EXPERIENTIA

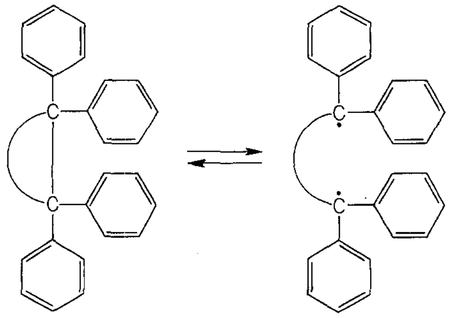
Vol. 28 - Fasc. 11 Pag. 1265-1400 15. 11. 1972

Eccentricities of Hydrocarbons on my Way from the Diyls to the Ylids

By GEORG WITTIG, Institut für Organische Chemie der Universität Heidelberg,
Im Neuenheimer Feld 7, D-69 Heidelberg (Germany).

The individuality of men and animals is expressed by their specific hehavior. Just as these living beings, chemical compounds can likewise show not only normal but also abnormal properties. Even hydrocarbons, which like the paraffins assume their identity primarily through functional groups, now and then allow a behavior to be detected that borders on the eccentric. We know from this that a deceptive structural formula can be indicated by seemingly strange behavior, therefore the cautious chemist speaks of the 'as though' until he is finally certain of a formulation. After such an adaptation process, structural knowledge is accepted as law and is ripe for textbooks. Also in my work, which has led me from the diyls to the ylids, I have encountered uncommon behaviors, about which I shall speak here.

About 45 years ago, as my fantasy strayed here and there from sensible thinking, I was captivated by an idea to which I was tempted to yield experimentally. The question was[1]: What influence does the ring strain exert on a ring opening if an accumulation of phenyl groups on a C–C bonding site predisposes the molecule to the formation of a biradical (designated in short as diyl I).

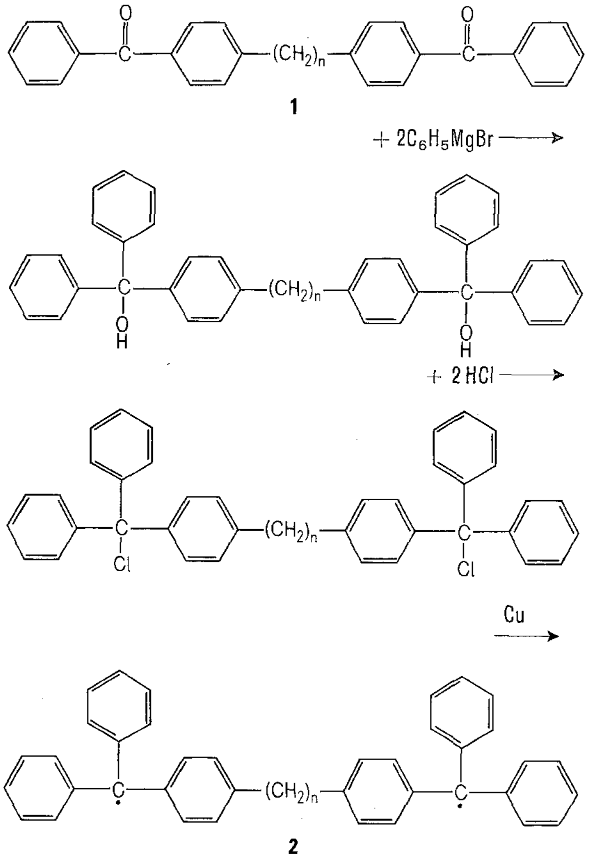


(I)

The biradicals 2 were synthesized in the following way. Phenylmagnesium bromide was allowed to react with the diketone 1; the resulting glycol was converted into the corresponding dichloride with hydrogen chloride and the halogen removed with elemental copper (II).

As the space models illustrate (Dreiding models did not exist at that time), the terminal radical groups for $n = 1$ and 2 can not close to form a strained ethane bond; in contrast to this $n = 3$ and 4 can cyclize (III).

Apparently in accordance with this is the finding that the diyls form a red solution for $n = 1$ and blue-violet for $n = 2$, whereas only light yellow solutions can be observed for $n = 3$ and $n = 4$, which are

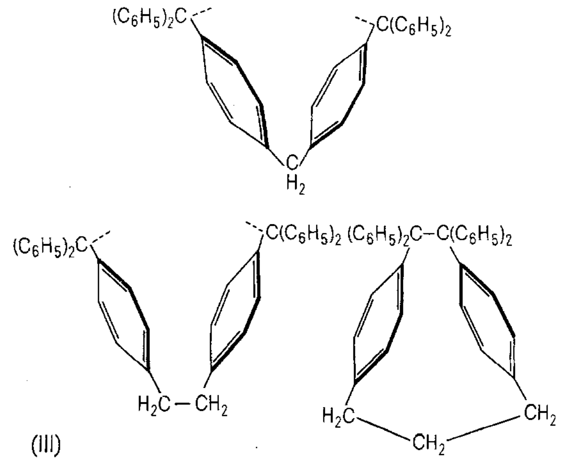


(II) $n = 1, 2, 3$ und 4

---

[1] G. WITTIG and M. LEO, Ber. dt. chem. Ges. *61*, 854 (1928); *62*, 1405 (1929).

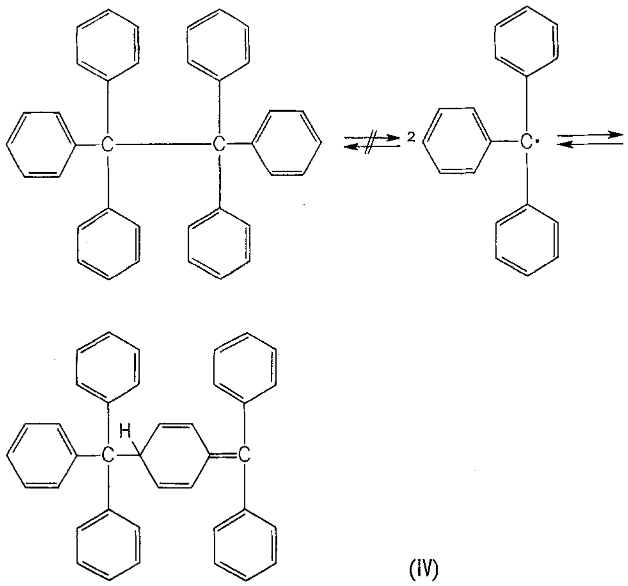
* Paul Karrer Lecture, presented 21 June 1972, in the Aula of the University of Zurich. German title: *Skurriles um Kohlenwasserstoffe auf meinem Wege von den Diylen zu den Yliden.*



(III)

characteristic color tones for triphenylmethyl[2]. All biradical solutions are air sensitive, since they can gape open like crocodiles opening their jaws to take in food. The molecular weight determinations show that in benzene solution strong association between molecules predominates for $n = 1$ and 2, whereas the radical valences for $n = 3$ and 4 are satisfied intramolecularly. Accordingly, ring formation results only when the ring strain permits it.

However, these conclusions are to be questioned, since in new investigations[3] triphenylmethyl does not dimerize to the ethane derivative, rather forms a *p*-quinoid system according to the following scheme (IV):



(IV)

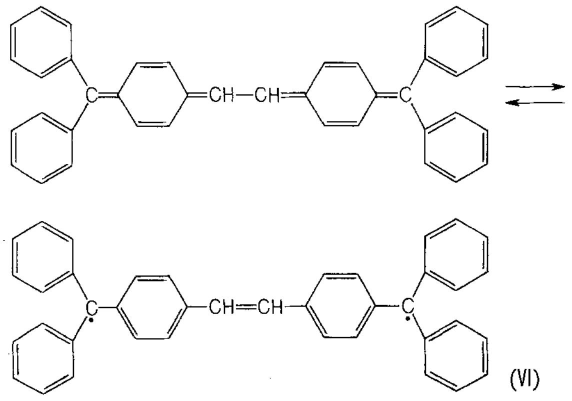
With this scheme, however, the state of affairs becomes so complicated that we did not resume work on these models again.

