1 shows the glass-forming region for slow and rapid cooling in the system Ge–Sb–Se. Glass-forming melts are semiconducting, with a wide forbidden zone (symbol ○). Far

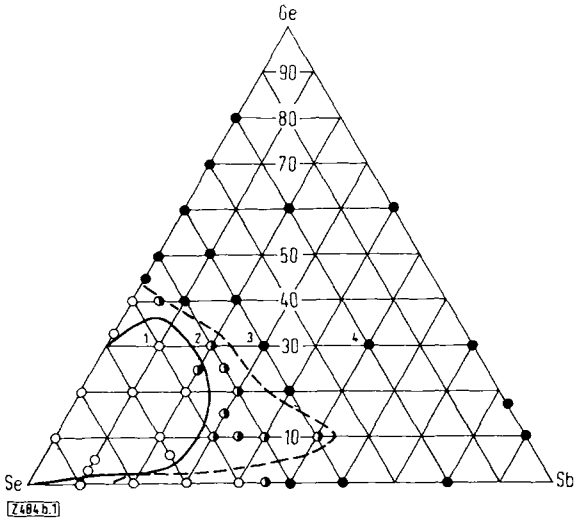

Fig. 1. Glass-forming region in the system Ge–Sb–Se on slow (——)[5] and rapid (- - -) cooling. Typical electrical conductivity curves for the compositions 1,2,3, and 4 are reproduced in Fig. 2.

outside the glass-forming region the melts have metallic conductivity (●). However, relatively high but non-metallic conductivity (◑) is found in a transition region; there the melts seem to be biphasic in microregions, containing metallic

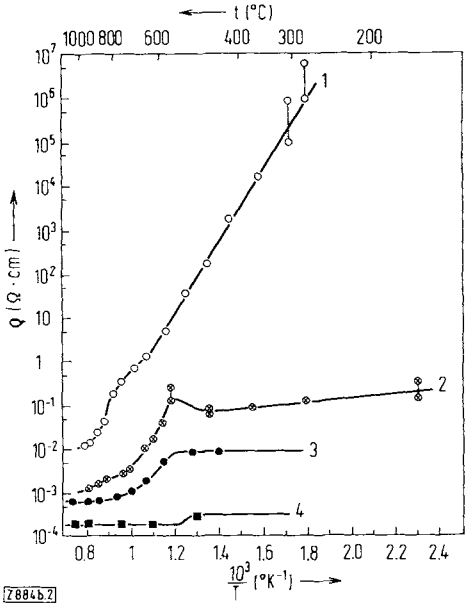

Fig. 2. Electrical conductivity of Ge–Sb–Se melts — curves for the compositions 1,2,3, and 4 (cf. Fig. 1).

conducting micelles (enriched in Ge and Sb) within a semiconducting matrix (enriched in Se). Crystallization of antimony-containing selenium melts is made easier by a catalytic influence of the antimony.

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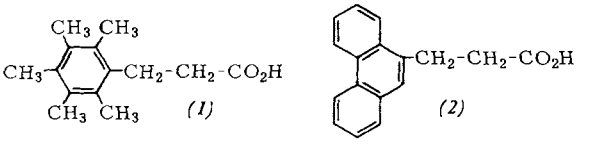
Formation of Electron-donor-acceptor Complexes as a Basis for Specific Adsorption

By *H. Stetter* and *J. Schroeder* [*]

We have begun a study of whether the formation of electron-donor-acceptor complexes can be used for specific adsorption in the chromatography of compounds of high molecular weight [1]. The most suitable substrates proved to be cellulose esters of 3-(pentamethylphenyl)- *(1)* and 3-(9-phenanthryl)-propionic acid *(2)* [2], which can be prepared from mercerized cellulose and the chlorides of the two acids [3]. Each glucose unit could be esterified with 2–3 equivalents of the acid.



The new cellulose esters permit appreciably better separation of aromatic nitro compounds and of quinones than is possible on commercial cellulose powder or silica gel (Figs. 1 and 2).

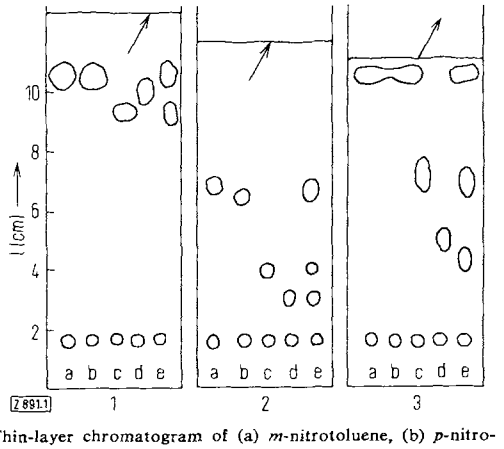


Fig. 1. Thin-layer chromatogram of (a) *m*-nitrotoluene, (b) *p*-nitrotoluene, (c) 2,4-dinitrotoluene, (d) 2,4,6-trinitrotoluene, (e) mixture. 1 = MN silica gel, 2 = cellulose ester of *(1)*, 3 = cellulose ester of *(2)*. Eluant: ether/light petroleum/acetone 50:40:10. Color of the complexes: yellow-red.

Moreover the position of the substances on the plate can be easily determined by the color of the donor-acceptor complexes formed. We consider this principle of specific adsorption to be capable of extension.

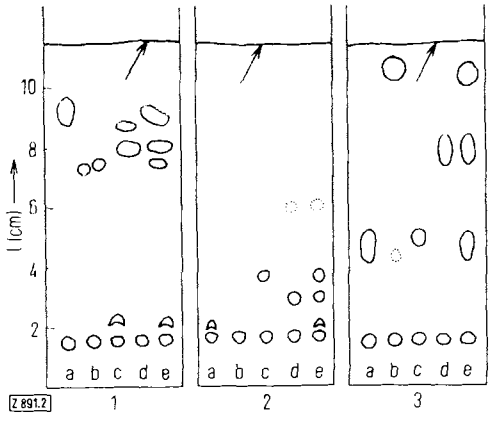


Fig. 2. Thin-layer chromatogram of (a) chloranil, (b) tetrachlorohydroquinone, (c) 1,2-naphthoquinone, (d) 1,4-naphthoquinone, (e) mixture. Adsorbant and eluant as for Fig. 1. Color of the complexes: yellow-red.

Cellulose ester of (1):

Mercerized cellulose[4] (10.6 g) is made into a slurry with pyridine (22 ml) and dioxane (78 ml). The acid chloride (56 g) of *(1)* in dioxane (200 ml) is added and the whole is heated at 95 °C for 24 h, and the ester is then precipitated by pouring the mixture into methanol (500 ml). The ester is isolated, boiled with acetone, triturated with a little methanol for 3 h in a ball mill, filtered off, and dried (yield 39.6 g; insoluble in alcohols, sparingly soluble in chlorinated hydrocarbons; sap. val: found 75.0% of acyl; calc. for diester 71.7% and for triester 79.3%).

Cellulose ester of (2):

Cellulose (11.3 g) in pyridine (23 ml) and dioxane (150 ml) is heated with the acid chloride (68 g) of *(2)* in dioxane (220 ml) as above for 48 h. The viscous solution is poured into methanol (1 l) + acetone (500 ml). The precipitated ester is filtered off, ground twice with methanol/acetone, and triturated with a little acetone in a ball mill for 2 h. It is insoluble in most organic solvents (yield 50 g; sap. val: found 75.3% of acyl; calc. 74.4% for diester).

For thin-layer chromatography 5 g of the cellulose ester of *(1)* is homogenized on a shaker with 0.3 g of gypsum, 8 ml of methanol, and 5 ml of water. For the ester of *(2)*, 4 g are similarly treated with 0.2 g of gypsum, 20 ml of methanol, and 5 ml of water. These materials are placed on plates, dried in the air, and heated at 90–100 °C shortly before use.

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1,5,9-Cyclododecatriene Complexes of Nickel(0) [**]

By *K. Jonas, P. Heimbach*, and *G. Wilke* [*]

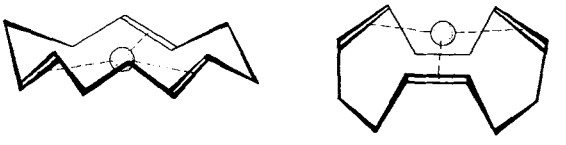
Cyclotrimerization of butadiene on 'naked' nickel leads to three isomeric cyclododecatrienes[1] (*cis,cis,trans*-CDT, *cis,trans,trans*-CDT, and all-*trans*-CDT). all-*cis*-CDT is not formed catalytically but can be prepared from all-*trans*-CDT[2]. Of the nickel complexes, so far only the deep red all-*trans*-CDT–Ni(0) *(1)* has been prepared[3]; its X-ray structure analysis[4] shows the nickel atom to occupy the center of the ring and to interact with all three double bonds. We have now studied the problem whether the other isomers can form defined complexes with nickel(0).

On treatment of bis(2,4-pentanedionato)nickel(II), $Ni(acac)_2$, with triethylaluminum (3:2; in ether) in the presence of *cis,cis,trans*-CDT or *trans,trans,cis*-CDT, red solutions are obtained from which $Al(acac)_3$ can be separated at −78 °C. If the filtrate therefrom is concentrated and cooled to −20 °C, pale red needles are precipitated whose composition corresponds approximately to $C_{12}H_{18}Ni$. The very soluble products decompose extremely easily so that attempts at further purification have so far failed.

However, all-*cis*-1,5,9-cyclododecatrienenickel(0) *(2)* can be very easily obtained in pure form by mixing the all-*trans*-complex *(1)* with all-*cis*-CDT in the molecular ratio 1:1 in ethereal solution at −78 °C and warming the whole slowly to room temperature. The color of the solution soon changes from deep red to yellow and on renewed cooling to −78 °C almost colorless needles of composition $C_{12}H_{18}Ni$ (mol. wt. 210, cryoscopic) in benzene are precipitated in 75% yield.

$$ttt\text{-CDT}\cdot Ni(0) + ccc\text{-CDT} \rightarrow ccc\text{-CDT}\cdot Ni(0) + ttt\text{-CDT}$$

This complex *(2)* reacts with CO, yielding $Ni(CO)_4$ and free all-*cis*-CDT. Its ^{1}H-NMR spectrum (in deuteriobenzene) shows two signals at τ = 5.24 (=CH–) and 7.68 ($-CH_2-$) with the intensity ratio 6:12, *i.e.*, all three *cis*-double bonds are bound to the nickel atom, as in *(1)*. It can be seen from the model that *cis*-CDT in *(2)* thus very probably occurs in the crown form.



(1) *(2)*

In the complex of this isomer there is maximum overlap of the metal orbitals with those of the double bonds, since both the bonding and the antibonding orbitals of all three *cis*-double bonds lie in one plane, whereas in the less stable complex *(1)* the three *trans*-double bonds are turned propellor-wise out of this plane[4].

There is clearly no relation between the stability of the individual complexes with nickel(0) and the isomer distribution of the cyclododecatrienes formed from butadiene on 'naked' nickel, since the isomer, all-*cis*-CDT, giving the most stable complex with Ni(0), is not formed catalytically.

The fourth coordination position of the nickel atom in *(2)* can be occupied by another ligand, as in *(1)*; but only tris-(*o*-biphenylyl) phosphite gives a stable 1:1 adduct with *(2)*, whereas phosphines also form stable 1:1 complexes with *(1)*.

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[**] Part of the dissertation by *K. Jonas*, Universität Bochum (Germany), 1968.

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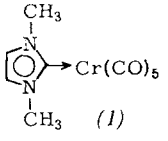
Pentacarbonyl(2,3-diphenylcyclopropenylidene)-chromium(0)

By *K. Öfele* [*]

All the stable transition-metal-carbene complexes known so far contain carbene ligands whose nucleophilic character is ascribed to delocalization of non-bonding electron pairs in hetero atoms to a vacant p-orbital of the carbene-carbon atom [1]. $(C_6H_5)_2C{=}CFe_2(CO)_8$, in which diphenylvinylidene occurs as carbene bridging ligand [2], represents an exception.

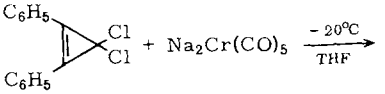
In pentacarbonyl(1,3-dimethylimidazolin-2-ylidene)chromium(0) [3] *(1)* and a series of analogous pentacarbonylchromium and tetracarbonyliron complexes with 1,2-dimethyl-

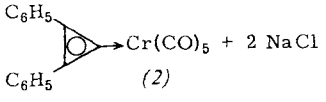


(1)

pyrazolin-3-ylidene, 3-methylthiazolin-2-ylidene, and 2,4-dimethyl-1,2,4-triazolin-3-ylidene as ligand [4], the nucleophilic character of the carbene ligands is particularly strongly developed because an aromatic 6π-electron system can arise by this delocalization. This may be the reason for the observed stability of the above-mentioned complexes and of the bis-(1,3-diphenylimidazolio)mercury salt prepared by *Wanzlick et al* [5].

