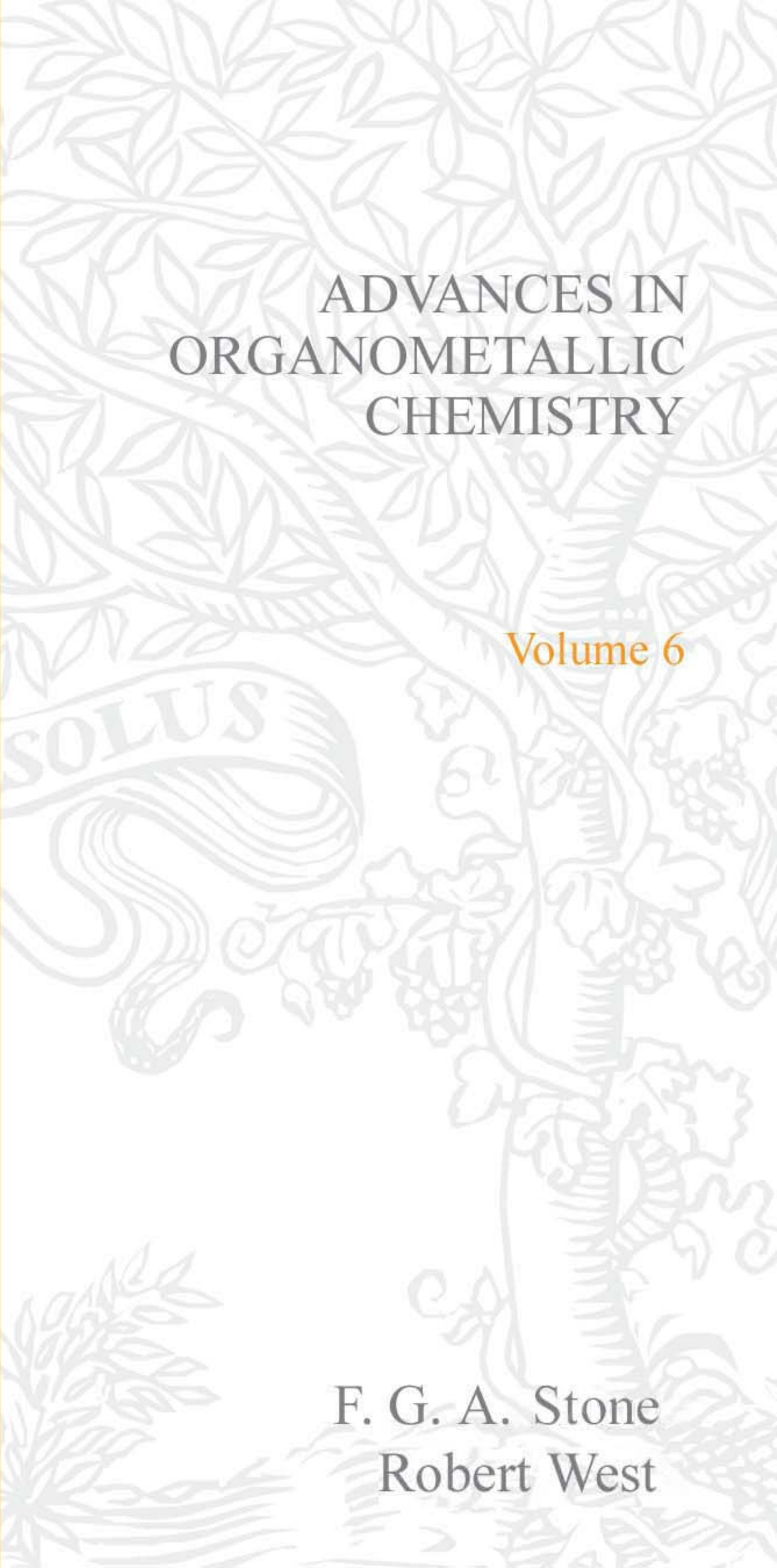

ADVANCES IN ORGANOMETALLIC CHEMISTRY

Volume 6

F. G. A. Stone
Robert West

Advances in

ORGANOMETALLIC CHEMISTRY

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Advances in ORGANOMETALLIC CHEMISTRY

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Preface

In the four years since the first volume of this serial publication appeared organometallic chemistry has continued the very rapid development which began some fifteen years ago. A continuing concern of the editors is how to make *Advances in Organometallic Chemistry* better serve the changing needs of this field.