Things are situated differently in the case of the biradical, in molecule **2** in which neither of the two phenylene group bridging methylene groups are available. I shall now concern myself with the consideration of the Chichibabin hydrocarbon **3** with inclusion of its phenyl homologs[4].

In the tabular series, the light absorption shifts to longer wavelengths with increasing lengths of the polyene chain between the two resulting diphenylmethylidene residues, and the reactivity toward oxygen increases accordingly. While the solution of the tetraphenyl-*p*-xylylenes (Thieles hydrocarbon) forms a peroxide only after days of action by oxygen, the same process requires minutes for the Chichibabin hydrocarbon **3** and ultimately only seconds for the final member **4**.

Differences of opinion have existed for a long time concerning the reason for the behavioral modes of the compounds mentioned. While I speculated on a valence tautomerism between the quinone structure and the corresponding biradical that is favored by the tendency of quinone groups to be transformed into aromatics, Müller[5] argued for a mesomerism on the basis of his measurements of the magnetic susceptibility.

I had, to be sure, expressed myself cautiously with the words that the valence tautomerism is by no means proven as long as the possibility exists that the valence shift to the diyl ensues only under the influence of the reagent, here, of the oxygen. I tried, therefore, to reach a decision between the alternative valence tautomerism and mesomerism with an optical method[6] (VI).



(VI)

If it is a question of a valence tautomerism between the quinones and a diradical form, in other words, of an equilibrium between two compounds, then the absorption curves at different temperatures should cross at a point (the isobestic point). Whereas, in the case of mesomerism, with changing temperatures the change

---

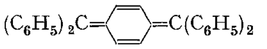
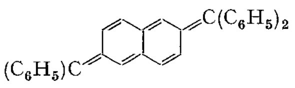
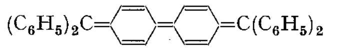
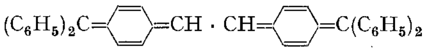
[2] The possibility was not excluded that the deep colors are to be traced back to by-products that form quinoid compounds through disproportion action.

[3] H. Lankamp, W. Th. Nauta and C. MacLean, Tetrahedron Lett. *1968*, 249. – H. A. Staab, H. Brettschneider and H. Brunner, Chem. Ber. *103*, 1101 (1970).

[4] G. Wittig and W. Wiemer, Justus Liebigs Annln Chem. *483*, 144 (1930); G. Wittig and A. Klein, Ber. dt. chem. Ges. *69*, 2087 (1936).

[5] E. Müller and I. Müller-Rodloff, Justus Liebigs Annln Chem. *517*, 134 (1935).

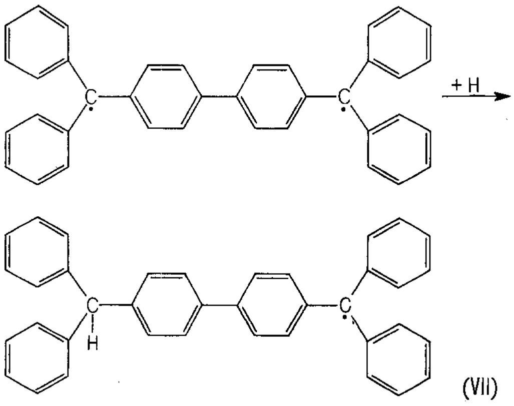
[6] G. Wittig and B. Fartmann, Justus Liebigs Annln Chem. *554*, 213 (1943).

Name	Formula	Color	Behavior with O_2; loss of color after:
Tetraphenyl-*p*-xylylene		Orange	Days
Naphthoquinone-2,6-*bis*-(diphenylmethylidene)		Red	Hours
Diphenylquinone-*p*, *p'*-*bis*-(diphenylmethylidene)	 **3**	Violet	Minutes
Diquinone of *p*, *p'*-*bis*-(diphenylmethenyl)-stilbene	 **4**	Blue	Seconds

of absorption should cause a displacement of the peak of the curve according to the wavelengths.

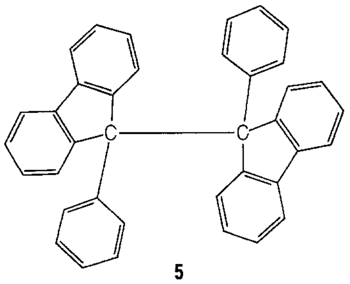
The measurements carried out on hydrocarbon **4** did not yield a clear picture since the experimentally possible temperature differences were too small.

In the meantime, the matter was cleared up by method of electrospin resonance[7] which is superior to susceptibility measurements. Accordingly, the Chichibabin hydrocarbon should contain 4% of the diracidal component, which remains in the valence tautomeric equilibrium with its paraquinoid form[8]. In recent times, it was finally theorized that the biradical constituent of the Chichibabin hydrocarbon probably abstracts a hydrogen atom from the solvent and that the observed paramagnetism is due to a monoradical[9]. However, the last word has not yet been spoken (VII).

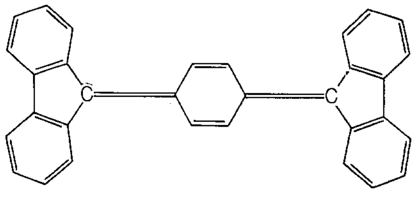

(VII)

The question presented itself of how does a compound of the type of Thiele hydrocarbon behave if two fluorenylid residues are inserted instead of the two diphenylmethylene groups. This problem was stimulating in that the dibiphenyleneethane **5**, whose structure was established by ^{13}C-NMR-spectroscopy, reveals no tendency toward radical dissociation in contrast to the 'isohexaphenyl ethane'[10] (VIII).

It was to be expected that the easily accessible 1,4-*bis*-[fluorenylidene-(9)-cyclohexadiene-(2,5)] **6**, corresponding to its parent substance, tends to form stable di- or polymerization products[11]. The colorless crystalline compound forms deep violet solutions in organic solvents from which it reforms colorless crystals with concentration under nitrogen. The osmometric molecular weight determination indicated that equilibrium lies on the side of the tetramers at the ascertained value of around 1600; the blue-violet solution color is accordingly to be traced back to the monomeric constituent **6**.


5

(VIII)


6

It could be shown on the basis of NMR spectroscopic measurements at different temperatures that

---

[7] G. J. Sloan and W. R. Vaughan, J. org. Chem. *22*, 750 (1957); G. A. Hutschison, A. Kowalsky and G. W. Wheland, J. chem. Physics *20*, 1485 (1952).

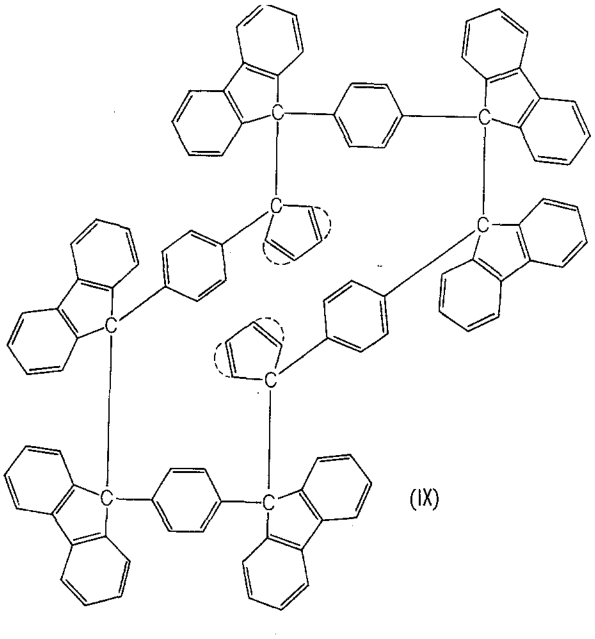
[8] I. D. Morozowa and M. E. Dyatkina, Russ chem. Revs *37*, 376 (1968).