To discover whether cyclic carbenes such as diphenylcyclopropenylidene [6] that contain an aromatic π-electron system but not any hetero atom would also form stable complexes with transition metals, 1,1-dichloro-2,3-diphenylcyclopropene was treated with $Na_2Cr(CO)_5$. A deep yellow, crystalline compound of m.p. 199–200 °C (decomp.), was formed, which was identified as pentacarbonyl(2,3-diphenylcyclopropenylidene)chromium(0) *(2)* by elemental analysis and by its mass spectrum.





(2)

The following ions occur in the mass spectrum [7] of *(2)*:

m/e	I_{rel}	Assignment
382	9.6	$(CO)_5CrL^+$
354	0.2	$(CO)_4CrL^+$
326	4.0	$(CO)_3CrL^+$
298	9.7	$(CO)_2CrL^+$
270	17	$(CO)CrL^+$
242	100	CrL^+
52	61	Cr^+

L = diphenylcyclopropenylidene.

A very weak peak occurs at *m/e* = 190 due to free carbene presumably split off thermally. The intensity distribution with the carbene-Cr fragment as base peak is similar to that observed for *(1)* [3] and other pentacarbonylchromium complexes with acyclic carbene ligands [8].

As in the case of *(1)*, the IR spectrum of *(2)* contains fewer ν(CO) bands than expected, namely, at 2061 (m) and 1938 cm^{-1} (vs) (in cyclohexane). In the ultraviolet region a solution of the compound in cyclohexane absorbs at 440 ($\log \varepsilon = 3.42$), 366 (4.16), and 248 nm (4.75). The ^{1}H-NMR spectrum of *(2)* in $CDCl_3$ shows two multiplets at $\tau = 1.68$ and 2.26 (intensity ratio 2:3) for the phenyl protons.

The new complex, with a carbene ligand but no hetero atom, is astonishingly stable. In the crystalline state it is stable to air; in an inert atmosphere it decomposes only above 192 °C, forming $Cr(CO)_6$, and in a vacuum it can be sublimed at 110 °C without decomposition. It dissolves readily in benzene, moderately in ether or acetone, and sparingly in light petroleum.

Experimental:

A solution of 1,1-dichloro-2,3-diphenylcyclopropene (1.5 g, 6.5 mmoles) in tetrahydrofuran (10 ml) was added dropwise to a solution of $Na_2Cr(CO)_5$ (1.6 g, 6.7 mmoles) in tetrahydrofuran (25 ml) at −20 °C with vigorous stirring and exclusion of air. After 1/2-hour's stirring at room temperature, the solvent was removed under reduced pressure, and the brown residue was taken up in ether (100 ml) and washed in a separatory funnel with two portions (each 20 ml) of water. The ethereal solution was then dried over sodium sulfate and filtered through Al_2O_3 on a G4 fritted filter. The ether was then distilled off in a vacuum and the residue was warmed for 1 h under high vacuum at 60 °C to remove $Cr(CO)_6$ and diphenylcyclopropenone. The crude product thus obtained was dissolved in benzene/ether (1:2) and freed from a dark brown impurity by chromatography with hexane and ether (column length 1 m; silica gel). The yield was 19.5%.

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Dipotassium Hexaamidoplumbate(IV) [**]

By *O. Schmitz-Du Mont* and *W. Jansen* [*]

The only purely inorganic lead(IV)-nitrogen compound to have been discovered up till now was obtained by *Schwarz et al.* [1] on ammonolysis of $PbCl_4$ in liquid NH_3. The product, which still contains chlorine, was assigned the empirical formula $Pb_5N_6Cl_4$; nothing is known about its structure. On ammonolysis of $Pb(C_6H_5)_4$ in liquid NH_3 and in the presence of KNH_2, we obtained a black, insoluble Pb^{IV} compound as a by-product that was so explosive that it could not be isolated [2]. The main reaction product, which was formed in the course of a redox reaction with liberation of N_2, was $K[Pb(NH_2)_3]$ *(1)*. We assumed that complete ammonolysis of $Pb(C_6H_5)_4$ first leads to dipotassium hexaamidoplum-

bate(IV), $K_2[Pb(NH_2)_6]$ *(2)*, which is unstable at 20 °C and mainly decomposes to form *(1)* and N_2. Lowering of the reaction temperature could possibly permit isolation of *(2)*.

Since tetraphenyllead, which is insoluble in liquid NH_3, does not react below 5 °C, readily soluble $(C_6H_5)_2PbI_2$ was subjected to ammonolysis at −75 °C in the presence of KNH_2. On addition of KNH_2 to the colorless solution of $(C_6H_5)_2PbI_2$ (1.2 g, 1.9 mmole) in NH_3 (60 ml) a voluminous yellow precipitate of $[(C_6H_5)_2Pb]_3N_2$ is first formed which redissolves after a total of 0.55 g (10 mmole) of KNH_2 has been added. If the yellow solution is then warmed to −25 °C, lustrous, colorless crystals gradually separate, which are filtered off after 3 h, washed with liquid NH_3 at −50 °C, and are freed from retained NH_3 under reduced pressure at −75 °C. Hydrolysis in a moist stream of oxygen-free nitrogen at −20 °C (absorption of liberated NH_3 in 2% aqueous boric acid; NH_3 determined conductometrically[2]) affords a brownish black precipitate. The analytical data correspond to the formula $K_2[Pb(NH_2)_6]$.

We assume the following reaction scheme to apply in the formation of *(2)*:

$$3\,(C_6H_5)_2PbI_2 \xrightarrow[-6\,KI,\,-4\,NH_3]{+\,6\,KNH_2\,(-75\,^\circ C)} [(C_6H_5)_2Pb]_3N_2 \text{ yellow precipitate}$$

$$[(C_6H_5)_2Pb]_3N_2 \xrightarrow{+\,6\,KNH_2,\ +\,4\,NH_3} 3\,K_2[(C_6H_5)_2Pb(NH_2)_4] \text{ yellow solution}$$

$$3\,(2) \xrightarrow[-\,6\,C_6H_6]{+\,6\,NH_3\,(-25\,^\circ C)} 3\,K_2[(C_6H_5)_2Pb(NH_2)_4]$$

In contrast to the analogous, highly stable tin compound $K_2[Sn(NH_2)_6]$, which has been known for a long time, compound *(2)* decomposes at room temperature with a black coloration, and with liberation of NH_3 and partial reduction of Pb^{IV} to Pb^{II} as well as formation of a black, highly explosive substance. Discoloration also occurs under liquid NH_3 at 0 °C. At 10 °C the black precipitate disappears within 40 h, with simultaneous evolution of N_2. After filtration of the solution and evaporation of NH_3 there remains a colorless, crystalline precipitate, which could be identified as a mixture of *(1)* and KNH_2 (analysis, Debye photograph).

Hydrazine and diimine[3] are probably involved in the decomposition of *(2)* according to the equation:

$$3\,(2) \rightarrow 3\,(1) + 3\,KNH_2 + 4\,NH_3 + N_2$$

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Fragmentation of Specifically Deuterated Tri-*n*-alkylchromium Compounds

By *R. P. A. Sneeden* and *H. H. Zeiss*[*]

Tri-*n*-alkylchromium compounds undergo fragmentation in tetrahydrofuran solution, on warming from −70 to +20 °C, to unequal quantities of *n*-alkane and 1-*n*-alkene plus a hydridochromium species capable of catalyzing the isomerization of the terminal olefins[1,2].

$$x\,(RCH_2CH_2)_3Cr(THF)_n \xrightarrow{-70\text{ to }+20^\circ} y\,RCH_2CH_3 + z\,RCH{=}CH_2 + x\,\text{"HCR"} (+\,m\,THF)$$

In order to determine the origin of the hydrogen atoms required for the formation of the alkane and hydridochromium species the fragmentation of the tris([2,2-D_2]-4-phenylbutyl)-chromium *(1)* and tris([1,1-D_2]-4-phenylbutyl)chromium *(2)* in tetrahydrofuran solutions has been studied[3,5].

At −40 °C both *(1)* and *(2)* are stable, undergoing methanolysis to essentially pure [2,2-D_2]- and [1,1-D_2]-4-phenylbutane [*(3)* and *(4)*] respectively.

After 0.5 h at 20 °C, *(1)* has undergone partial fragmentation (Table 1, exp. 1). The products, after hydrolysis, consist of hydrogen and hydrogen deuteride, *(3)* containing some [1,2,2-D_3]-4-phenylbutane *(5)*, plus [2-D]-4-phenyl-1-butene containing some [1,2-D_2]-4-phenyl-1-butene.

$$(C_6H_5CH_2CH_2CD_2CH_2)_3Cr(THF)_n \xrightarrow[2)\,H_2O]{1)\,0.5\text{ h at }20^\circ C} \begin{cases} C_6H_5CH_2CH_2CD_2CH_2(H, D) \\ C_6H_5CH_2CH_2CD{=}CH(H, D) \\ H_2 + HD \end{cases}$$

After 20 h at 20 °C, the organochromium compound has undergone complete fragmentation and the isomerization of the 1-alkene is complete. The products after hydrolysis (Table 1, exp. 2) now consist of hydrogen and hydrogen deuteride, *(3)*, and *(5)*, plus deuterated *cis*- and *trans*-2- and 3-alkenes.

Table 1. Fragmentation of tris([2,2-D_2]-4-phenylbutyl)chromium and tris([1,1-D_2]-4-phenylbutyl)chromium. Isotopic compositions of hydrolysis products.

Exp. No.	Product	Quantity [a]	Isotopic Composition [b] D_0	D_1	D_2	D_3	D_4
1	alkane	86.2	0.3	3.4	81.3	14.4	0.6
	1-alkene	13.2	6.3	77.1	13.7	1.6	1.1
	H_2/HD	0.6 [c]	93.7	6.3	0.0		
2	alkane	76.0	2.3	7.6	60.1	27.2	2.6
	1-alkene	0.7	[d]	[d]	[d]	[d]	[d]
	H_2/HD	0.75 [c]	98.7	1.3	0.0		
3	alkane	78	1.3	4.8	87.7	5.1	1.1
	1-alkene	10	8.0	29.3	47.0	15.0	0.7
	H_2/HD	0.5 [c]	97.4	2.6	0.0		

[a] Unless otherwise stated, these are the relative percentages present in the total hydrocarbon mixture.
[b] Expressed in relative percentages and corrected for natural isotopic abundances.
[c] Expressed in mmoles per mmole chromium.
[d] Not measured.

After 0.5 h at 20 °C, *(2)* has undergone extensive fragmentation and the resulting 1-alkene has been partially isomerized. The products after hydrolysis (Table 1, exp. 3) are hydrogen and hydrogen deuteride, *(4)* containing some trideuterated 4-phenylbutane, a complex mixture of non-deuterated 4-phenyl-1-butene and mono-, di- and tri-deuterated 4-phenyl-1-butenes, in which the deuterium is distributed over C^1, C^2, and C^3, plus *trans*- and *cis*-2-alkenes.

$$(C_6H_5CH_2CH_2CH_2CD_2)_3Cr(THF)_n \xrightarrow[2)\,H_2O]{1)\,0.5\text{ h at }20^\circ C} \begin{cases} C_6H_5CH_2CH_2CH_2CD_2H \\ C_6H_5CH_2CH(H, D)C(H, D) = CD(H, D) \\ \textit{trans}\text{- and } \textit{cis}\text{-2-alkene} \\ H_2 + HD \end{cases}$$

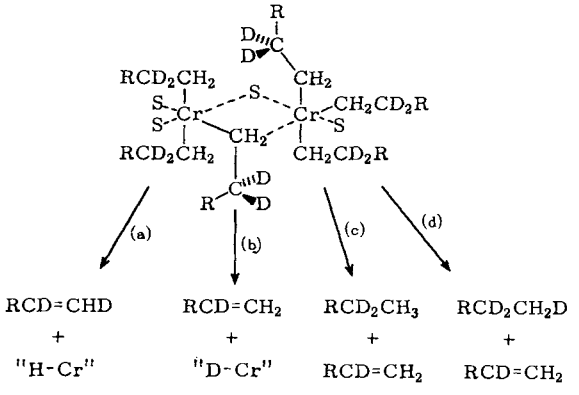
The present results prove that in the fragmentation of tri-*n*-alkylchromium compounds:

(i) the hydrogen (deuterium) atoms present on the carbon atoms α and β to the metal center are transferred to the metal[6] (HD on hydrolysis);

(ii) the hydrogen (deuterium) on the carbon atom β to the metal center is acquired by one of the alkyl groups originally bonded to the chromium (presence of trideuterioalkane);

(iii) prior to the isomerization process (and perhaps during it) there is transfer of hydrogen and deuterium over C^1, C^2, and C^3, this occurring without concomitant double bond migration.