As a relatively young discipline, organometallic chemistry is fortunate in that many of the people who pioneered this field of endeavor are still actively contributing to it. Thus we have available to us a priceless opportunity to learn at first hand from these distinguished chemists something of what will be the "early history" of the field. Beginning with this volume, we plan to include brief introductory chapters of a personal and historical nature by scientists who have contributed greatly to organometallic chemistry. These essays will provide a first-hand record of the circumstances leading up to the more important discoveries which have shaped the field, and may also give insight into the research philosophy and methodology of the most important contributors.

We hope that these historical chapters will be of interest both to present and future organometallic chemists, and so may give this publication a lasting value beyond that of even most authoritative reviews.

F. G. A. STONE
ROBERT WEST

November, 1967

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A Forty Years' Stroll through the Realms of Organometallic Chemistry

KARL ZIEGLER

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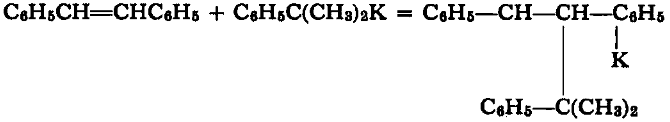
The idea to write this article was suggested to me by my colleague R. West, Madison, Wisconsin. He wrote to me: "Beginning with this volume, we would like to include ... an essay of a personal and historical nature by a scientist who has contributed to organometallic chemistry."

I have indeed done some work on metal alkyls, but as a matter of fact I am not a very enthusiastic writer, except, from time to time, for original publications of new experimental findings in a form as complete as possible under any given circumstances. Nevertheless there have been some occasions during recent years to write articles "of a more personal and historical nature" (*31*, *33–36*). Would it not involve too many recurrences and might it not lead to the impression for all readers of former articles of mine that "this man now is telling nearly the same over and over again"? There is no doubt that the focus of many researches initiated by me has now entirely moved on, partly to the best of my own former co-workers, partly to many capable authors all over the world. Will this not lower the value of such an article?

However, I do not want to overestimate the number of potential readers of this article who may have read earlier articles by me. Especially for readers belonging to the younger generation, I will begin this article as if it were the result of an interview: "Professor Ziegler, you have now been active in the field of organometallics for exactly 43 years and you have opened up some new areas of that field and found some technical uses for organometallic compounds. Can you tell us: what were, in your personal opinion of today, the most impressive individual experiments or observations having the widest consequences for your later work?" In an article of limited size, the answer to such a question from a fictitious interviewer cannot be anything else but a series of spotlights on single discoveries.

I

I will start with a certain moment in one of the last days of November 1927, when Bähr and I (*37*) observed that the deep red color of phenylisopropylpotassium in ether rapidly changed to a deep yellow on addition of stilbene. This indicated that—unexpectedly—the potassium compound had added to the stilbene



$$C_6H_5CH{=}CHC_6H_5 + C_6H_5C(CH_3)_2K = C_6H_5{-}\underset{\substack{|\\ C_6H_5{-}C(CH_3)_2}}{CH}{-}\underset{\substack{|\\ K}}{CH}{-}C_6H_5$$

This represented the discovery of the first addition of an organometallic (organoalkali) compound to a C=C double bond. The organopotassium compound used had at that time been known for only 4 years. It was found by the author and Schnell (*46*) as the result of a systematic search for the simplest ether to be split by an alkali metal according to the equation

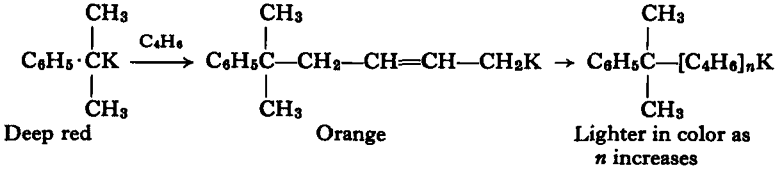
$$ROR' + 2\,M = RM + MOR'$$
$$M = \text{alkali metal}$$

We had discovered this reaction earlier using an ether of rather more complicated structure.

II

The 1:1 addition of an organometallic compound to a double bond certainly did not attract particular attention at the time, even though the reactivity demonstrated exceeded that of the well-known Grignard compounds. Even more significant was the finding that with suitable components the reaction could be repeated again and again. Given that the first 1:1 addition takes place, it might seem surprising that such repetitive reaction should not be possible for any two components. However, we found that the so-called "stepwise organometallic synthesis" could only be realized with a limited number of alkali alkyls and only a few ("activated") olefinic hydrocarbons, notably butadiene, its homologs, and styrene (*26*, *40*, *43*).