[9] H.-D. Brauer, H. Stieger, J. S. Hyde, L. D. Kispert and G. R. Luckhurst, Molec. Physics *17*, 457 (1969); W. J. van der Hart and L. J. Oosterhoff, Molec. Physics *18*, 281 (1970).

[10] H. A. Staab, K. Sundarsano Rao and H. Brunner, Chem. Ber. *104*, 2634 (1971).

[11] G. Wittig, E. Dreher and W. Reuther; H. Weidinger and R. Steinmetz, Justus Liebigs Annln Chem. *726*, 188 (1969).

the tetrameric constituent in solution and the colorless crystals possess the following structure (IX):



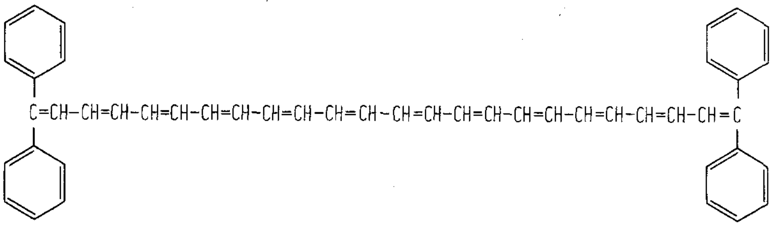
(IX)

It is a matter here of one of the stable conformations which allows itself to be built completely strain-free with Dreiding models. The fragility of the structure is indicated by the observation that the colorless crystals may themselves assume a deep blue color upon gentle pressure. One can write and draw on paper impregnated with it with a wooden rod. To be sure, the colors produced are not stable very long since the pressure-produced monomer in this fine distribution is sensitive to oxygen in air.

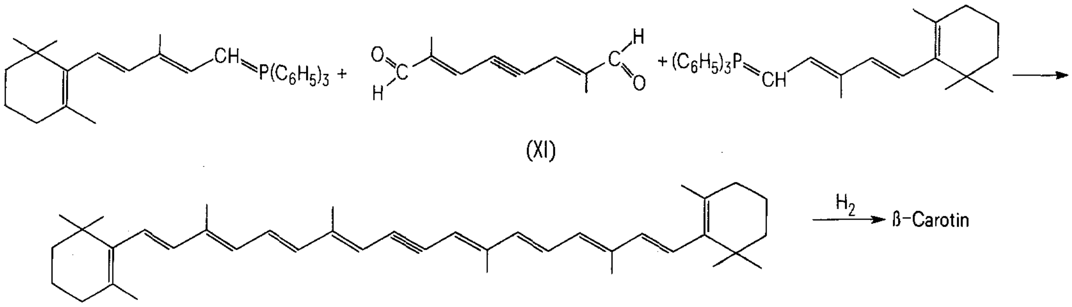
Now, what is the behavior of ω, ω'-tetraphenylpolyenes, which indeed carry 4 radical formation-favoring aryl residues on the end of the chain but do not permit a possibility of aromatization within the polyene chain? Corresponding to the work by KUHN and WINTERSTEIN[12] who synthesized diphenylpolyenes, we succeeded in synthesizing all *trans*-tetraphenylpolyenes up to the compound which is colored red-violet with 12 double bonds[13] (X).

However, the hydrocarbons collectively proved to be inert in the presence of oxygen. Even the highest members of this series gave no indication detectable by electronspin resonance[14] that biradicals occur.

In this connection, the naturally occurring carotinoids could be pointed out; the replacement of carbonyl oxygen by methylene groups with the help of the phosphonium ylid method proved to be very advantageous for their synthesis[15]. I mention here, as one example of many, the β-carotene prepared according to POMMER[16] on the synthetic principle of $C_{15} + C_{10} + C_{15} = C_{40}$ (XI):



(X)



(XI)

After the pioneer work of PAUL KARRER and RICHARD KUHN, the research groups of the BASF and Hoffmann-La Roche (under POMMER and ISLER) have made outstanding achievements. None of these unsaturated hydrocarbons contain diyls as valence tautomeric impurities.

While, as reported, the Chichibabin hydrocarbon contains a monoradical component, the meta-isomeric

---

[12] R. KUHN and A. WINTERSTEIN, Helv. chim. Acta *11*, 88 (1928).

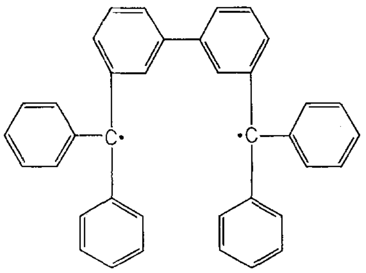
[13] H. BURGER, Dissertation (Tübingen, 1958); G. WITTIG and R. WIETBROCK, Justus Liebigs Annln Chem. *529*, 162 (1937).

[14] K. H. HAUSSER, Angew. Chem. *68*, 729 (1956).

[15] U. SCHÖLLKOPF, Angew. Chem. *71*, 260 (1959); *Carotinoids* (Ed. O. ISLER, Birkhäuser; Publisher, Basel and Stuttgart 1971).

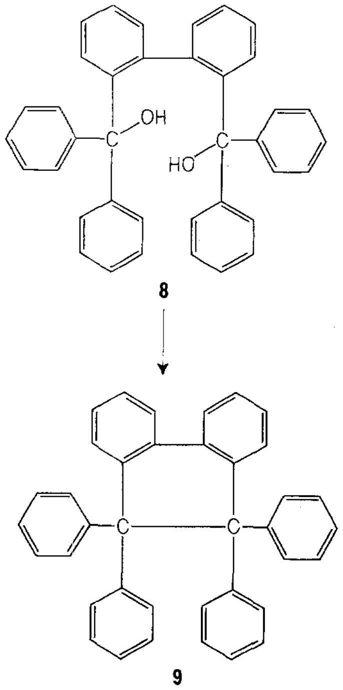
[16] DBP 954247 Kl 120, Patent G. WITTIG and H. POMMER, C. *1958*, 1843.

compound **7** shows the behavior of a normal biradical, as detected by Schlenk[17]. The reason for this is readily available; a deviation in a quinoid formation is here structurally forbidden (XII).