It is now clear that the fragmentation of tri-*n*-alkylchromium compounds involves at least two fundamental processes, the first is a homolytic or one-electron transfer process in a monomeric or dimeric chromium species and the second is β-elimination of metal hydride[7]. These can be summarized, for the dimeric species, as follows: (R = $C_6H_5CH_2CH_2-$; S = THF):



(a): α-elimination of metal hydride. (b): β-elimination of metal hydride. (c): attack on solvent. (d): attack on alkyl group.

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[4] All isotopic compositions were kindly determined mass spectrometrically by Dr. *W. E. Koerner* and his associates of Monsanto Company, Research Center, St. Louis, Mo. USA.

[5] The individual organic compounds were isolated by preparative scale gas chromatography and identified by comparing their infrared and ^{1}H-NMR spectra with authentic specimens. The isotopic compositions of the pure compounds were determined by mass spectrometry [4], the location of the deuterium atoms follows from the proton count of the ^{1}H-NMR spectra. The gaseous products were isolated using a vacuum line and their identities and compositions established by mass spectrometry [4].

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Ring Closure of 2-Hydroxyadipaldehyde

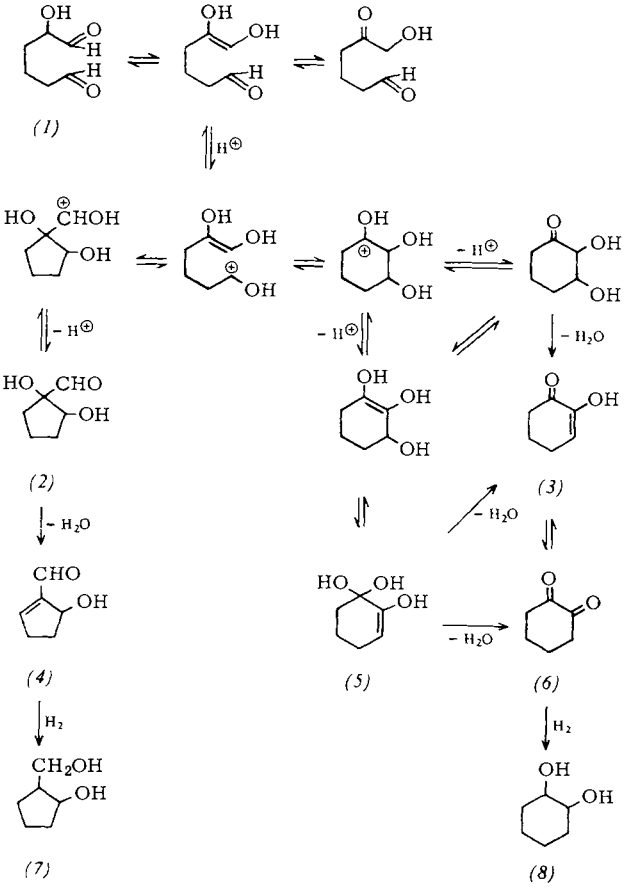
By *H. Mathais, J. P. Schirmann*, and *F. Weiss*[*]

Feichtinger and *Noeske*[1] recently reported that 1,2-cyclohexanediol *(8)* is formed on discontinuous pressure hydrogenation of aqueous solutions of 2-hydroxyadipaldehyde *(1)* to 1,2,6-hexanetriol, ring closure being assumed to occur with 1,6-linkage and elimination of the hydroxyl group from the α-position.

However, as we have found, the ring is closed before the hydrogenation occurs. 1,2-Cyclohexanediol *(8)* is formed by hydrogenation of 1,2-cyclohexanedione *(6)* or its enol *(3)* or hydrate *(5)* (see Scheme 1), which are formed by intramolecular aldol formation merely on warming an aqueous solution of *(1)*[2–5]. If, for instance, 200 g/h of a 20% aqueous, slightly acid (pH 5) solution of *(1)* is passed through a copper tube (length 500 mm, diameter 10 mm) at 140–170 °C in a stream of nitrogen (12 l/h), the aldehyde is completely cyclized. Several extractions with dichloromethane afford 1,2-cyclohexanedione *(6)* in 48% yield and 5-hydroxy-1-cyclopentene-1-carboxaldehyde *(4)* in 34% yield; if the experiment is conducted at about 80 °C, then only the dione is detectable by gas chromatography.

The reaction is extremely fast in the hot, *e.g.*, when a solution of *(1)* is injected into an evaporation cell for gas chromatography. A certain amount of *(6)* may be formed, as shown by thin-layer chromatography, when an aqueous solution of 3,4-dihydropyran-2-carbaldehyde is heated to prepare *(1)*.

The varying results of continuous and discontinuous pressure hydrogenation of *(1)* are thus explained as follows: in discontinuous experiments, *(1)* is exposed to heat for relatively long times and at relatively high concentrations and can thus cyclize partly before hydrogenation occurs. Experimentally, *cis*- and *trans*-1,2-cyclohexanediol *(8)* and 2-hydroxycyclopentanemethanol *(7)* are formed, which proves this stepwise process; further, 1,2-dihydroxycyclopentanemethanol – a hydrogenation product of *(2)* – was found on hydrogenation of *(1)* over copper at 200 °C[6]. However, in the continuous process the concentrations of *(1)* are kept so low by immediate hydrogenation that the ring-closure mechanisms cannot operate.



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Ion Pair Formation in Benzene Radical Anion Solutions[**]

By *G. L. Malinoski jr.* and *W. H. Bruning*[*]

Our investigations of electron transfer effects on the ESR spectrum of benzenide ion produced by alkali metal reduction in tetrahydrofuran (THF), dimethoxyethane (DME), and mixtures of these two solvents lead us to believe that extensive ion pairing occurs with metal ions in solution[1].

However, our results do not agree with the spectra or discussion recently reported by *Köhnlein, Böddeker,* and *Schindewolf*[2]. These authors reported a spectrum of about 15 lines obtained after warming the solution (in THF/DME) to 0 °C and then recooling to −30 °C in the absence of alkali metal alloy. In addition, during this cycle they observed a color change from deep green to brown-yellow. They also reported that if alkali metal was visibly present in the solution the color remained deep green and the normal 7 line ESR pattern of $C_6H_6^-$ was obtained. They concluded that the 15 line pattern arose from interactions with metal ions causing the lifting of the orbital degeneracy in $C_6H_6^-$.

We have tried unsuccessfully to repeat their experiments. Great care was taken in our work to purify solvents and benzene. (A. R. grade solvents were exhaustively dried over Na–K alloy, distilled from the alloy, degassed and transferred from one vacuum storage bottle, containing Na–K alloy, to another several times. Spectroquality benzene was dried over Na–K alloy in vacuum storage bottles, for periods of months, until use.) In a given glass apparatus several preparations of anion radical were usually made and discarded *via* glass sidearms in an attempt to scavenge all possible impurities in the system before producing the final solution for ESR analysis. The resulting solutions were always blue or slightly blue green in color and repeated warming-cooling cycles, with or without metal present, caused no color changes and did not affect the ESR spectra obtained. (Warming and cooling without metal present did lead to some reduction of signal intensity, presumably due to decomposition of $C_6H_6^-$.)

Many different samples were prepared with initial neutral benzene concentrations in the range 0.1 M to 4 M using solvents from different sources. Reductions were carried out with either Na–K alloy in mixed solvents or with K in DME, THF, or the mixed solvents. Our spectra always gave the basic 7 line pattern of benzenide ion, often broadened due to electron transfer. (The spectra could be collapsed to the exchange narrowed limit depending on the concentration of neutral benzene and temperature.) Computer simulation of these spectra in the broadening limit could be accomplished using solutions to the density matrix equations[3]. An alkali metal coupling constant of approximately $a_M = 0.5–0.7$ gauss was included along with $a_H = 3.6$ gauss[4] (Figure 1).

Our experiments indicated that a_M depends on concentration of neutral benzene as well as temperature. (As $[C_6H_6]$ increases a_M seems to increase. The dielectric constant of benzene is ~3 times smaller than THF or DME[5] and the increase in a_M is not unreasonable.) At no time however, did we observe spectra attributable to a predominant interaction of the electron spin with the symmetrical E_{2u} state of benzene.

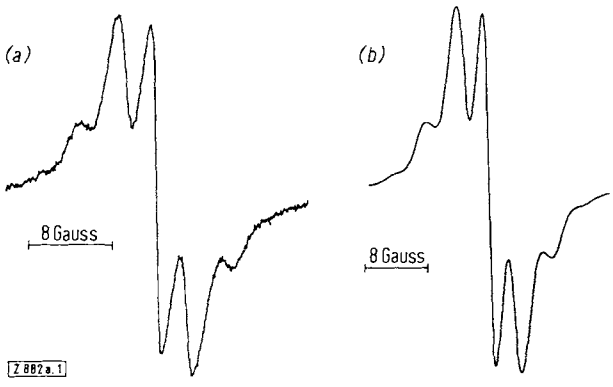

Fig. 1. (a) ESR spectrum of $C_6H_6^-$ produced by reduction of benzene (≈ 4 M in DME) with potassium. $T = -24$ °C.

(b) Computer simulation of the same spectrum: $a_H = 3.6$ gauss, $a_K = 0.7$ gauss, mean lifetime of species $\tau = 3.75 \times 10^{-7}$ sec. With $a_K = 0$, a completely different pattern results.

Alkali metal splitting was not observed at temperatures between −85 and +30 °C. Time dependent electron transfer, metal ion transfer, or rapid interconversion processes between various types of ion pairs may be responsible for this[6]. In addition, as temperature is lowered metal splittings generally decrease and relatively slow processes can still lead to averaging effects which wipe out small splittings[5]. (There is always neutral benzene present in these systems and electron transfer is important, even at −50 °C.)

We believe *Köhnlein et al.* did observe a species related to $C_6H_6^-$; however, our results indicate that their spectrum cannot be attributed to interaction with the gegenion. The warming-cooling cycle dependence they reported, with or without metal present, could perhaps be explained if $C_6H_6^-$ abstracted a proton from a trace impurity in their system. Protonation could lead to a depression in energy of the symmetric orbital and a 15 line pattern would result if the magnetic interaction of the extra proton was very weak. Subsequent contact with alkali metals could then destroy such a species, with evolution of H_2 in the system.

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A Reinterpretation of the ESR Spectrum Attributed to a Non-degenerate State of the Benzene Radical Anion[**]

By *Pamela Wormington* and *J. R. Bolton*[*]

Köhnlein, Böddeker, and *Schindewolf*[1] recently reported a fifteen-line ESR spectrum which they attributed to the benzene anion confined in the symmetrical (E_{2u}) state[2] of the degenerate ground state of the benzene anion. They reported a large triplet (1:2:1) hyperfine splitting of 6.5 G and a smaller quintet (1:4:6:4:1) splitting of 1.7 G. Indeed these hyperfine splittings are close to those expected for a benzene anion confined to the symmetrical state.

On reinvestigation of this system ($C_6H_6^-$ in THF/DME[1]), we find that each line of the original fifteen-line spectrum splits into at least twelve components; this finding clearly demonstrates that the spectrum does not arise from any form of the benzene radical anion.

The ESR spectra were recorded on a modified Varian V 4502 spectrometer; a sample of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine in methanol was used for field calibration[3]. The solvent (Mallenckradt Chromatographic spectro grade) was purified by distillation from CaH_2 and subsequent vacuum distillation from $LiAlH_4$ into a solvent vessel containing sodium and an involatile aromatic hydrocarbon such as perylene; the benzene (Coleman, Matheson and Bell "spectrograde") was used as received.

At −60 °C a "normal" 7-line benzene anion spectrum[4] was obtained. As the temperature was raised, the spectrum broadened and all but disappeared at 0 °C. At 20 °C a triplet structure began to appear which then resolved into three quintets. However, on reducing the microwave power below 1 milliwatt and using a very low modulation amplitude, each of the fifteen lines resolved into at least twelve components. We have been able to analyze this substructure as arising from a doublet (one proton), a triplet (2 protons), and a quintet (4 protons).