The decisive experiments: By adding more and more butadiene to the deeply red-colored solution of phenylisopropylpotassium the color rapidly changes, with the first mole of butadiene, to a light orange, and with more butadiene passing over to paler and paler yellows.



$$C_6H_5\cdot\overset{CH_3}{\underset{CH_3}{C}}K \xrightarrow{C_4H_6} C_6H_5\overset{CH_3}{\underset{CH_3}{C}}{-}CH_2{-}CH{=}CH{-}CH_2K \rightarrow C_6H_5\overset{CH_3}{\underset{CH_3}{C}}{-}[C_4H_6]_nK$$

Deep red — Orange — Lighter in color as *n* increases

In contrast, colorless solutions of lithium alkyls in ether turn yellow with butadiene, the color passing through a maximum and changing to lighter yellow with more and more butadiene. In this way (and of course by many other observations) the occurrence of stepwise organometallic syntheses was indicated.

$$C_4H_9Li \xrightarrow{C_4H_6} C_4H_9{-}CH_2{-}CH{=}CH{-}CH_2{-}Li \rightarrow C_4H_9{-}(C_4H_6)_nLi$$

Colorless — Strong yellow — Paler yellow as *n* increases

It is obvious that these old experiments of ours are the prototypes of recent revivals of a type of reactions concerned with the so-called "living polymers" (*16*, *17*). It was apparent to us at that early time (1930–1935) that in our examples the chains were able to grow so long as nonconsumed monomer was still present. Moreover, growth stopped as soon as all the monomer had added stepwise to the active (organometallic) end, but could be revived with more monomer, the molecules eventually "dying" when the organometallic ends were destroyed. Recently, theories have been developed to account for these observations and experimental techniques have been considerably improved. In this way remarkable progress has been achieved by younger colleagues. See Th. L. Brown (*1*).

III

Now I should like to recall a day—its date is not exactly known—in 1930, spent in the laboratory at Heidelberg studying an experiment so primitive, and in today's context so commonplace, that some readers may be surprised to see it appear here in a collection of those experiments which were the most important for me. On that day my co-worker H. Colonius, upon my wish, brought together butyl halides and lithium chips in various chemically indifferent solvents and found that butyllithium formed in all cases investigated, the optimum yield being attained in benzene and with butyl chloride (*38*). The generality of the reaction [also in the combination of bromobenzene with lithium in (*38*, *39*)] soon became evident. With this discovery Grignard techniques were extended to organolithium compounds.

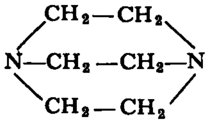
The lithium compounds themselves had then been known for 13 years (*14*), but lacked an easy method of preparation. Developments from 1930 on proved, as had happened 25 years earlier after the discovery of the Grignard reaction, what great progress can be made, and how large an extension of an area of research can occur as soon as a new synthetic tool of great reactivity becomes easily accessible.

There were two reasons why Colonius and I were favored to be the first to hit on this very simple reaction in 1930. First, it was just then that lithium was first used for certain technical applications (e.g., as an alloy component for bearing metals), and therefore became easily accessible at a tolerable price. Second, the experiments described under II above had induced us to study the kinetics of certain lithium alkyl reactions. From these we had found that ethyllithium and alkyl halides, especially chlorides, essentially do not react with each other. Therefore the course of our decisive experiments had been predictable (*38*). This impetus had been necessary to overcome the prejudice about the Wurtz synthesis originating from the textbooks.

IV

The center of activity in the field of organolithium compounds soon shifted from Heidelberg, where their easy availability had first been discovered. I shall have to return later to some former developments of my own. The spotlight shifts for some time to other places and authors. The observation that organolithium compounds often function as "super Grignards," their ability to metallate other compounds, the famous lithium–halogen exchange (Gilman, Wittig), the role organolithium compounds play in aryne chemistry, are among some of the most striking developments in this field. But to come back to my own story: The next most important experiment was the discovery of the equivalency of ethylene and butadiene with regard to the "stepwise organometallic synthesis" or to the "growth reaction."