(XII) **7**

One compound is missing in this series, the *ortho* isomer, the tetraphenyl-dihydrophenanthrene **9**, which was troublesome for us[18] but was later prepared in the following simple manner[19] (XIII):

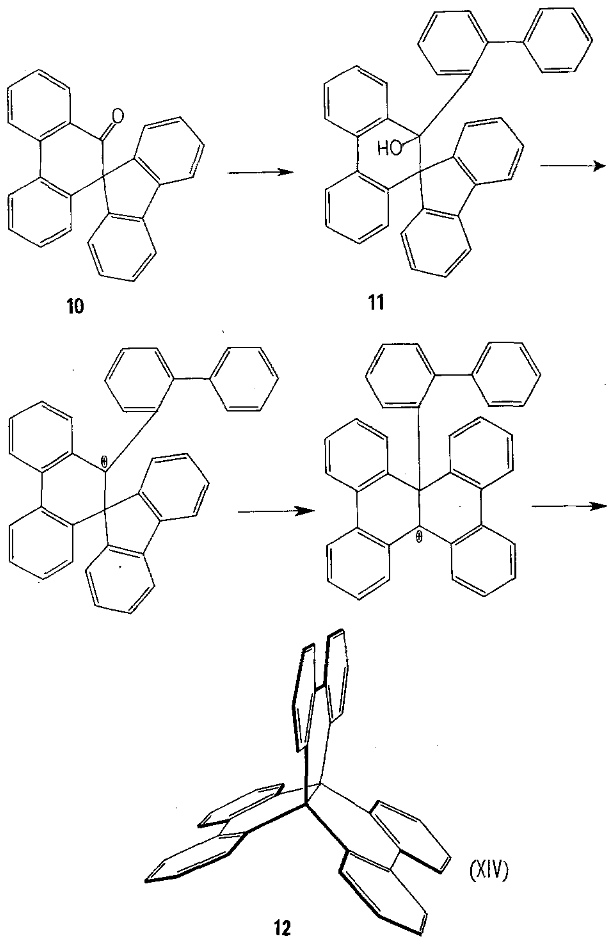


(XIII) **9**

The glycol **8** obtainable from diphenyl acid ester and phenyllithium was reduced immediately with tin-(II)-chloride and hydrochloric acid in acetic acid to the cyclic hydrocarbon **9**.

The compound **9**, whose structure was recently proven NMR-spectroscopically, is very stable in spite of its hexaphenylethane analog structure. This stability was not changed when we introduced 2 methoxyl groups into the *o*- and *o'*-positions of the diphenyl system to increase the ring strain. While compound **9** which melts at 340° was also insensitive to oxygen in solution, it was cleaved straight forwardly with sodium-potassium alloy to the dipotassium derivative. Apparently, the ring closure contributes to a stabilization of the ethane bond.

In support of this work, it appeared worthwhile to synthesize the *tris*biphenyleneethane **12**, which is interpreted as *ortho*-linked hexaphenylethane[20] (XIV).



The ketone **10** formed the corresponding carbinol **11** by reaction with *o*-lithiumdiphenyl which yielded the desired hydrocarbon **12** in acidic medium via a twofold Wagner-Meerwein rearrangement.

This first aromatic propellane, whose mere appearance in my opinion causes a certain feeling of well-being, melts at 475°. Its actual spatial structure **12a** was proved by NMR-spectroscopy. **12a** showed the almost symmetrical ABCD spectrum that is produced by 4 types of aromatic protons in the ratio 1:1:1:1 (XV).

The central ethane bond could not be cleaved with sodium-potassium alloy to the corresponding dipotassium derivative. Evidently the dense aryl packing here prevents a penetration into the center of the molecule by alkali metals.

---

[17] W. Schlenk and M. Braun, Ber. dt. chem. Ges. *48*, 725 (1915).

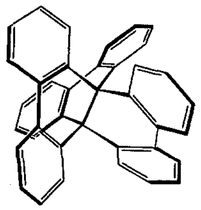
[18] G. Wittig and H. Petri, Justus Liebigs Annln Chem. *505*, 17 (1933).

[19] W. Schoch, Dissertation (Heidelberg 1970).

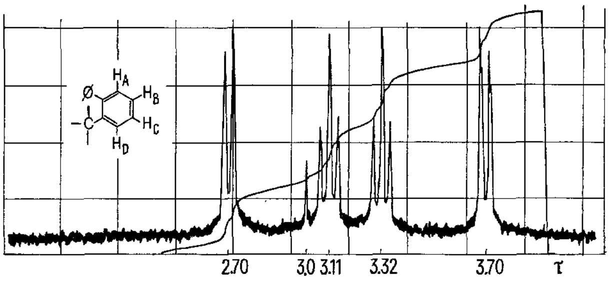
[20] G. Wittig and W. Schoch, Justus Liebigs Annln Chem. *749*, 38 (1971).

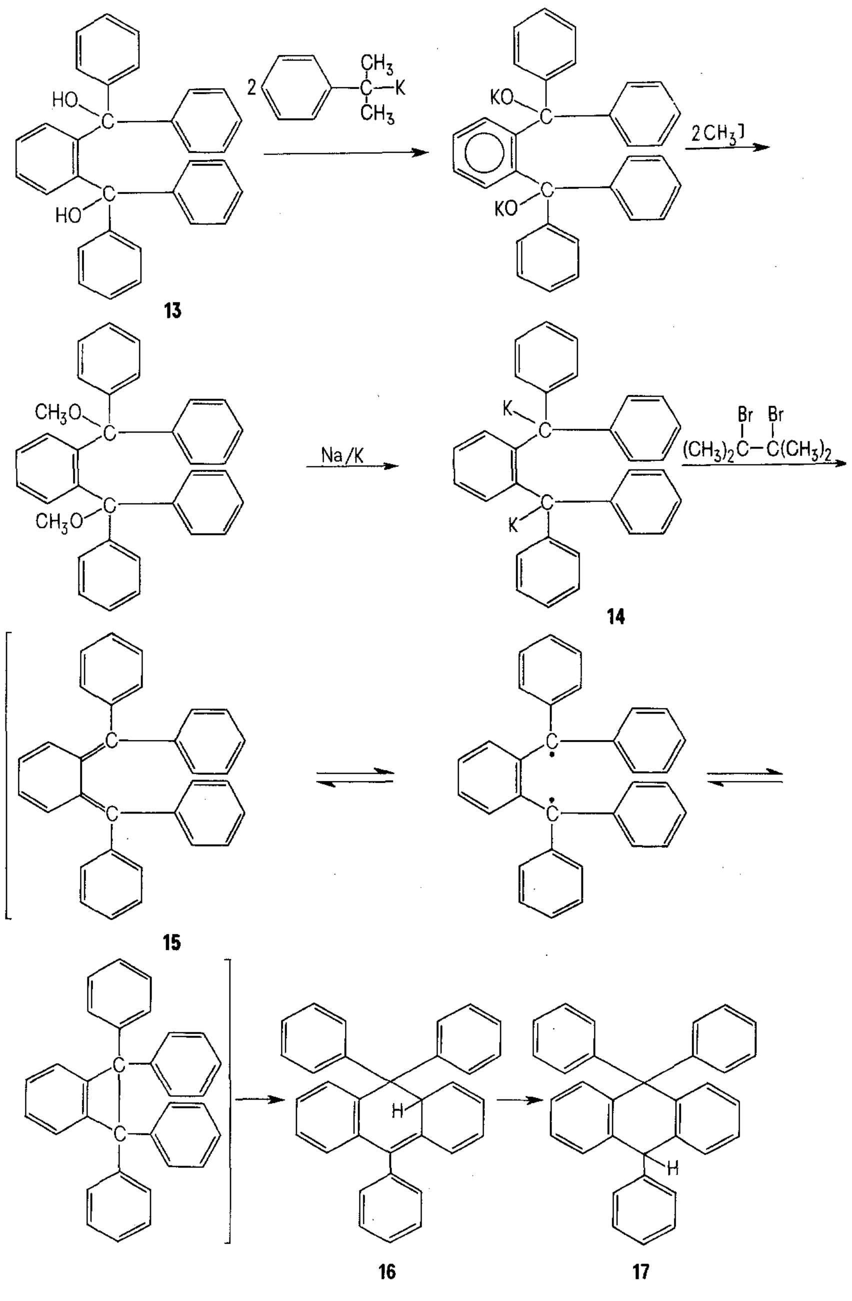
In this connection, the *ortho* isomer of the Thiele hydrocarbon was of interest; we were able to produce it in the following complicated way. Glycol **13** prepared from phthalic acid ester with phenyllithium (phenylmagnesium bromide proved unworkable) was etherified through its potassium glycolate with methyl iodide. The compound **14**, which was cleaved to the dipotassium compound with potassium, was demetalated with tetramethylethylenedibromide. However, the expected tetraphenyl-*o*-xylylene **15** was not formed, rather the triphenyldihydroanthracene **17** at —50° (XVI).