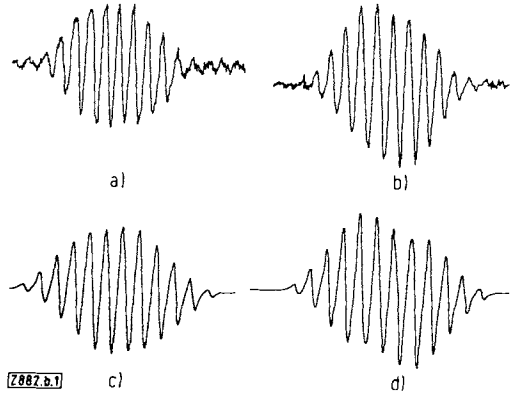

Table 1. Hyperfine splittings found for the ESR spectrum observed from the reaction of benzene with a Na—K alloy in THF/DME.

T(°C)	a_H (Gauss)				
	2 H	4 H	1 H	2 H	4 H
−65			0.413 ± 0.004	0.235 ± 0.002	0.116 ± 0.002
−63	6.505 ± 0.013	1.774 ± 0.011	0.407 ± 0.002	0.234 ± 0.001	0.119 ± 0.001
−60			0.386 ± 0.003	0.226 ± 0.002	0.114 ± 0.002
−37			0.383 ± 0.004	0.236 ± 0.002	0.119 ± 0.002
−36	6.432 ± 0.007	1.800 ± 0.007			
−34			0.363 ± 0.002	0.228 ± 0.001	0.117 ± 0.001
− 3	6.252 ± 0.001	1.774 ± 0.001	0.349 ± 0.003	0.232 ± 0.002	0.117 ± 0.002
+22	6.116 ± 0.003	1.758 ± 0.002	0.326 ± 0.006	0.231 ± 0.005	0.115 ± 0.005

The above Figure shows the resolution of the central line at +22 °C (a) and at −37 °C (b) as well as the corresponding computer simulations based on the coupling constants given in Table 1 [(c) and (d)].

The improved resolution of the original fifteen-line spectrum[1] provides clear evidence that the radical producing this spectrum is not the benzene radical anion since at least thirteen protons are contributing hyperfine splittings. The radical is obviously a product of some coupling reaction; however, we are not willing to speculate as to its identity at this stage.

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[1] a) *W. Köhnlein, K. W. Böddeker,* and *U. Schindewolf*, Angew. Chem. *79*, 318 (1967); Angew. Chem. internat. Edit. *6*, 360 (1967). Cf. b) *G. L. Malinoski jr.* and *W. H. Bruning*, Angew. Chem. *80*, 996 (1968); Angew. Chem. internat. Edit. *7*, 953 (1968) and c) *K. W. Böddeker, G. Lang,* and *U. Schindewolf*, Angew. Chem. *80*, 998 (1968); Angew. Chem. internat. Edit. *7*, 954 (1968).

[2] *J. R. Bolton* and *A. Carrington*, Molecular Physics *4*, 497 (1961).

[3] *W. Knolle*, private communication, the coupling constants used for *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (Wursters Blue) are $a_H = 1.989$, $a_{CH_3} = 6.773$, and $a_N = 7.051$ gauss.

[4] *T. R. Tuttle* and *S. J. Weissman*, J. Amer. chem. Soc. *80*, 5342 (1958); *J. R. Bolton*, Molecular Physics *6*, 219 (1963).

Influence of Solvent Pretreatment and Electrolyte Addition on the ESR Spectra of Aromatic Radical Anions

By *K. W. Böddeker, G. Lang,* and *U. Schindewolf*[*]

In the ESR spectroscopic investigation of the benzene radical anion, $C_6H_6^-$, in tetrahydrofuran (THF)/dimethoxyethane (DME), the ESR septet occurring at low temperatures was found to give way on warming (up to ≈ 0 °C) to a new spectrum whose fine structure could be interpreted[1] as resulting from a preferred occupation of the symmetrical (E_{2u}) state of the two states contributing to the ground state of $C_6H_6^-$. Further experiments with and without addition of electrolyte, which have been extended to cover simple benzene derivatives, have shown that the behavior of the radical anions differs according to whether the solvent has been dried over $LiAlH_4$ or has been pretreated in some other way.

Preparation of samples: Each of the samples was prepared under vacuum conditions in a Pyrex vessel (Fig. 1) furnished with a suitable side-arm for the recording of ESR spectra (flat cell).

The K/Na alloy (0.1 ml; 3:1 or 5:1) was introduced into the apparatus by vacuum distillation *via* the side-arm A which subsequently was sealed off. 0.5 ml of the aromatic hydrocarbon to be investigated and 6 ml of THF/DME mixture (THF:DME usually 2:1) were then introduced into the reaction vessel through B. The ethers, which had been dried either over $LiAlH_4$ or over K/Na alloy, were first distilled into a measuring cylinder connected to the

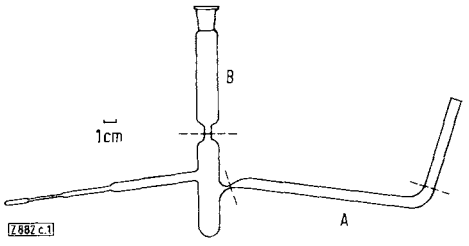

Fig. 1. Pyrex glass vessel for preparation and measurement of ESR samples; the tube is sealed off at the position marked — — — — —.

vacuum line and thence into the reaction vessel. After sealing off, the sample was thoroughly mixed at room temperature (as fine a division of the liquid alloy as possible) and then cooled in Dry-ice/methanol. Similarly, corresponding samples were prepared with addition of about 50 mg LiCl, which had been baked-out in the reaction vessel at 200 °C under vacuum before distillation of the other components.

Results: 1. THF and DME dried over $LiAlH_4$. — After warming the samples, or in the presence of LiCl typical ESR spectra were obtained of the radical anions formed with C_6H_6, C_6H_5D, and $C_6H_5CH_3$ (see Fig. 2). In LiCl-free solution these spectra only developed at temperatures above

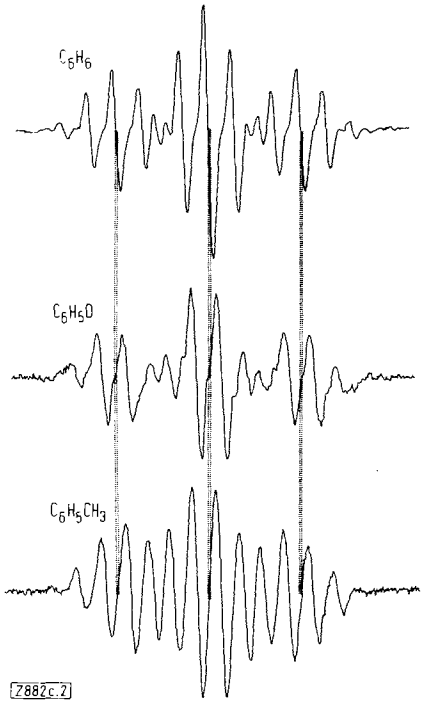

Fig. 2. ESR spectra of radical anions obtained in solvents pretreated with $LiAlH_4$ (the triplet structure is indicated by gray lines).

$\approx$ 0 °C from the "normal" spectra initially appearing at low temperatures; however in the presence of LiCl the new spectra were obtained immediately, even at low temperature, in the case of C_6H_6 and C_6H_5D [2].

The common feature exhibited by the spectra is the triplet structure with splitting of about 6.2 to 6.8 gauss (20 to −80 °C) that is indicated in Fig. 2 by gray lines and which points to a preferred occupation of the symmetrical state characterized by an increased spin density on two oppositely situated ring positions. According to this interpretation the radical anions are analogous to the radical anion of *o*-xylene which has similar triplet coupling constants and likewise exhibits a total splitting $Q < 22.5$ gauss [3]. A qualitatively similar charge distribution also occurs in the pyridine radical anion [4] whose tendency to form bipyridyl [5] finds a parallel in the formation of biphenyl in LiCl-containing benzene samples as observed by us.

The superhyperfine structure in the 15 line spectrum of benzene found by *Wormington* and *Bolton* [6] suggests that a complex structure is present in the case of these anion radicals [7] which, nevertheless must be intrinsically related to the original hydrocarbons.

2. THF and DME dried over K/Na alloy. — Whereas on increasing the temperature the ESR spectrum of the benzene radical anion in LiCl-free solution exhibits the behavior observed by *Malinoski* and *Bruning* [8], we obtained in the presence of LiCl, the spectrum shown in Fig. 3 which

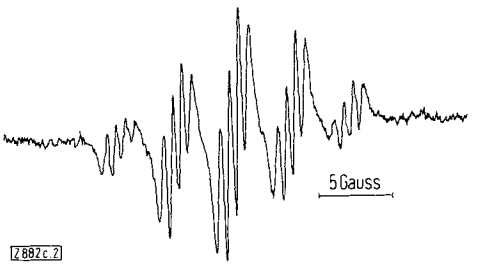

Fig. 3. ESR spectrum of the benzene radical anion in THF/DME (1:1) at −40 °C in the presence of LiCl; the solvent was dried over K/Na alloy. (The outermost groups of lines, intensity $^1/_{20}$ of that of the central groups, are just recognizable.)

indicates, by a quartet splitting of each of the seven lines of the "normal" $C_6H_6^-$ spectrum [9], an association with alkali metal cation.

In the presence of $LiAlH_4$, which was introduced into the reaction vessel under protective gas before the distillation of the residual components, we also observed in the case of benzene the 15 line spectrum shown in Fig. 2 when the temperature was raised.

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[1] *W. Köhnlein, K. W. Böddeker*, and *U. Schindewolf*, Angew. Chem. *79*, 318 (1967); Angew. Chem. internat. Edit. *6*, 360(1967). See also [6] and [8].

[2] In LiCl-free solution of C_6H_5D at temperatures > 0 °C, the 15 line spectrum of the benzene radical anion formed by isotopic exchange is superimposed upon the 12 line spectrum of the monodeuteriobenzene radical anion. — The "new" spectrum of the toluene radical anion occurs preferentially on warming LiCl-free solutions having a high THF content.

[3] *T. R. Tuttle*, J. Amer. chem. Soc. *84*, 2839 (1962); *J. R. Bolton*, J. chem. Physics *41*, 2455 (1964).

[4] *R. L. Myers* and *C. Talboty*, cited in *F. Gerson*: Hochauflösende ESR-Spektroskopie. Verlag Chemie, Weinheim 1967, p. 113.

[5] *A. Carrington* and *J. dos Santos-Veiga*, Molecular Physics *5*, 21 (1962).

[6] *P. Wormington* and *J. R. Bolton*, Angew. Chem. *80*, 997 (1968); Angew. Chem. internat. Edit. *7*, 954 (1968).

[7] This interpretation is also advocated by *A. Weller*; private communication.

[8] *G. L. Malinoski jr.* and *W. H. Bruning*, Angew. Chem. *80*, 996 (1968); Angew. Chem. internat. Edit. *7*, 953 (1968).

[9] The degree of splitting depends on the composition of the solvent.

Analysis of Foodstuffs with Particular Reference to Quality Control

The Foodstuff and Juridical Chemistry Group of the Gesellschaft Deutscher Chemiker and the Selskabet for Levnedsmiddelteknologi og -hygiejne, anerkendt selskab under Dansk Ingeniørforening, held a joint meeting in Kiel from 17 to 19 September 1968. Four of the fourteen lectures are reported below.

Recent Results concerning the Fate of Sulfurous Acid in the Organism

By *W. Diemair* (Lecturer) and *G. Pfleiderer* [*]

In order to follow the fate of sulfite in the organism we first prepared $^{35}SO_3^{2-}$, by *Griess*'s method, namely, by evaporating copper sulfate and carrier-free $Na_2{}^{35}SO_4$ solution on a water bath to complete dryness (87% yield). The yield measured with a Packard liquid scintillation spectrometer was 94%.

Sulfite can be determined in biological material by *Engelhardt*'s method, namely, distillation in a modified Reith-Willems apparatus with Tillmann's reagent. For determination of ^{35}S the organic tissues were freeze-dried. Combustion in pure oxygen and absorption of the radioactive gaseous combustion residues permits the very tedious chemical oxidation of the ^{35}S compound to be avoided. The apparatus described by *Kalberer* and *Rutschmann* was used.