During my time in Heidelberg, that is, earlier than 1936, we found, in the course of experiments to distill butyllithium under high vacuum, that the lithium alkyl smoothly decomposed into lithium hydride and 1-butene. In carrying out similar experiments with ethyllithium immediately after the war, Gellert and I (*41*) found firstly that the lower lithium alkyls were distillable under suitable conditions, and secondly that 1-butene was formed from ethylene in contact with ethyllithium. From this observation it was a very short step to discover the "stepwise organometallic synthesis" (*42*) occurring when ethyllithium or its homologs were heated with ethylene under pressure, especially in ether as a solvent. Quite recently this old reaction found by Gellert and myself in 1950 has stimulated most remarkable research by Eberhardt, (*4*, *5*) on reactions between lithium alkyls, ethylene, and aromatic hydrocarbons in the presence of certain amines, e.g.,



as catalysts, the results going far beyond our original findings. Gellert and I added polyformaldehyde to the reaction products of propyllithium and butyllithium with ethylene, and obtained the series of even- and uneven-membered straight-chain aliphatic alcohols from hexyl to dodecyl and from heptyl to tridecyl alcohols, respectively. Without any doubt, simple autoxidation of our reaction products would also have led us to straight-chain primary alcohols (with one carbon atom less on an average). Not much more than 10 years later, compounds of the same type were manufactured in a similar way in amounts of several thousands of metric tons at Lake Charles, Louisiana (*12*), the only difference being that alkyl compounds of aluminum were used instead of those of lithium. From these observations of purely academic interest it became obvious that organometallic compounds could have potential value for the synthesis of straight-chain aliphatic compounds from ethylene. But nobody could have imagined that this would culminate, 4 to 5 years later, in a new process for making linear extremely long chains of plasticlike polyethylene, and to a kind of revolution in polymerization techniques.

V

The spotlight falls next on a solution of lithium aluminum hydride in ether which Gellert, in my institute, heated with ethylene under pressure (*27*). He obtained a mixture of pure α-olefins, from butene up to tetradecene.

$$n(C_2H_4) = (C_2H_4)_n \qquad n = 2 \text{ to about } 7$$

This successful experiment represented the last attempt to find a polymerization, or better oligomerization, of ethylene by heating it together with lithium hydride. Since we had already observed the decomposition of lithium alkyls into olefins and lithium hydride

$$C_nH_{2n+1}Li \rightarrow C_nH_{2n} + LiH$$

and also the growth reaction

$$C_nH_{2n+1}Li + C_2H_4 = C_nH_{2n+1}\text{—}CH_2\text{—}CH_2\text{—}Li$$

nothing more was necessary but to write the → arrow in the first equation as a double arrow $\leftrightarrows$ of an equilibrium in order to come to the conclusion that the predicted catalysis of the oligomerization of ethylene by lithium hydride should exist (*30*). Actually we did not discover it then—at least not as a smooth and practicable reaction—but with $LiAlH_4$ the whole thing worked quite nicely. I often have mentioned that this experiment solved a crisis in our whole work, because in elucidating the mechanism of this smooth catalysis we discovered the following reactions (*28*):

$$LiAlH_4 + 4\ C_nH_{2n} = LiAl(C_nH_{2n+1})_4 \qquad (1)$$

$$AlH_3 + 3\ C_nH_{2n} = Al(C_nH_{2n+1})_3 \qquad (2)$$

$$Al(C_nH_{2n+1})_3 \rightleftarrows HAl(C_nH_{2n+1})_2 + C_nH_{2n} \qquad (3)$$

$$\begin{tikzcd} R\text{—al} + C_2H_4 = R\text{—}CH_2\text{—}CH_2\text{—al} \arrow[d, "\text{more } C_2H_4"] \\ R\text{—}(CH_2\text{—}CH_2)_n\text{al} \end{tikzcd} \qquad (4)$$

$$(\tfrac{1}{3}Al = al)$$

The most astonishing of these new results was the discovery of reaction (4), that is, the existence of our well-known stepwise organometallic synthesis, our so-called "growth" reaction, also in the field of the aluminum chemistry. I think nobody would have predicted this analogy between corresponding compounds of alkali metals and of aluminum. It should be understood that obviously the monovalent group R_2Al ($R = C_nH_{2n+1}$ and the like) is behaving similarly to an alkali metal, especially lithium. Of course, the special reactions arising from this analogy are then characteristic for all three Al—C bonds of the aluminum trialkyls as long as they exist as such in the reaction mixture. Consequently, the reactivity of the aluminum trialkyls changes considerably when passing over to the types $XAlR_2$ and X_2AlR wherein X may be neither a hydrogen atom nor an organic group. (*29*).