In the last step, the Nauta-analogous addition of diradicals was executed to form **16**, which was converted by H shift to the end product **17**[21].



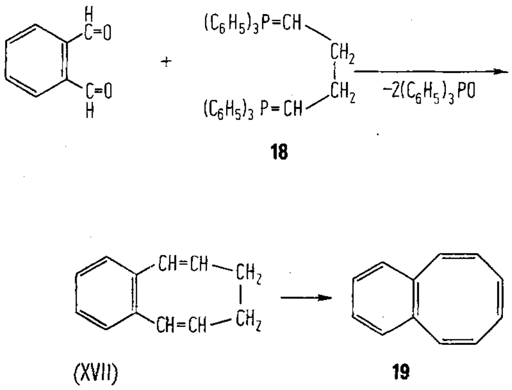
12a (XV)





(XVI)

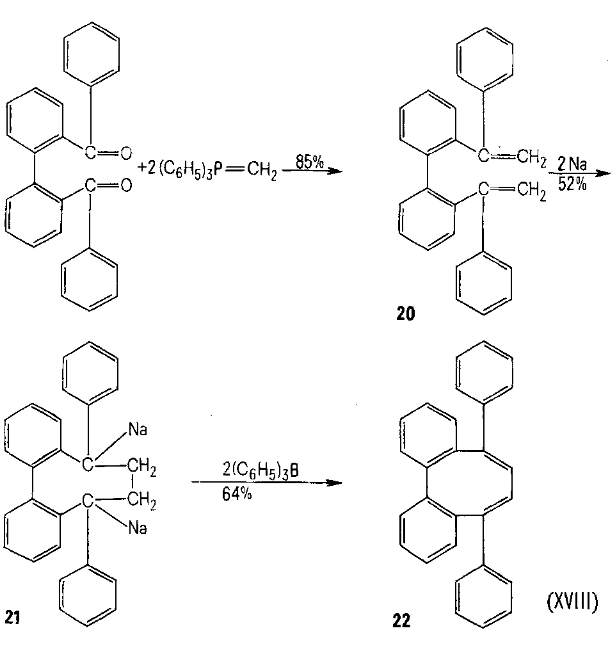
I turn now to a new chapter, to the *cyclic* polyenes, a few of which were synthesized. From *o*-phthalaldehyde and the bifunctional phosphonium ylid **18**, 1,2-benzocyclooctatriene was produced. By way of its bromo derivative and following this the acetoxy derivative benzocyclooctatetraene **19**[22] was formed by thermal degradation (XVII).



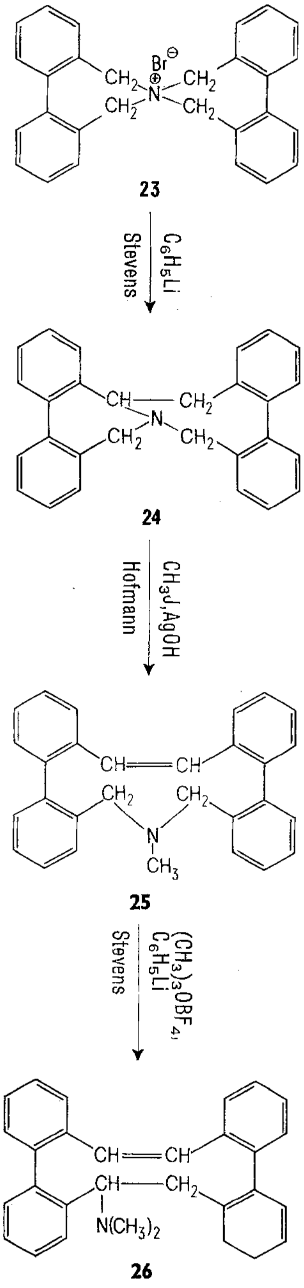
This yellow hydrocarbon which melts at 51° was previously unknown.

We were able to synthesize a compound which also belonged to the benzocyclooctatetraene by a method which is original because all of the intermediates except the first are very unusual[23].

For the synthesis of the 5,8-diphenyl-1,2,3,4,-dibenzocyclooctatetraenes **22**, *o,o'*-dibenzoyldiphenyl was allowed to react with 2 moles of triphenylphosphinemethylene, and the resulting *bis*-olefin **20** was altered to **21** by lengthy action of sodium. Then **22**, was produced by cleavage of **21** with triphenyl-boron (XVIII).



The *ammonium* ylids also proved useful for the production of cyclic polyenes. Thus the already known 1,2,7,8,-dibenzocyclooctatetraene[25] could be prepared from di-*o*-xylylene ammonium bromide[24] through a series of synthetic steps which are analogous to those in the production of the 1,2,3,4,7,8,9,10-tetrabenzocyclododecahexaenes[26] which are now to be described.



Formula XIX continued on p. 1272

---

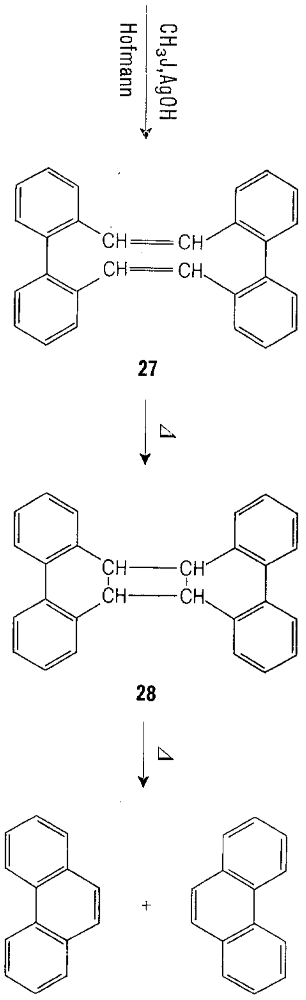
[21] G. Wittig and M. Leo, Ber. dt. chem. Ges. *64*, 2395 (1931); G. Quinkert, W. W. Wiersdorff, M. Finke and K. Opitz, Tetrahedron Lett. *1966*, 2193.

[22] G. Wittig, H. Eggers and P. Duffner, Justus Liebigs Annln Chem. *619*, 10 (1958).

[23] G. Wittig and W. Stilz, Justus Liebigs Annln Chem. *598*, 93 (1956).

[24] G. Wittig, Angew. Chem. *63*, 15 (1951).

Formula XIX continued from p. 1271

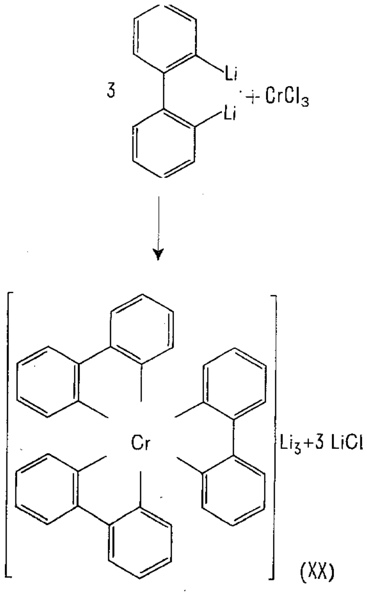


The starting compound was the cyclic ammonium salt **23** whose ylid, produced with phenyllithium, underwent the Stevens rearrangement to the amine **24** (XIX).

The methyl iodide derivative was converted to the corresponding quartenary base with silver oxide, which gave the cycloolefin **25** by heating under Hofmann degradation conditions. The difficulties of quarternizing **25** could be overcome by the use of trimethyloxoniumtetrafluoroborate. The ammonium iodide obtainable therefrom was converted into its ylid which in turn yielded the amine **26** in a new Stevens rearrangement. Its methyl iodide derivative was converted via the hydroxide by the Hofmann degradation to the tetrabenzocyclododecahexaene **27**.