It was observed that sulfite taken perorally is oxidized rapidly but not completely in the ileum. All ions resobed in the ileum proceed first to the liver; the rapid diminution in the amount of sulfite indicates a sulfite oxidase activity in *Lang*'s sense. The proportion of sulfite oxidized in the ileum is smaller the emptier are the stomach and ileum. After 40 min most of the sulfite in the jejunum is already oxidized to the extent of 40%. The residual sulfite is excreted almost wholly through the kidneys. Sulfite can be detected only in traces in the liver. At least in the liver the total activity is accounted for as sulfate; introduction of ^{35}S from sulfite is not observed.

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Studies of the Occurrence of Aflatoxin B_1, Migration and Changes in Content in the Preparation of Some Foods

By *E. Hanssen* [*]

Aflatoxin B_1 can be formed by *Aspergillus* [1–4] and other types of mold [2], being contained both in the mycelium and in the spores of this mycotoxin. That means that foodstuffs may have toxic action even if not visibly contaminated with mold. *Penicillium* species seem particularly liable to form aflatoxin. In *Penicillium* species discovered on preserved gherkins, stored at a temperature of 4 °C, we found 0.150 ppm of aflatoxin B_1, and in orange peel on which *Penicillium* was growing we found 0.010 ppm.

The medium must fulfil definite requirements for growth of *Aspergillus flavus* [5]. We found that there is a minimum of vitamin B content necessary for its growth. It could not be grown on white bread dough or biscuit dough (vitamin B_1 content 0.50 ppm), though it grows very well on whole wheat dough (vitamin B_1 content 3.00 ppm). We have followed the separation of aflatoxin in the interior of the attacked material, in a foodstuff whose cell structure had been destroyed (whole wheat dough), and in a foodstuff with undamaged cell structure (opened coconut). After about one week the content of aflatoxin B_1 in the mycellium was 0.250 ppm; in the layer 7 mm below the mycellium it was about 0.085 ppm, both for cellular and non-cellular material. In the lowest layers (between 2 and 7 cm) we found a very high content of aflatoxin (about 0.800 ppm).

The aflatoxin B_1 content of peanuts is decreased by 40% on dry roasting (130 °C, 5 min); it is reduced by about 20% of the original content on oil roasting (120–150 °C, 6 min).

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[1] *E. Bodin* and *L. Gautier*, Ann. l'Inst. Pasteur *20*, 209 (1906).
[2] *D. A. A. Mossel*, Goldschmidt informiert *1*, 21 (1967).
[3] *K. H. Frank*, Arch. Lebensmittelhyg. *17*, 237 (1966).
[4] *F. Bär*, Med. Ernährung *7*, 180 (1966).
[5] *R. I. Mateles* and *J. C. Adye*, J. appl. Microbiol. *13*, 208 (1965).

Fluorimetric Determination of Some Antioxidants

By *H.-P. Thier* [*]

Alkyle sters of gallic acid, dihydronorguaiaretic acid (NDGA), and the mixture of 2- and 3-*tert*-butyl-4-hydroxyanisole (BHA) (2- and 3-*tert*-butyl-4-methoxyphenol) are used in many countries as antioxidants for fats and fatty foodstuffs. Sensitive fluorimetric methods have been worked out for their quantitative determination.

Treatment in dimethylformamide/water (85:15) with 1% of ethylene diamine is suitable for the determination of 0.01 to 10 μg/ml of the gallic esters. A blue fluorescence (λ_{max} = 455 nm) is formed, which is measured after 2–3 h; its intensity is greatest for the propyl ester.

Condensing the guaiaretic acid with 5% of ethylene diamine in methanol/water (7:3) leads to a product that fluoresces green (λ_{max} = 530 nm). The intensity of fluorescence is measured after 7–24 h, enabling 0.1–5 μg/ml of the acid to be determined quantitatively. Gallic esters must be removed previously.

When dissolved in acetonitrile and oxidized with cerium(IV) sulfate in sulfuric acid, both the methoxyphenols gave 2-*tert*-butyl-*p*-benzoquinone. When taken up in chloroform, this quinone reacts with a 0.02% solution of potassium cyanide in dimethyl sulfoxide/water (96:4) in 20 min, yielding 5-*tert*-butyl-2,3-dicyanohydroquinone, which fluoresces blue (λ_{max} = 475nm), whence 0.5–5 μg/ml of total methoxyphenol can be determined.

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Trypsin and Chymotrypsin Inhibitors in Foodstuffs

By *J. Weder* (Lecturer) and *H.-D. Belitz* [*]

Trypsin and chymotrypsin inhibitors have been shown to be present in a very large number of foodstuffs, *e.g.*, in milk, in egg-white, in some animal organs, and in legumes, potatoes, root crops, and cereals. Disturbances in which these inhibitors seem to have played a part have been observed from time to time when these materials were fed to animals or man. The inhibitors can be completely destroyed by sufficient heat treatment. Data in the literature and our own observation [1] show that, for instance in legumes, the thermal stability of the trypsin and chymotrypsin inhibitors can vary very greatly from species to species.

To obtain more precise information about this differing behavior, we have isolated the trypsin and chymotrypsin inhibitors from the legumes *Pisum sativum* var. *balticum*, *P. sativum* var. *Schneebergeri*, *Phaseolus vulgaris* var. *nanus*, *Ph. coccineus*, *Lathyrus odoratus*, and *Vicia faba*, by extraction of the ground seeds with H_2SO_4 and fractional precipitation with ammonium sulfate or, for *Vicia faba*, with acetone. The specific activities of these crude inhibitors were 0.2 to 1.6 TIE ^{cas}/mg [**] and 0.3 to 0.8 CTIE ^{cas}/mg, or, for *Vicia faba*, 83 TIE ^{cas}/mg and 54 CTIE ^{cas}/mg. The pure inhibitor obtained, as described by *Werle et al.* [2], from *Lathyrus odoratus* by use of an insoluble trypsin derivative had 30 times the activity of the crude preparation.

The following molecular weights were found by gel filtration on Sephadex G 50 (sequence as above): 10800 and 15800 (2 fractions), 10900, 17100, 14600, 11700, and 10200. No correlation could be found between thermal stability and molecular weight.

The pure inhibitor from *Lathyrus odoratus* had a strikingly high cysteine content, and an excess of acidic over basic amino acids, but methionine was absent.

[VB 173 IE]

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[**] TIE^{cas} are trypsin inhibitor units and CTIE^{cas} are chymotrypsin inhibitor units determined with casein as substrate, see ref. [1].

[1] *H.-D. Belitz, H. P. Wassner*, and *J. Weder*, Z. Lebensmittel-Unters. u. -Forsch. *137*, 211 (1968).

[2] *H. Fritz, H. Schult, M. Hutzel, M. Wiedemann*, and *E. Werle*, Hoppe-Seylers Z. physiol. Chem. *348*, 308 (1967).

SELECTED ABSTRACTS

The growth of anodic mercuric sulfide films on a mercury electrode in solutions containing sulfide and the effect of such films on the anodic dissolution of mercury have been studied by *R. D. Armstrong, D. F. Porter*, and *H. R. Thirsk* by measurement of potentiostatic switching curves. In the initial stage of film formation, black mercuric sulfide (metacinnabarite, identified by electron diffraction) is deposited on the electrode surface in two successive monolayers. Each of these layers considerably reduces the rate of dissolution of mercury to form HgS_2^{2-}. The current-voltage curve shows a discontinuity for the formation of each monolayer of HgS. It is mentioned that passivation processes on solid metal electrodes could be similar in nature. / J. physic. Chemistry *72*, 2300 (1968) / –Hz. [Rd 921 IE]

The reaction of mercury atoms with chlorine atoms has been investigated by *D. G. Horne, R. Gosavi*, and *O. P. Strausz*. The chlorine atoms were obtained by flash photolysis of CF_3Cl sensitized by mercury vapor; the kinetics of the reaction were deduced from the absorption of HgCl at 2790 Å. The extinction coefficient of HgCl at 2790 Å was determined as $(1.6 \pm 0.6) \cdot 10^5$ mole^{-1} cm^{-1}; the rate constant (second order) of the reaction amounts to $3 \cdot 10^{10}$ mole^{-1} sec^{-1} in 720 torr CF_3Cl and $0.9 \cdot 10^{10}$ mole^{-1} sec^{-1} in 10 torr CF_3Cl + 710 torr Ar, and it is temperature-independent between 110 and 170 °C. The rate constant (second order) of dimerization of HgCl in the gas mixtures named has the value $(3.0 \pm 1.8) \cdot 10^{11}$ or $(1.9 \pm 1.3) \cdot 10^{11}$ mole^{-1} sec^{-1}. / J. chem. Physics *48*, 4758 (1968) / –Hz. [Rd 925 IE]

The superconducting properties of ternary intermetallic compounds having a β-tungsten structure were studied by *G. Otto*. The samples, which all had the composition $Nb_3(X_{1-x}M_x)$ with X = Al, Sn, or Ga and M = Ga, Ge, In, or Sn, were obtained by melting the powder-form elements under argon in an electric arc and were studied in the quenched and in the tempered state. In order to relate the transition temperature to other quantities that were not directly dependent on superconductivity, the lattice constants and micro-hardness of the samples were measured. The highest transition temperature was found for $Nb_3(Al_{0.7}Ge_{0.3})$ at 20.05 °K. As x varies in a mixed-crystal series the transition temperature passes through a maximum when a valence electron density of 0.26 Å^{-3} is reached. Further, the lowest micro-hardness and the highest transition temperature occur together in one mixed-crystal series. Tempering raises the transition temperature over that of the quenched sample by a maximum of 1.3 °C. / Z. Physik *215*, 323 (1968) / –Hz. [Rd 926 IE]

The course of the synthesis of cyclooctatetraene by tetramerization of acetylene in the presence of nickel compounds has been the subject of attempted quantum-chemical explanation by *E.-A. Reinsch*. As well as fixing the geometrical relations of the four acetylene molecules in a complex *cis*-$[Ni(C_2H_2)_4X_2]$ where X is a further unidentate ligand, the nickel has the function of orienting two unpaired electrons spatially to two acetylene ligands in such a way that a new C–C bond can be formed. The orbitals necessary for this catalytic assistance are singly occupied only in magnetically normal d^8 complexes (high spin); other electron configurations do not come into consideration for this purpose. The special feature of paramagnetic nickel complexes in catalysis of this reaction is thus explained. / Theor. chim. Acta *11*, 296 (1968) / –Hz. [Rd 927 IE]

Amide ions NH_2^- as color centers in crystalline KCl, KBr, and KI were investigated by *R. Windheim*. In an electric field or under uniaxial mechanical strain the crystals show peculiarities due to the fact that the color centers are not centrosymmetric; the oscillator strengths of the UV bands at 295 nm are larger in the HNH plane than perpendicular to it. The NH_2^- ions orient themselves, so far as possible, with their dipoles in the (100) direction. The orientation favored under uniaxial strain is that where the protons are separated as

widely as possible from their nearest K^+ neighbor. The dipole moment of NH_2^- in KCl and KBr is 0.23 D (that of the amide radical 0.26 D), but in KI it is 0.44 D. The large difference is explained by assuming that in the large I^- anion holes the NH_2^- is not central but lies towards the edge, thus creating an addition to the dipole moment. / Z. Physik *215*, 152 (1968) / –Hz.

[Rd 928 IE]

The reaction cross-section of ammonium salts for scattering of subthermal neutrons (wavelength 8.5 Å) as a function of temperature has been evaluated by *P. S. Leung, T. I. Taylor,* and *W. W. Havens jr.* The increase S_T in the reaction cross-section, calculated for each hydrogen atom and for unit change of temperature, does not change appreciably in the region of the lambda transformations, which correspond to the change from ordered to disordered spatial orientation of the NH_4 ions; on the other hand, for the chloride, bromide, and iodide the reaction cross-section per H atom increases as much as 18–20 barn (1 barn = 10^{-24} cm^2) at the transformation point of first order, where the torsional vibration of the NH_4 ions passes into relatively free rotation and, in this connection, the CsCl structure is substituted by the NaCl structure. S_T increases in a defined manner with decreasing torsional frequency or rotation potential threshold. Calibration of the values for the halides enabled the hitherto unknown rotation-potential thresholds for ammonium sulfate (3.4 kcal/mole) and perchlorate (0.4 kcal/mole) to be determined. For the halides, hindrance to free rotation in the NaCl phase decreases in the order Cl, Br, I. / J. chem. Physics *48*, 4912 (1968) / –Hz.