VI

Reaction (4) suggested a rather attractive synthesis of higher primary aliphatic compounds from ethylene, especially the synthesis of higher fatty alcohols by autoxidation (*50*), these alcohols being desirable for many purposes. It was soon found that in this case all three Al—C bonds undergo autoxidation with oxygen to form alcoholates. However, oxidation does not occur with the same ease for all three bonds, the third presenting some difficulties. But nevertheless the synthesis of fatty alcohols through aluminum alkyls and our growth reaction seemed to be a practical fatty alcohol synthesis, provided the aluminum alkyls were easily available. When we discovered the reactions (1) to (4) and some others which seemed to be of potential interest, simple syntheses for aluminum alkyls did not yet exist. Here one of the few points arises where our own discoveries forced us to look for the solution of another chemical problem in order to make the results of our own earlier work bear fruit.

VII

The so-called "direct synthesis" of aluminum alkyls (*49*), particularly those of triisobutylaluminum and triethylaluminum, by adding together aluminum metal, hydrogen, and the corresponding olefin were found by a systematic but not very long search. The process is now, I believe, common knowledge.

$$Al + 1\tfrac{1}{2}\ H_2 + 3\ CH_2{=}C(CH_3)_2 = Al(CH_2{-}CH(CH_3)_2)_3$$

$$Al + 1\tfrac{1}{2}\ H_2 + 3\ C_2H_4 = Al(C_2H_5)_3$$

Aluminum trialkyls dissolve aluminum with hydrogen under pressure affording dialkylaluminum hydrides. The reaction products add to olefins in the next step (b) to give 50% more aluminum alkyl than the amount originally employed, a sequence which finally leads to any desired amount.

$$\text{(a)} \quad 2\ Al(C_nH_{2n+1})_3 + 3\ H_2 = 3\ HAl(C_nH_{2n+1})_2$$

$$\text{(b)} \quad 3HAl(C_nH_{2n+1})_2 + 3\ C_nH_{2n} = 3\ Al(C_nH_{2n+1})_3$$

Reactions (a) and (b) may be combined into one operation (e.g., for triisobutylaluminum), or may be carried out in separate steps [e.g., for $Al(C_2H_5)_3$].

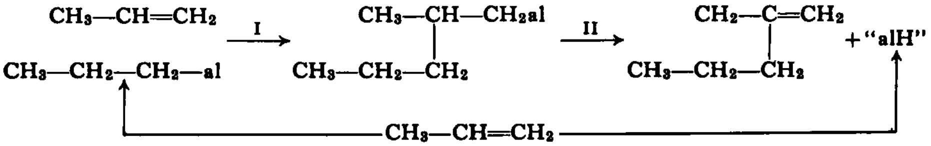
With this process the groundwork for the technical synthesis of fatty alcohols from ethylene had been laid, and indeed a few years later—not very long for a detailed technical development—there existed three good-sized plants for making such products: one operating since 1962 in Lake Charles, Louisiana (*12*), one since 1965 in Pasadena, Texas (*2*), and one in operation since 1964 in Germany (*25*). From the economic point of view the low equivalent of aluminum, namely 9, is a great advantage. Moreover, it is essential that alumina or salts thereof should find good markets.

VIII

Let us review our story: It began with the addition of a few grams of stilbene to some milliliters of phenylisopropylpotassium in ether, and it ended—up to this point—with the transformation of ethylene into straight-chain aliphatic compounds of medium-sized length on an industrial scale. But the essential part of the chemistry involved in the two so entirely different reactions was the same: the addition of metal–carbon bonds to C═C double bonds, which means nothing else but a widening of the old principle of the organometallic synthesis. Soon after our first observation with stilbene, butadiene played an essential role in our work. I will have to come back to butadiene later during this chapter. But at this point some relations between our new chemistry and its next homolog isoprene fit better into the sequence of my story.

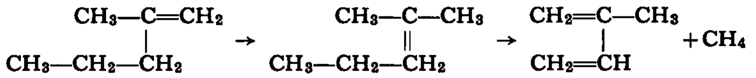
Isoprene has a very close relation to processes which we call catalytic organometallic syntheses and which are possible on the basis of additions of organometallic compounds to C═C double bonds. We discovered this very useful principle when Dr. Gellert heated to 150–200° C some grams of tripropylaluminum dissolved in some hundreds of grams of propylene under pressure. During several hours, the pressure dropped from about 200 to only a few atmospheres. We distilled off the reaction product directly from the autoclave, added to the remaining small quantity of the organo-aluminum compound in the autoclave a new portion of propylene, and repeated these operations again and again, each time with the same small sample of the aluminum compound as initiator of the transformation of the propylene. Provided the propylene was pure enough and contained no oxygen or moisture, the whole procedure could be repeated many times without change. The distillate was practically pure 2-methyl-1-pentene (*51*).