The synthetic pathway to **27**, described here in a simplified manner, produced in further steps the cyclobutane derivative **28** and phenanthrene, which were also subsequently to be obtained through heating of **27** by way of the now isolatable **28**. One actually obtained two hydrocarbons **27** which were recognized as *cis-trans* isomers. The hydrocarbon found to be the *cis-trans* compound in recent studies of SKIPKA[27] forms the four-membered ring.

I should now like briefly to discuss the atropisomeric *o*-hexaphenylenes, which also belong to the series of the cyclic polyenes. One obtains them by conversion of ate-complex **29**, which is produced from 2,2'-dilithiumdiphenyl and chrome (III) chloride, with halides of transition metals[28]. We realized the best yield of **30 B** with copper (II) chloride (XX).



(XX)

29

It could be determined with the help of the IR-, UV- and NMR-spectra that for the 2 compounds were the centrally symmetrical *o*-hexaphenylene **30 A** and the helical stereoisomer **30 B** (XXI).

In contrast to the centrally symmetrical *o*-hexaphenylene **30 A**, **30 B** possesses only 3 binary axes of rotation but no axis of rotary reflection or plane of symmetry and is accordingly chiral. Actually the latter hydrocarbon could be separated into optical antipods by spontaneous crystallization and column chromatography on (—)-α-[2,4,5,7-tetranitro-9-fluorenylideneaminooxy]-propionic acid.

Whether or not the dibenzo [g.p.] chrysene **31** is also obtainable in optically active form, is at the present time being investigated. We would explain a possible optical activity by the steric hindrance of the circled *ortho*-fixed hydrogen atoms, which force the aromatic system a little out of plane.

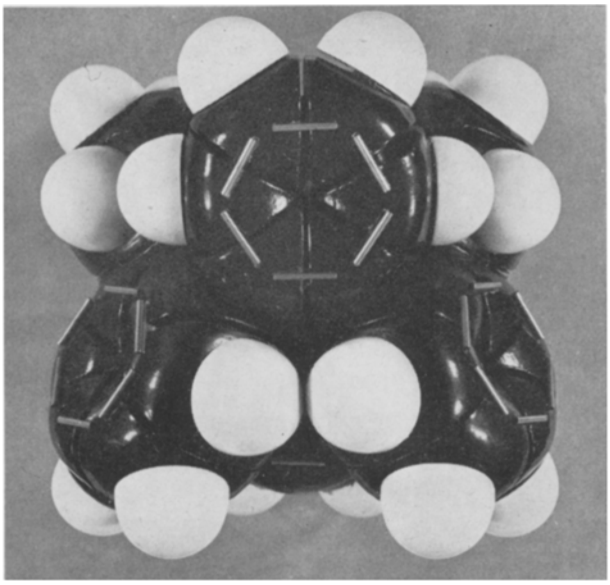
---

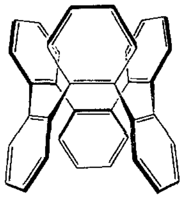
[25] L. FIESER and M. M. PECHET, J. Am. chem. Soc. *68*, 2577 (1946).

[26] G. WITTIG, G. KÖNIG and K. CLAUSS, Justus Liebigs Annln Chem. *593*, 127 (1955).

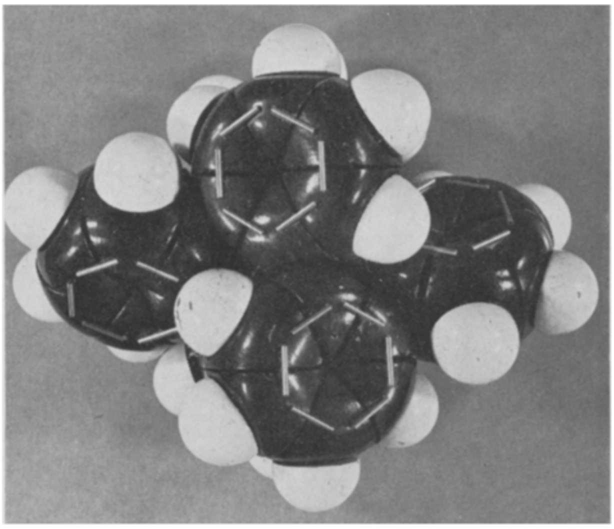
[27] G. SKIPKA, Dissertation (Heidelberg 1971).

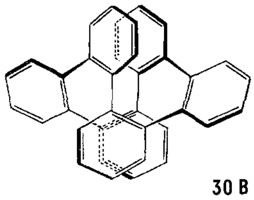
[28] G. WITTIG and K.-D. RÜMPLER, Justus Liebigs Annln Chem. *751*, 1 (1971); G. WITTIG and G. KLAR, Justus Liebigs Annln Chem. *704*, 91 (1967); G. WITTIG and G. LEHMANN, Chem. Ber. *90*, 875 (1957).





30 A

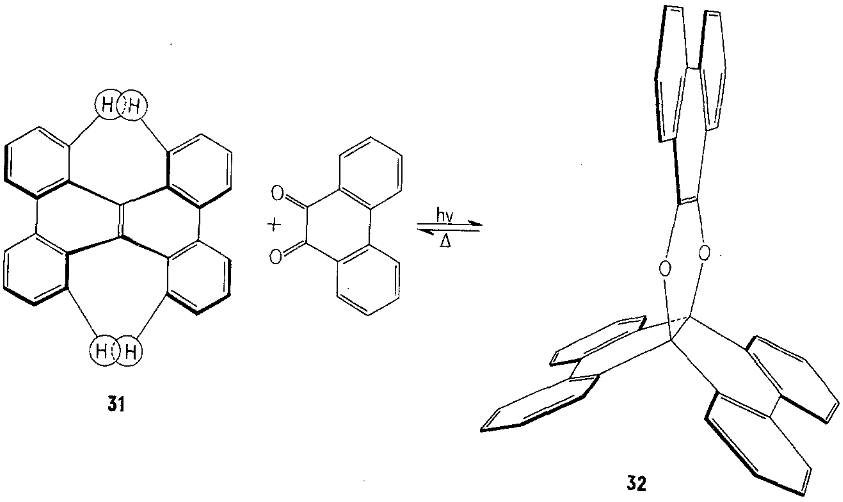




30 B

(XXI)

That the inner aromatic C=C bond is distinguished by a special reactivity was impressively shown by the observation that phenanthrene quinone reacted with irradiation with UV-light in the following way (XXII): It is added to form the propellane derivative **32**, which is cleaved reversibly to the initial components by heating[29]. These reactions show that today's customary characterization of aromatic systems with halos in the



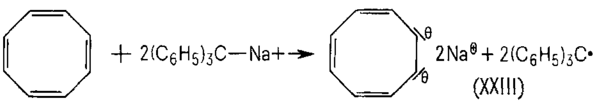
31

32

(XXII)

aromatic six-sided figures can deceptively veil the actual different electron densities.

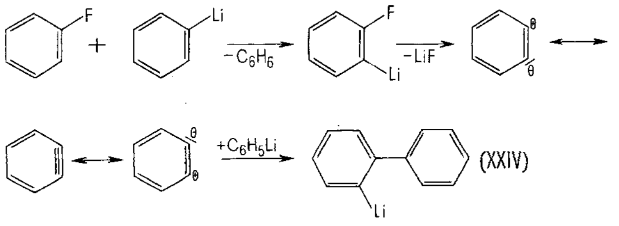
A noteworthy reaction is included here, which forms the transition to the closing chapter of the dehydrobenzenes. In this connection cyclooctatetraene was reacted with trityl sodium. Although these reactants yield polymers in tetrahydrofuran solution, the cyclooctatetraene is reduced in ether to the disodium adduct. In doing so, the 'isohexaphenylethane' is simultaneously formed[30] (XXIII).