[Rd 929 IE]

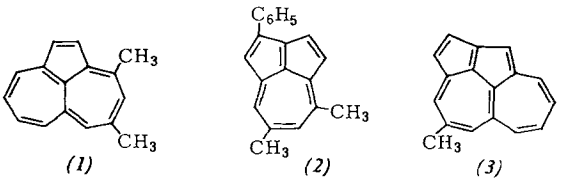
Shifts in the fluorescence bands at different wavelengths of excitation were observed by *A. N. Fletcher* for the following organic compounds: 2-aminopurine, biphenyl-2,2'-diol, 6-methoxy- and 6-ethoxy-quinaldine, 3-aminophthalhydrazide, 6-methoxyquinoline, and quinine. The effect depends on the presence of rotatable auxochromic groups in the molecule and on the solvent; shifts of up to 50 nm in the emission maximum can occur. To explain the effect it is assumed that the molecule can exist in at least two conformations which are stabilized or destabilized by the solvent to different extents in the ground and the excited state. A change in the wavelength of excitation then leads to a change in the distribution of the excitation energy between the two conformers and thus to a shift in the emission. It should be noted that quinine, which is used as a fluorescence standard, also shows this effect! / J. physic. Chemistry *72*, 2742 (1968) / –Hz.

[Rd 930 IE]

Proof of the existence of I_4 in iodine vapor has been provided by *A. A. Passchier* and *N. W. Gregory*. The temperature- and pressure-dependence of the absorption band at 265 nm, to which both I_2 and I_4 contribute, was used to determine the equilibrium constants of the reaction $2\ I_2 \rightleftharpoons I_4$ between 150 and 420 °C, and thence the bond enthalpy $\Delta H^\circ_{605\,°K} = -2.9 \pm 0.4$ kcal/mole and the bond entropy $\Delta S_{605} = 123 \pm 2$ cl/mole. These values are those to be expected if only van der Waals forces are effective between the two iodine molecules. As an example of how little I_4 is formed it is stated that at 240 °C and 2.5 atm total pressure, only 1.4% of the vapor exists as I_4. / J. physic. Chem. *72*, 2697 (1968) / –Hz.

[Rd 931 IE]

The fluorescence of *peri*-condensed non-alternant polycyclic hydrocarbons has been studied by *R. C. Dhingra* and *J. A. Poole*. Like azulene, *(1)* and *(2)* show fluorescence from the second excited singlet state. The absorption spectrum of *(3)*

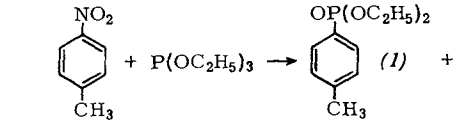


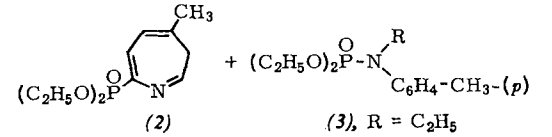
(1) *(2)* *(3)*

is not wholly assigned, but the fluorescent state is in this case also at least the second, and perhaps a still higher, singlet state. Normal fluorescence from the first singlet state was not found in a single case. / J. chem. Physics *48*, 4829 (1968) / –Hz.

[Rd 934 IE]

A new possibility of removing nitro groups from non-activated nitro compounds such as *p*-nitrotoluene is described by *J. I. G. Cadogan, D. J. Sears,* and *D. M. Smith*. Reaction of boiling triethyl phosphite with *p*-nitrotoluene gives 5% of diethyl *p*-toluenephosphonate *(1)* together with 6% of diethyl 4-methyl-3*H*-azepine-7-phosphonate *(2)*, 24% of diethyl *N*-ethyl-*N*-*p*-tolylphosphoramide *(3)*, and 26% of diethyl *N*-*p*-

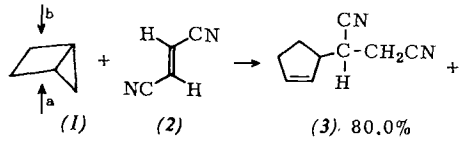




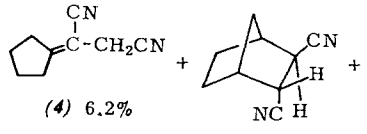
tolylphosphoramide *(4)*. *p*-Nitroanisole and *p*-ethylnitrobenzene behave analogously. *o*- and *m*-Nitro analogs cannot be converted into diethyl arylphosphonates. / Chem. Commun. *1968*, 1107 / –Ma.

[Rd 936 IE]

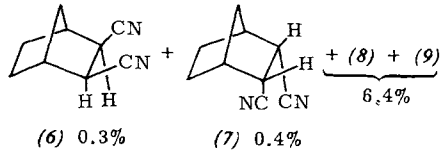
The mechanism and stereochemistry of the addition of olefins to bicyclo[2.1.0]pentane *(1)* were studied by *P. G. Gassman, K. T. Mansfield,* and *T. J. Murphy*. On using fumarodinitrile *(2)* they obtained compounds *(3)*–*(7)* in the relative yields



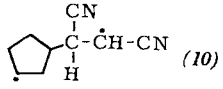
(1) *(2)* *(3)* 80.0%



(4) 6.2% *(5)* 6.7%



(6) 0.3% *(7)* 0.4%



(10)

shown, together with two unidentified products *(8)* and *(9)*. Use of maleodinitrile afforded the same compounds, yields being 88.7, 2.2, 1.2, 2.1, 3.0, and 2.8% [for *(8)* + *(9)*], respectively. This can be explained only by assuming an intermediate stage that permits rotation. Since *(3)*–*(7)*, as well as fumaro- and maleo-dinitrile are stable under the reaction conditions and a zwitterionic intermediate was previously excluded, the intermediate product must be the diradical *(10)*. The question whether the olefin approaches the bicyclic system from "below" (a) or "above" (b) could be answered by studying addition of maleic anhydride to [2,3-D_2]bicyclo[2.1.0]pentane *(1)*; the olefin approaches from "below". / J. Amer. chem. Soc. *90*, 4746 (1968) / –Kr.

[Rd 940 IE]

The adsorption of trace elements from sea water on to the surface of containers has been studied by *D. E. Robertson* for the radioactive isotopes ^{46}Sc, ^{59}Fe, ^{60}Co, ^{65}Zn, ^{85}Sr, ^{86}Rb, ^{110}Ag, ^{114}In, ^{124}Sb, ^{134}Cs, and ^{235}U, when these are added to the sea water as soluble salts. After storage for 20 days at the normal pH (8.0) of sea water in polyethylene flasks, indium, scandium, and iron were adsorbed to the extent of about 95, 45, and 40%, respectively; losses of the other elements remained below 20%. Except for scandium and iron, the losses on Pyrex glass were less than 10%. Polyethylene containers came off best when the sea water was acidified to pH = 1.5; then, after 20 days, only about half of the scandium had been adsorbed, while the amounts for other elements were less than 10%. / Analyt. Chim. Acta *42*, 533 (1968) / –Kr.

[Rd 937 IE]

Bis(triphenylstannyl)mercury *(1)*, the first compound containing a Hg–Sn linkage, was obtained by *C. Eaborn, A. R. Thompson,* and *D. R. M. Walton,* as a yellow solid, on treatment of triphenylstannane with bis[bis(trimethylsilyl)amido]-mercury at room temperature:

$$2\,(C_6H_5)_3SnH + Hg[N(Si(CH_3)_3)_2]_2 \rightarrow Hg[Sn(C_6H_5)_3]_2 + 2\,[(CH_3)_3Si]_2NH$$

(1)

(1) is stable for several months in the dark at room temperature, but decomposes rapidly in light, in solution, or when heated. The Hg–Sn bond is not formed from triethylstannane and dibenzylmercury at 100 °C or from bromotriphenylstannane and sodium amalgam, the analogy to Hg–Si and Hg–Ge bonds failing. / Chem. Commun. *1968*, 1051 / –Kr.

[Rd 938 IE]

BOOK REVIEWS

Chromatographisches Praktikum (Practical Chromatography). By *G. Hesse*. Vol. 6 in the series "Methoden der Analyse in der Chemie" (Methods of Analysis in Chemistry) edited by *F. Hecht, R. Kaiser, H. Kriegsmann,* and *W. Simon*. Akademische Verlagsgesellschaft, Frankfurt/M. 1968. 1st Edit., 1967, 244 pp., 50 figs., 28 tables, linen. DM 39.–.

This book gives an introduction to the most important chromatographic procedures and describes in the two main chapters the chromatography of solutions (column, thin-layer, and paper chromatography) and gas chromatography. The above procedures and their variants are described with the aid of numerous easily reproducible examples. The author addresses himself predominantly to chemistry and biology students in their final year at school or the first year at university. The comprehensive presentation of chromatographic methods and the emphasis laid on their essential similarity are particularly welcome. Theoretical explanations are only given insofar as they are necessary for the solution of examples. Anyone who has worked through the experiments should have no difficulty in solving problems of separation in analogous cases.

With this selected class of readers in mind, it is of course understandable that various methods important in research (such as exchange chromatography of amino acids and nucleotides, countercurrent distribution, *etc.*) are mentioned only briefly or not at all. In conjunction with the connection between the activity of the adsorbent and the polarity of the substances and the eluent, so very important in practice, one would have liked to see – besides the eluotropic series (p. 27) – a reference to the 'microcircular technique' (*E. Stahl*) which often allows one to determine from TLC the proper conditions for separation on a column. The ninhydrin reaction (p. 103) is not solely a means for the detection of α-amino acids.

In accordance with the subtitle 'Introduction to the Critical Performance of Chromatographic Procedures' the possible pitfalls are clearly indicated in each chapter, especially in the section on 'Changes in Materials During Chromatography'. The convincing critical assessment of R_f values is particularly pleasing.

The reviewer finds the book very suitable as an introduction to the field of chromatographic separation.

W. Barz [NB 752 IE]

Fortschritte der Arzneimittelforschung. (Progress in Drug Research). Volume 10. Edited by *E. Jucker*. Birkhäuser Verlag, Basel-Stuttgart 1966. 1st Edit., 603 pp., DM 128.–.

The introductory article, "Drug Research – Whence and Whither", to this new volume[2] has been written by *R. G. Denkewalter* and *M. Tishler*. After a short historical introduction, the authors attempt to sketch out the position of pharmaceutical research in the present day and in the future, and to fathom and establish the factors that could play an important role. In so doing, they point to the uncertainty of all predictions: "The true nature of a discovery is that it is unexpected" (31 pages). – The article by *G. Ehrhart* "Considerations on the Development of Medicaments" deals with a number of examples; the author refers to the fact that "significant advances can only be made when new territory is opened up by new fundamental discoveries" (13 pages). – *J. H. Beil* and *B. K. B. Lum* give a 36-page review of "The β-Andrenergic Blocking Agents, Pharmacology and Structure-Activity Relationships". After a critical discussion of the receptor theory, relationships are considered between chemical constitution and exciting or blocking action, a number of relevant compounds are listed, and their clinical pharmacology is briefly touched upon (165 references).

[1] Angew. Chem. *79*, 911 (1967); Angew. Chem. internat. Edit. *6*, 892 (1967).

[2] Cf. Angew. Chem. *79*, 386 (1967); Angew. Chem. internat. Edit. *6*, 892 (1967).

A 45-page report on "Value and Valuation of Drugs" has been written by *J. Büchli*. A short introduction on the development of drugs and the role played therein by the pharmaceutical industry precedes a discussion of methods used in their evaluation: analytical-chemical methods, pharmacological problems regarding mechanism of action, toxicity and side effects, and the carrying out and evaluation of clinical tests. The chapter (64 references) closes with a section dealing with state controls in a number of countries. – The article by *C. A. Winter* "Nonsteroid Antiinflammatory Agents" covers 50 pages. A short introduction on the nature and mechanism of the formation of inflammation and chemical intermediate carriers that could play a role is followed by a description of methods for the production of inflammation in animal experiments, a special section being devoted to arthritis, which is regarded as a symptom but not as a primary cause. Finally, the groups of antiinflammatory compounds are discussed. The relatively sparse and uncertain results regarding theory and therapy of diseases of connective tissue invite further research into this important topic (64 pages, 500 references). – There follows a detailed 156-page treatment of "The Effect of Form on the Action of a Drug" by *K. Münzel* (472 references). "The therapeutic action of a medicament undoubtedly depends mainly on its chemical structure..... The action can, however, be influenced decisively and changed by the form in which the pharmaceutical is administered", as is shown with the aid of many examples.

A review of "New Drugs" is given by *W. Kunz*. The many new introductions are arranged in groups according to their applications, and subdivided further according to parent substance. The structural formula, trade name, and international name are given for each substance (69 pages, 419 references). The theme "Molecular Pharmacology, a Basis for Drug Design" is dealt with in 101 pages by *E. J. Ariens*. A discussion of the mode of action, based mainly on the receptor theory, represents a starting point for positive planning (numerous structural formulas, 384 references).