Unfortunately, it eluded us at the time that the disodium adduct with its 10 π electrons represents a stable aromatic system according to the Hückel rule [$(4n + 2)$ π electrons]. The true state of affairs was discerned only much later by KATZ et al.[31], who also isolated the same aromatic system by direct action of alkali metals.

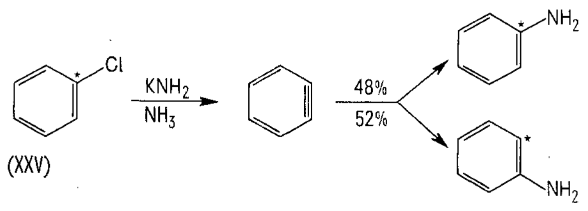
In conclusion, I turn to *dehydrobenzene*, a hydrocarbon which is to be detected only fleetingly in solution or in the gaseous state.

We happened upon this problem because of an unexpected reaction sequence[32]. For the study of diphenyl formation, we had reacted the 4 halogen benzenes with etherial phenyllithium under identical experimental conditions and found to our surprise that the supposedly sluggish fluorobenzene reacts unusually rapidly to diphenyl giving a 75% yield, while the remaining halogen benzenes give only 5–7% yield. Our explanation for this result was that the diphenyl formation proceeds through an *ortho* metalation of the halogen benzene which is favored by the inductive-substituent effect of the electronegative fluorine. Supporting this explanation was the demonstrable *o*-lithiodiphenyl that resulted rather than diphenyl. From this it was concluded that following the metalation a metallohalide cleavage takes place which leads to the dehydrobenzene[33] (XXIV).

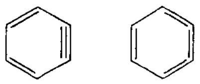


Phenyllithium adds to this to form the *o*-lithiodiphenyl which was found.

Strong evidence for the intermediary occurrence of dehydrobenzene was later provided independently by ROBERTS[34], when he reacted 1-^{14}C-chlorobenzene with potassium amide in liquid ammonia and isolated the two expected anilines in yields of approximately 50% each (XXV).

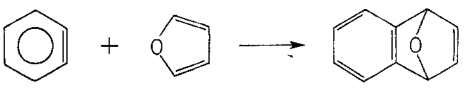


This short-lived intermediate product was named benzyne, a nomenclature which appears to me less than successful since it is based on a carbon-carbon triple bond, in contrast to which one can show a triple cumulative system of double bonds with the same authority because of the benzene structure. In order to escape this dilemma, the formula **33** with the halo in the six-membered ring seems to me to be more reasonable (XXVI).


(XXVI)


33

Later the identification of the short-lived dehydrobenzene succeeded on a totally different basis, on the theory that it should react as a dienophile[35] (XXVII).



(XXVII) **34**

As the diene, we first chose furan which should, as an ethereal solvent, favor the metalloorganic formation of dehydrobenzene and, at the same time, act as a diene trapping agent. In an exciting experiment, we reacted *o*-fluorobromo-benzene with lithium-amalagam in furan from which we isolated the endo-oxide **34** as a Diels-Alder adduct in good yield.

[29] G. WITTIG and W. SCHOCH, Justus Liebigs Annln Chem. *749*, 24 (1971).

[30] G. WITTIG and D. WITTENBERG, Justus Liebigs Annln Chem. *606*, 8 (1957).

[31] TH. J. KATZ, CH. R. NICHOLSON and C. A. REILLY, J. Am. chem. Soc. *88*, 3832 (1966).

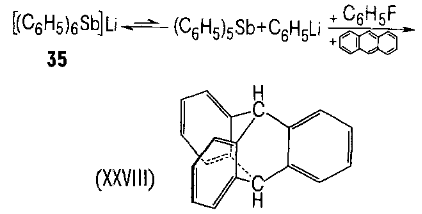
[32] G. WITTIG, G. PIEPER and G. FUHRMANN, Ber. dt. chem. Ges. *73*, 1193 (1940).

[33] G. WITTIG, Naturwissenschaften *40*, 696 (1942).

[34] J. D. ROBERTTS, H. E. SIMMONS JR., L. A. CARLSMITH and C. W. VAUGHAN, J. Am. chem. Soc. *75*, 3290 (1953).

[35] G. WITTIG and L. POHMER, Chem. Ber. *89*, 1334 (1956).

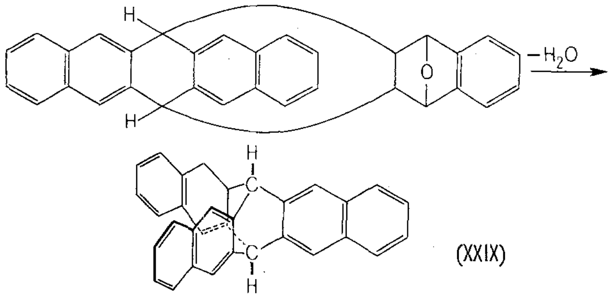
Among other diene additions, I mention only the addition of dehydrobenzene to anthracene to form triptycene which BARTLETT had already prepared in a totally different way. His reaction could be remarkably simplified if one reacted the more easily accessible *fluorobenzene* with phenyllithium which one maintained in lower concentration by means of a trick. We accomplished this by adding the ate-complex **35**[36], which yields only a little phenyllithium in reversible equilibrium (XXVIII).



35

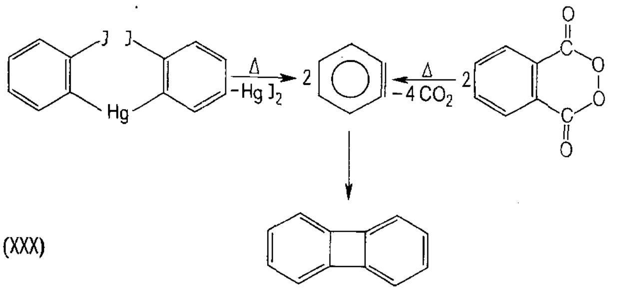
(XXVIII)

In this connection, an additional triptycene synthesis should be pointed out, which ultimately is based on the intermediary occurence of dehydrobenzene[37a]. It involves the addition of dihydronaphthalene-endo-oxide, which is easily accessible from dehydrobenzene and furan to *pentacene*. This addition product was transformed by dehydration in acetic anhydride and hydrochloric acid into the previously unknown tribenzotriptycene, which melts at 389° and whose IR-spectrum corresponds to that of the similarly prepared *mono*benzo-triptycene in its characteristic bands (XXIX).



(XXIX)

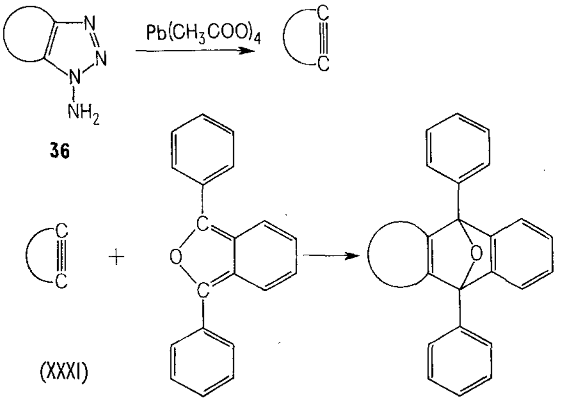
The life-span of dehydrobenzene[37] in the gaseous state was determined by thermal decomposition of *bis-o*-iodophenylmercury as well as phthaloylperoxide to biphenylene at 600° in an argon atmosphere under reduced pressure. With furan, which was injected behind the zone of decomposition, α-naphthol formed as a secondary product of the primarily formed dihydrohaphthalene-endo-oxide (XXX).



(XXX)

The lifetime amounted to a maximum of 20 msec under these conditions. In the light of this and other research not reported here[38], we acknowledged the actual existence of dehydrobenzene and became accustomed to the occurrence of this surprising compound[39]

Distinguishing it from dehydrobenzene, cyclohexyne contains an actual acetylene bond[40]. This hydrocarbon and other cycloalkynes were prepared abundantly from the N-amino-triazole derivatives **36** by oxidation with lead tetraacetate (XXXI):



36

(XXXI)

While cyclooctyne—as was already known can be isolated, cycloheptyne exists for only a few hours in solution[41]. Cyclohexyne and cyclopentyne, on the contrary, could only be trapped in the presence of cyclic dienes as their Diels-Alder adducts. Especially 2,5-diphenyl-3,4-benzofuran reacted promptly under the in situ conditions[42].

---

[36] G. WITTIG and E. BENZ, Tetrahedron *10*, 37 (1960).

[37] G. WITTIG and H. F. EBEL, Justus Liebigs Annln Chem. *650*, 20 (1961); H. F. EBEL and R. W. HOFFMANN, Justus Liebigs Annln Chem. *673*, 1 (1964).

[37a] G. WITTIG, H. HÄRLE, E. KNAUSS and K. NIETHAMMER, Chem. Ber. *93*, 951 (1960).

[38] R. W. HOFFMANN, *Dehydrobenzene and Cycloalkynes* (Verlag Chemie and Academic Press, New York 1967).

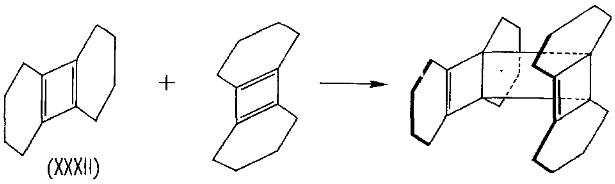
[39] Considering the short lifespan of dehydrobenzene, the following episode must prove surprising. During my Tübingen time, my coworkers had placed a flask labelled crystallized dehydrobenzene on the table of my private laboratory for me as a Christmas gift. An American colleague, who saw the flask on the occasion of his visit, reported in California that I had succeeded in cultivating crystallized dehydrobenzene in flasks. This news broke like a bomb but cleared itself up as time passed with the explanation that as a practical joke the flask with the ominous label had been filled with sodium thiosulfate, which forms especially beautiful crystals with 5 moles of water of crystallization.

[40] G. WITTIG and H.-L. DORSCH, Justus Liebigs Annln Chem. *711*, 46 (1968); G. WITTIG and P. FRITZE, Justus Liebigs Annln Chem. *712* 79 (1968).

[41] G. WITTIG and J. MESKE-SCHÜLLER, Justus Liebigs Annln Chem. *711*, 65 (1968).

[42] G. WITTIG, Angew. Chem. *74*, 479 (1962).

Should the resulting cycloalkynes be allowed to stand, an auto-addition to the cyclobutadiene derivative ensues which combines, in the case of cyclohexyne, to form tetramers[43] (XXXII):



(XXXII)

The structure and the reaction pathway were proven.

Hereby I am at the end of my exposition. We have seen that the eccentric cases, in respect to the enumerated hydrocarbons, documented themselves either in mode of formation, or in their structure, or ultimately in their behavior.

E. Th. A. Hoffmann, who lived around 1800 and was professionally a government official was simultaneously a poet, composer, conductor and designer and in his character and appearance himself an eccentric person, might have been able to fashion the material under discussion more effectively into his 'Tales of Hoffmann'. But the modern chemist would overlook this and become meaningfully engrossed in the 'Tales of another Hoffmann,' Roald Hoffmann, who, together with Woodward, with his line of reasoning, brought bizarre relationships onto a strict scientific base.

Zusammenfassung. In dem vorliegenden Artikel werden Kohlenwasserstoffe behandelt, die – im Laufe einer etwa 45jährigen Forschung des Autors synthetisiert – entweder in ihrer Bildungsweise oder in ihrer Struktur oder schliesslich in ihren Eigenschaften ein wenig skurril sind.

In Modellverbindungen wurde der Einfluss der Spannung auf die Tendenz der Ringöffnung zu Diradikalen (kurz Diyle genannt) untersucht und weiterhin am Tschitschibabinschen Kohlenwasserstoff und Analogen die Alternative studiert, ob es sich um eine Valenztautomerie oder Mesomerie zwischen chinoiden Derivaten und Diradikalen handelt.

Während die anstehenden Probleme hier noch nicht restlos geklärt sind, zeigen die ω,ω'-Tetraphenylpolyene auch mit längerer Polyenkette, ferner das β-Carotin keinen Diylcharakter. Auch Tetraphenyldihydrophenanthren **9** und das aromatische Propellan **12** sind inert gegenüber Sauerstoff.

In diesem Zusammenhang wurde über die Präparierung von Cyclopolyenen wie **19** und **22** berichtet. Besonderes Interesse bietet das auf der Ammoniumylid-Basis bereitete Tetraphenylcyclododecahexaen **27**, das beim Erhitzen über das Cyclobutanderivat **28** zum Phenanthren zerfällt. Von den ebenfalls zu den Cyclopolyenen gehörenden beiden stereoisomeren *o*-Hexaphenylenen **30 A** und **30 B** konnte den Erwartungen gemäss **30 B** in optische Antipoden zerlegt werden. Tetrabenzonaphthalin **31**, in dessen Molekül die mittlere C=C-Bindung besonders reaktiv ist, bildete mit Phenanthrenchinon beim Bestrahlen das Propellan **32**, das beim Erhitzen wieder in die Ausgangskomponenten zerfiel.

Abschliessend wird über die Bildungsweise von Dehydrobenzol und seine Struktur berichtet und das dienophile Verhalten des nur kurzlebigen Kohlenwasserstoffs aufgezeigt. Zum Unterschied von Dehydrobenzol enthalten die niedergliedrigen Cycloalkine eine echte Acetylenbindung. Sie sind ebenfalls kurzlebig; das Cyclohexin tetramerisiert sich über sein nicht-isolierbares Cyclobutadien-Derivat.

---

[43] G. Wittig and U. Mayer, Chem. Ber. *96*, 329 and 342 (1963).

ACTUALITAS

International Cell Research Organization (ICRO)

1. *Training Courses.* One of the main activities of ICRO is the organization of training courses on topics of high novelty and on modern techniques in cellular and molecular biology: Principles and techniques of tissue and organ culture; Genetics and Physiology of Bacterial viruses; Energy transducing systems on the sub-cellular level; Methods in mammalian cytogenetics; Membrane Biophysics; DNA-RNA Hybridization; Biogenesis of Mitochondria; Embryology and Epigenetics; Interaction between Animal Viruses and host cells, application of computers to experimental work in biology and chemistry; Methods in molecular biology, etc. The courses generally last 3–5 weeks, and include 16–20 young participants (sometimes more). The ICRO courses are fully international, both the teaching staff and the participants coming from the largest possible number of countries.

2. *The Problem of Developing Countries.* Most of the past ICRO courses have been organizing in European countries – east and west – but the demand from developing countries is increasing steadily. ICRO activities in developing countries may tend to give preference to topics of potential economic usefulness, such as applied microbiology, microbial protein production, fermentation industries, soil microbiology, plant genetics, etc.

Inquiries for more information should be addressed to: Dr. Adam Kepes, International Cell Research Organization, c/o Unesco – AVS, Place de Fontenoy, 75 Paris 7e, France.