The volume closes with an article by *F. Labhardt* dealing with "The Application of Psychopharmaceuticals in Psychosomatic Medicine". A short introduction on the term psychosomatic medicine and a statement of the problems involved precede a discussion of the most important psychosomatic disturbances and their symptoms, and of relevant methods of investigation. There follows a consideration of modern psychopharmaceuticals and their applications, dosages, and side effects. Finally the author points out that, in spite of the proportions that psychopharmacotherapy has assumed in recent years, a certain degree of uncertainty still surrounds its effects, a fact that invites further scientific research and clinical observation (84 references). – A detailed subject index for the present volume and indexes of the authors and articles in the ten volumes that have so far been published increases the value of the series. The production of the book, with its many figures, tables, and structural formulas, is once again exemplary.

O. Schaumann [NB 744 IE]

Fortschritte der Arzneimittelforschung (Progress in Drug Research) Vol. 11. Edited by *E. Jucker*. Birkhäuser-Verlag, Basel-Stuttgart 1968 1st Edit., 572 pp., numerous figs. and tables, bound DM 116.–.

In a 37-page paper entitled "Mescaline and Related Compounds" *A. R. Patel* reports on their natural occurrence, their biogenesis, the various syntheses, their physical constants, and the analytical methods. The behavior of mescaline in the body and its biochemical and neurophysical action on animals and men are then discussed, as well as the theory of the mechanism of this effect. Finally, there is a brief section on the derivatives of mescaline (370 references).

"The Photochemistry of Drugs and Related Substances" is discussed by *S. T. Reid* with the aid of more than 300 structural formulas and 500 references. After a brief theoretical introduction concerning the mechanism of photochemical transformation, each class of compounds is discussed separately (alkenes, dienes, trienes, aldehydes, ketones, aromatics, and finally nitrogen-containing compounds) (72 pp.).

An extensive report on "Investigations on the Biochemistry and Pharmacology of Thymoleptics" is given by *M. H. Bickel*. With the introduction of the iminodibenzyl derivative imipramine (Tofranil ®) in 1958 as a prototype thymoleptic, a new and successful era began in the drug treatment of endogenous depressions. The next sections give a detailed description of the testing methods, metabolism, the relationship between constitution and action, as well as the manner of action of compounds in this class (102 pp., 475 references).

A very extensive report on "Oral Anticoagulants" is given by *E. Renk* and *W. G. Stoll*. The chemistry of coumarin and 1,3-indanedione is discussed first, with reference to their constitution and methods of synthesis and to the relationships between constitution and action. This is followed by a section on the physiology of coagulation and its inhibition by substances contained in the body, as well as the influence of synthetic compounds on this process. After a discussion of the general pharmacology and the metabolism of anticoagulants, the report finishes with a detailed section on their therapeutic application (129 pp., 899 references).

A. Kreutzberger reports on "The Amidine Structure in Pharmaceutical Research" (87 pp.). Following an historical introduction the syntheses are described and the naturally occurring amidines listed. This is followed by a discussion of their therapeutic applications, as antidiabetics, as antiprotozoan and antibacterial agents, as well as cytostatics, local anesthetics, and virostatics. The reading of this very full report is simplified by the inclusion of 400 structural formulas.

The present volume is made particularly valuable by the inclusion of a general subject index of all 11 published volumes, which lists about 14,000 entries in 115 pages and thus makes the whole work into an invaluable source of information. Once again the book ends with an author index and a list of contents of the volumes already published. The production is again exemplary.

O. Schaumann [NB 753 IE]

The Mass Spectra of Organic Molecules. By *J. H. Beynon, R. A. Saunders*, and *A. E. Williams*. Elsevier Publishing Company, Amsterdam-London-New York, 1968. 1st Edit., ix, 510 pp., 181 figs., 20 tables, bound, Dfl. 97.50.

One of the first books in which mass-spectrometric methods were collected for the chemist was *J. H. Beynon*'s "Mass Spectrometry and its Application to Organic Chemistry", published in 1960[1]. *J. H. Beynon, R. A. Saunders*, and *A. E. Williams* have now again attempted to collect and compare the often widely scattered information given in the literature. Comparison of equivalent chapters in the two books dealing with fundamental apparatus and methods of mass spectrometry shows that the new book does not replace the earlier monograph but rather supplements it. While in the former the mass spectrometers and measuring techniques were fully discussed in more than 300 pages, the authors summarize this subject in the present work in 37 pages. Because of this cramped presentation, a newcomer to the field receives only an inadequate impression of the problems connected with the recording and evaluation of mass spectra.

The book is mainly intended to give instruction and assistance in mass-spectrometric structural analysis of organic compounds. To avoid errors, it is necessary to know the properties of the ionic types formed in the mass spectrometer. These are discussed in the second chapter, which contains a full and very good section on metastable ions. The formation of rearranged ions, which often gives rise to great difficulties in structural analysis, is explained. At this point one would

[1] Cf. Angew. Chem. *73*, 634 (1961).

have liked to see a reference to the work of *Brown* and *Djerassi*[2], which forms a good supplement to this section of the book.

The work presented to date on the mass-spectrometric behavior of organic substances has shown that mass spectra are determined by the heteroatoms and the functional groups. In discussing mass spectra, the authors have therefore classified the organic compounds according to their heteroatoms, as hydrocarbons and compounds of oxygen, nitrogen, sulfur, halogens, boron, phosphorus, and silicon. It is understandable that this classification is somewhat arbitrary if several different heteroatoms are present in the molecule. However, the index at the end of the book simplifies the search for a particular class of compounds.

The important characteristics necessary for identification and structural analysis are here presented more forcibly than in similar works, without necessarily a full discussion of the mechanism by which the fragments are formed. The treatment covers not only the mass spectra of monofunctional compounds, which gave a particularly clear picture of fragmentation, but also the mass spectra of polyfunctional compounds and natural products with complicated structures, such as steroids. The methods of mass-spectrometric structure analysis are illustrated by numerous well-chosen examples. The possibilities and limits of the method are discussed in the concluding chapter, with reference to 17 examples.

Random checks have shown that the literature up to 1967 has not, after all, been covered completely. This limits to some extent the use of the book as a reference work, as is suggested by the text of the dust-cover. The book can be recommended as an extensive introduction to organic mass spectrometry and as a good introduction to mass-spectrometric structure analysis. *H. F. Grützmacher* [NB 749 IE]

Chemie der Eiweisskörper (The Chemistry of Proteins). By *E. Waldschmidt-Leitz* and *O. Kirchmeier*. Ferdinand Enke-Verlag, Stuttgart 1968. 3rd Edit., xi, 258 pp., 8 illustrations, 37 tables. Cloth-bound DM 57.00.

The long established work under review has been extended by a few chapters to indicate the new developments that have taken place since the publication of the 2nd edition. The description of the synthesis and degradation of amino acids in living organisms deserves especial mention. The reader is given a good and concise review with ample literature references.

The book deals primarily with the classical chemistry of amino acids (coherent treatments of this subject are hard to find), with the synthesis, preparation, and structure analyses of peptides, the properties of proteins, and elucidation of their amino-acid sequences, and finally describes, in brief, a considerable number of proteins. In only a few instances would it have been desirable to discuss new developments in greater detail, *e.g.* the denaturation of proteins or the determination of the tertiary and quaternary structures of proteins as they are known today. All chapters are carefully supported by literature citations, which enables the student to deepen his understanding by contact with the original work. The book is well produced and, as usual, the presentation is very clear; in all, it is a very suitable reference work. *H. Fasold* [NB 760 IE]

Atlas of Electron Spin Resonance Spectra. By *B. H. J. Bielski* and *J. M. Gębicki*. Academic Press Inc., London-New York 1967. 1st Edit., xiii, 664 pp., numerous figures and tables, bound, $ 27.00.

A collection of ESR spectra has long been awaited by research workers in this field. The two authors must be commended for undertaking this laborious task of collecting spectra from the widely scattered data in the published literature. The atlas contains well over a thousand reproductions of ESR spectra derived from paramagnetic species in solution, in gases, in glasses, and in powders – but not, however, in single crystals. The reproductions are neatly executed and well arranged. Most of the spectra were published before the end of 1964; only a few are taken from more recent or from unpublished work. A certain selectivity limits the completeness of the work, but increases its reliability. No attempt has been made to verify the correctness of the data. Apart from the ESR spectra, ancillary information – such as the paramagnetic species, their preparation, the recording conditions, and coupling constants – is listed.

While the atlas largely comes up to our expectations, indeed its usefulness has already been proved several times in the reviewer's laboratory, certain shortcomings should not be overlooked. In the first place, the spectra have not been selected carefully enough. This is particularly true of the spectra of radicals that have been recorded under similar conditions, without essentially differing from each other. Such spectra could have been omitted, together with the line diagrams showing the schematic hyperfine structure, which are largely superfluous. The spin densities calculated from the measured coupling constants using a somewhat arbitrary proportionality factor are also unnecessary.

Frequent errors are found in the formulas of the paramagnetic species and in the coupling constants indicated. For instance three different formulas are used for the three spectra given for the allyl radicals (pp. 29 and 30):

$CH_2{=}CH{-}\dot{C}H_2$; $CH_2{=}CH{-}\dot{C}H_2 + \dot{C}H_2{-}CH{=}CH_2$; and $H_2C{=}CH{=}CH_2$. They appear as different species; moreover, in the mesomeric notation the + sign should be replaced by the usual double-headed arrow (↔).

The radical cation whose spectrum is reproduced on p. 538 was obtained from 1,3,6,8-tetraazapyrene and not from the 4,5,9,10-tetradeuterio derivative as quoted.

For the radical anion of pyrene the coupling constant of the two equivalent protons in positions 2 and 7 is erroneously given twice on p. 533 ($a_2^H = -1.09$ G and $a_{2,7}^H = 1.05$ G). The first value is correct, apart from the incorrect negative sign which cannot be determined from the spectrum given.

The numerical indices of the coupling constants of the *p*-nitrotoluene radical anion (p. 628, top) are meaningless, since the numbering is missing on the corresponding formula. If the numbers are taken to be those normally used in chemical nomenclature for *p*-nitrotoluene they are actually misleading.

When all is said and done, however, this atlas is a very useful and commendable aid which every ESR laboratory should posses. Nevertheless, a critical approach is indicated, and it would be wise to consult the original literature at the same time. *F. Gerson* [NB 757 IE]

Nuclear Magnetic Resonance Spectra and Chemical Structure. Vol. 1: The Spectral NMR Parameters of Compounds with Analyzed Spectra. By *W. Brügel*. Academic Press, New York-London / Dr. Dietrich Steinkopff-Verlag, Darmstadt 1967. 1st Edit., xviii, 235 pp., loose-leaf, $ 35.00.

In comparison to the familiar "infra-red Brügel" the present volume offers not just another spectroscopic method but an entirely different selection. Whereas the older book was – and is – an introduction, this work is almost exclusively a summary, an ambitious atlas of spectra which no longer merely lists the spectra themselves, as produced by the spectrograph, but lists them in an extracted form.

To pass on to the form and content, it might be said that this is not really a book at all, but rather a file of medium thickness in the A 4 format. The work is divided into an introduction in German and English (7 pp.) tables (212 pp., English text), a bibliography (520 citations), and an alphabetical subject index (English, about 2500 entries).

[2] Cf. *P. Brown* and *C. Djerassi*, Angew. Chem. 79, 481 (1967); Angew. Chem. internat. Edit. 6, 477 (1967).

The part containing the tables is divided into two major groups. The first deals mainly with substances in which only the protons are capable of nuclear resonance, or in which only proton resonance was measured, and the second, relatively small, group contains data relating to nuclei other than H. Inorganic substances and polymers are not considered except for isotactic polystyrene. The tables contain the nuclear resonance parameters (chemical shift and coupling constants) of the particular substance, with the solvent used, its concentration, and the literature reference. Only those substances are listed whose spectra had been accurately evaluated. The literature has been included up to 1966.

The alphabetical division into 88 basic substances and their derivatives is very easy to refer to but in some cases a little confusing. The tables under the heading 'anthracene' or 'naphthalene' do not contain all the data on these compounds; the reader still has to refer to the voluminous chapter on benzene, under the subheading of 'condensed aromatics'. Numerous benzo compounds are listed under 'benzene', while others – like benzimidazole, benzofurazan, *etc.* – are listed under their own names. However, all the substances are easily found in the subject index.

This work has been printed on good, strong paper – a necessary precaution if frequent use is envisaged. It will be very useful to anyone engaged in the practice of nuclear resonance spectroscopy, not least because he can rely on the author's critical treatment of the literature.

This work should be brought up to date from time to time. Perhaps the recently published data on polymers could then also be taken into account. *D. Hummel* [NB 758 IE]

The Chemistry of Non-Aqueous Solvents. Vol. 1: Principles and Techniques. Edited by *J. J. Lagowski*. Academic Press, New York-London 1966. 1st Edit., xi, 403 pp., 18 figures, 6 tables, $ 16.50.

This book covers the more important aspects of reactions and physical measurements in non-aqueous media – including theoretical fundamentals – as well as the methods generally used in investigations in low-boiling media and molten salts. The following topics are treated: 1. Lewis acid-base exchange in polar non-aqueous media (*D. W. Meek*); 2. Solvation of electrolytes and solvent equilibria (*E. Price*); 3. Acid functions in amphiprotic media (*R. G. Bates*); Electrode potentials in non-aqueous solvents (*H. Strehlow*); 5. Solvent extraction of inorganic substances (*L. J. Katzin*); 6. Experimental techniques for low-boiling media (*J. Nassler*); 7. Experimental techniques for the investigation of molten salts (*R. A. Bailey* and *G. J. Janz*).

The first chapter is written in a fluent and easily understandable style. All essential aspects and modern points of view are discussed. The reader is first familiarized with the out-of-date concepts (*e.g.* $SOCl_2$ as electrolyte in liquid SO_2), which are appropiately corrected in another part of the book. This consideration of the historical course of the topic under review is an attractive and interesting feature of the work. The reviewer would, however, have preferred the text to have been based on more modern and up-to-date knowledge and the historical development to have been brought more into the margin.

Section 2 contains a precise and clearly arranged treatment of the influence of solvation on ionization equilibria. Modern techniques of investigation are taken into consideration, *e.g.* NMR measurements for the evaluation of interactions between cations and solvent molecules.

Section 3 is somewhat exacting and demands a great deal of the reader. For example, the reviewer is of the opinion that *Izmailov*'s ideas for the derivation of the solvation energy of the proton is treated far too briefly. However, it must be emphasized that the section as a whole is very clearly written. Section 4 is written with remarkable didactic skill. Those who are acquainted with the fundamentals of electrochemistry and thermodynamics will have very little difficulty in understanding this contribution. The reader is given such an excellent and impressive survey of the measurement and evaluation of electrode potentials in non-aqueous media that he has no need to refer to the original literature.

The author of Section 5 has been confronted with the difficult task of working through the extensive amount of original literature concerning the separation of substances by distribution between two solvents. He has, however, succeeded in compiling a representative review of the principles of the many methods presently being used.

Section 6 is of immense value to all chemists who are concerned with, or are likely to concern themselves with non-aqueous solutions. The techniques used for preparation of solutions are described mainly for lower-boiling media. Particular interest attaches to solutions of solids on which physical measurements or chemical reactions are to be carried out. All the physical methods that have become of importance in the chemistry of non-aqueous solvents, *e.g.* polarography, Raman spectroscopy, *etc.*, are so treated that one can perform experiments as a rule without further ado, mainly because of numerous and well illustrated figures of apparatus and experimental set-ups that have been included.

The experimental side is also to the fore in Section 7; however, for a complete understanding of the fundamentals of processes the necessary theoretical explanations are also included. Methods for the determination of magnetic susceptibility, electrochemical and spectroscopic methods, and methods for the investigation of transport phenomena are treated, as are also and techniques such as calorimetry cryoscopy. Adsorption chromatography and chemical reactions in molten salts are also dealt with.

All sections are supplemented with a fully comprehensive bibliography. This work, which will appear in several volumes, has closed a gap in the "secondary literature". For this reason, our thanks goes out to the editor, who has made a name for himself particularly through his investigations on solutions in liquid ammonia. All chemists with an interest, or potential interest, in the field of non-aqueous solutions will welcome the appearance of this work.

O. Schmitz-Du Mont [NB 745 IE]

Halogen Chemistry. Edited by *V. Gutmann*. Academic Press, London-New York 1967. Volume 2: 1st Edit., xii, 481 pp., many figures and tables, 115 s; Volume 3: 1st Edit., xiv, 471 pp., many figures and tables, 115 s.

In this three-volume work on halogen chemistry the editor gives a review of the present-day position of the subject. Unfortunately, the date of publication chosen is somewhat late, for a number of the topics dealt with have recently been treated in standard text books of fluorine chemistry and of inorganic chemistry.

Volume 2 is concerned primarily with preparative chemistry and with covalent halogen compounds; halogen oxides and halogen acids have, however, been rather neglected. Compounds of halogens with elements of the 3rd and 6th main groups are likewise unconsidered.

This volume contains the following chapters: 1. Sulfur-Nitrogen-Halogen Compounds (*O. Glemser* and *M. Fild*); 2. Fluorophosphoranes (*R. Schmutzler*); 3. Halides of Arsenic and Antimony (*L. Kolditz*): 4. Inorganic Silicon Halides (*E. Hengge*); 5. Organoelement Halides of Germanium, Tin, and Lead (*J. Ruidich, H. Schmidbauer,* and *H. Schumann*); 6. Equilibria Involving Halide Complexes in Aqueous Solution (*G. P. Haight jr.*); 7. Halogenation and Halogen Exchange in Fused Salt Media (*N. R. Thompson* and *B. Tittle*); and 8. Covalent Oxychlorides as Solvents (*V. Gutmann*).

The authors of the individual articles, who are undoubtedly experts in their fields, have all contributed to the development of halogen chemistry by their own work.

In the first five chapters, structures, fluorine magnetic resonance data, and a number of reaction mechanisms are given, in addition to chemical properties and reactions. The

articles are clearly arranged, make for easy reading, and are readily comprehensible. Chapter 6 describes the properties of halogen ions as ligands; chapter 8 deals with solvent properties of oxychlorides on the basis of a "solvent definition of acids and bases" and of a "coordination model of nonaqueous solutions". Chapter 7 provides a review of the application of salt melts in the preparation of fluorine-carbon compounds. The formation of complex ions in the melt is also discussed and examples of the manufacture of metals are given.

Volume 3 likewise contains eight chapters, the first three being devoted mainly to theoretical aspects of halogen chemistry. The others deal with the preparation and properties of metal-halogen compounds. 1. Halides containing Multicentered Metal-Metal Bonds (*D. L. Kepert* and *K. Vrieze*); 2. The Nature of the Metal-Halogen Bonds (*R. G. Pearson* and *R. J. Mawby*); 3. Review of Metal-Halogen Vibrational Frequencies (*R. J. H. Clark*); 4. The Halides of Niobium and Tantalum (*F. Fairbrother*); 5. Pentahalides of the Transition Metals (*A. D. Beveridge* and *H. C. Clark*); 6. Halide Chemistry of Chromium, Molybdenum, and Tungsten (*J. E. Fergusson*); 7. Halogen Chemistry of the Actinides (*K. W. Bagnall*); and 8. Halogeno-Metal Carbonyls and Related Compounds (*F. Calderazzo*).

Apart from the somewhat arbitrary choice of subject matter and a certain amount of duplication in the individual articles, these two volumes certainly represent a welcome addition for the chemist interested in these topics. With their help he can rapidly gain a comprehensive picture of the latest results in halogen research. Furthermore, since the volumes also contain various stimuli for further work they should on no account be absent from any chemical library.

A. Haas [NB 740 IE]

Porous Carbon Solids. Edited by *R. L. Bond.* Academic Press London-New York 1967, 1st Edit., xi, 311 pp., numerous illustrations and tables, bound $ 14.50 / 80 s.

This book deals with the possible methods for determining the pore structure of solids. The title is misleading insofar as nearly all the methods are generally applicable. Only in the results quoted as examples do synthetic graphites, activated carbons, and natural coals receive special treatment.

The theoretical and experimental aspects of the methods are described in eight sections in which, however, some procedures are treated too briefly. This is particularly true of the description of the evaluation of the gas adsorption isotherm which is the most important procedure in the determination of pores having a radius of less than 100 Å. Better and more detailed information on this subject can be found elsewhere. The recently developed t-plot method of *de Boer* and *Lippens* is not mentioned at all. The next section describes the possible methods of determining the pore size distribution by adsorption of molecules of various sizes from solutions and also by the use of gaseous molecular 'probes' which give a good measure of the molecular sieve properties of coals and narrow pore carbons. Density measurements by displacement of helium or liquids are also described. The characterization of pore structure by permeability measurements of gases and liquids is described very thoroughly and critically; the limits of validity of the theoretical assumptions are particularly discussed. The same is true of mercury porosimetry, the standard method for the determination of pore sizes with radii between 10 μ and 100 Å. The last chapters describe direct representation of relatively large pores, using radiographic methods. In this, the pores are filled with a liquid that absorbs X-rays more strongly than carbon, for instance liquid bismuth or silver

This book certainly enriches the literature, particularly in the treatment of the less well-known procedures. The reviewer especially liked the criticism of the various methods. The standard procedures are, however, described more clearly and thoroughly in other works. *H. P. Boehm* [NB 754 IE]

The Solid-Gas Interface. Vol. 2. Edited by *F. A. Flood.* Marcel Dekker Inc., New York 1967. 1st Edit., xiii, 660 pp., numerous illustrations, $ 27.50.

Shortly after the appearance of the first volume[1], which dealt essentially with the foundations and theory of physical adsorption, a second volume has now appeared. Acknowledged experts report on modern methods of measurement and their application to the problem of physical adsorption.

R. L. McIntosh deals with dielectric measurements on adsorption systems and discusses the results obtained. *P. W. Selwood* discusses the application of the investigation of magnetic properties of suitable systems for the study of adsorbent-adsorbate interactions and adsorption bonding.

In an extensive article *R. M. Barrer* treats the problems of material transport in porous media and in adsorption phases. *H. W. Habgood* deals with the theoretical foundations of gas chromatography and shows how this method can be applied to investigations on adsorption, in particular to the determination of adsorption isotherms and heats of adsorption. *S. Ross* and *E. D. Tolles* deal with the sorption of gases by solids covered with liquids. Finally, *W. Prins* discusses the take-up of adsorbate by the adsorbent and the resulting volume changes of the adsorbent.

The thermodynamic and kinetic aspects important in the study of adsorption are discussed by *B. E. Conway. P. J. Sereda* and *R. F. Feldman* show how the mechanical properties of the adsorbent are influenced by the presence of an adsorbate.

Measurements of surface potentials provide valuable information on bonding of the adsorbate. *F. C. Tompkins* deals with the most important methods of determination, discusses the results obtained in several systems, and comments on the conclusions to be drawn. By means of a band model *A. C. Zettlemoyer* and *R. D. Iyengar* discuss the interaction between adsorbates and semi-conductor surfaces.

The relationships during the impingment of a molecule on the surface of a solid and particularly its accommodation, is dealt with in two articles: *F. M. Devienne* deals mainly with the experimental results, and *E. A. Flood* and *J. P. Hobson* discuss the possibilities of a theoretical treatment of the problem.

J. N. Hodgons reports on the optical properties of the solid-gas interface; *C. H. Amberg* explains the methods and applications of IR spectroscopy.

The measurements of electron spin resonance and nuclear magnetic resonance, first applied to the study of adsorption only a few years ago, are described by *J. G. Aston*, and *M. J. D. Low* describes the application of the Mössbauer effect. *E. D. Eanes* and *A. S. Posner* put forward small-angle X-ray scattering as a valuable method of studying the adsorbing surfaces.

J. R. Dacey describes the adsorptive properties of activated carbon in comparison with other adsorbents. *B. G. Linsen* and *A. van den Heuvel* draw the reader's attention to the significance of pore structure in adsorption. The problem of hysteresis in the field of adsorption is discussed by *D. H. Everett.*

As in the first volume, *G. D. Halsey* ends by reviewing critically each chapter of the book.

This two-volume work is not a textbook on physical adsorption – the structure is too heterogeneous and the chapters are too little attuned to one another for this purpose. The book is rather directed to those already occupied with problems of adsorption, acquainting them with the most recent theoretical and experimental developments. The 1050 references in the first volume and those numbering over 2000, in the second volume include work from 1966. It should be particularly emphasized that not only are the commonly used methods dealt with, but also the more special procedures, often with very illuminating results. *G. Wedler* [NB 751 IE]

[1] Cf. Angew. Chem. *80*, 325 (1968); Angew. Chem. internat. Edit. *7*, 319 (1968).

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