The mechanism of the reaction was easy to explain.



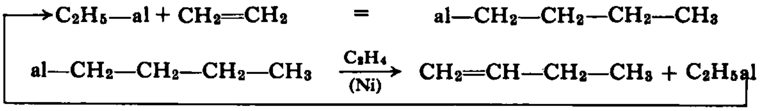
The organometallic synthesis of step I is the decisive reaction step. But contrary to an analogous Grignard reaction (e.g., $CH_3CH_2CHO + BrMgC_3H_7$) the metal does not migrate but is conserved as "alH" [$=(C_3H_7)_2AlH$] and immediately retransformed to propylaluminum with propylene. The reaction takes place in a very selective way, and largely in one direction. It is clear that there are many variations of such a catalytic organometallic synthesis. The oligomerization of ethylene—which we looked for and eventually found, as I mentioned above, not only with $LiAlH_4$ but also with $Al(C_2H_5)_3$—belongs to the same type of reaction. These are all homogeneously catalyzed processes in their purest form, illustrated in a particularly impressive way in the conversion of propylene to 2-methyl-1-pentene.

That this latter reaction has become the basis of a very large isoprene production is not to be credited to my institute but to the cooperation between the two American companies, Goodyear Tire & Rubber Co. and Scientific Design Co. These two firms added to our dimerization of propylene the rearrangement of the 2-methyl-1-pentene into 2-methyl-2-pentene and then cracked this product to give isoprene and methane (*10*).



IX

I hope the reader will not be too disappointed that he had to accompany me through some fields of small-molecule or at the most "middle-sized" molecule chemistry and has not up to here read a word about macromolecular chemistry, in which according to a quite general opinion, well known to me, I am said to be a special expert. As a matter of fact, except for my former activity in the field of polybutadiene and polystyrene chemistry which touched the problems later on referred to as "living polymers," I was never closely connected with macromolecular chemistry. But my own life contained some surprises, and I believe the most astonishing event was my sudden confrontation with macromolecules in consequence of an experiment which led from monomeric ethylene to its lowest possible "polymer," the dimer 1-butene. At the end of 1952 it happened that my co-worker Holzkamp (*47*) was duplicating one of our best-known experiments, the addition of ethylene to ethylaluminum. The reaction no longer gave a trace of a "growth" product as it should have, but instead quantitatively transformed ethylene into 1-butene, the organoaluminum compound functioning purely as a catalyst. After a strenuous investigation we found that an extremely small trace of metallic nickel caused this change in the course of the reaction. The nickel strongly catalyzes a so-called replacement reaction of 1-butene from butylaluminum by ethylene.



$$C_2H_5\text{—al} + CH_2\text{=}CH_2 \quad = \quad \text{al—}CH_2\text{—}CH_2\text{—}CH_2\text{—}CH_3$$

$$\text{al—}CH_2\text{—}CH_2\text{—}CH_2\text{—}CH_3 \xrightarrow[(Ni)]{C_2H_4} CH_2\text{=}CH\text{—}CH_2\text{—}CH_3 + C_2H_5\text{al}$$

No chain longer than that of a C_4 hydrocarbon is found because the C_4 chain is cleaved off immediately after its growth on the aluminum.

This discovery happened just as we had finished a series of experiments attempting to let our growth reaction proceed up to the addition of 1000 and more molecules of ethylene. A synthesis of such very long aluminum alkyls would have involved a new method of making a strictly linear "polyethylene," since the molecular weight of the commercial polyethylene was said to lie in the region of 30,000–50,000. Our attempts had not been successful. We had reached molecular weights of perhaps a few thousand. Obviously also in these experiments a replacement reaction

$$\ldots\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—al} + C_2H_4 = \ldots CH_2\text{—}CH_2\text{—}CH\text{=}CH_2 + C_2H_5\text{al}$$

caused a "chain transfer" and hindered the chain growth. The reader will recognize that the idea of developing a new process for polyethylene arose logically from our growth reaction. This process worked between 100 and 200 atm, about one-tenth of the pressure of the conventional process. To have reduced the required pressure by so much appeared to be quite desirable at that time.

Now we were suddenly confronted with the fact that there were trace catalysts like nickel catalyzing the chain transfer of the growth reaction at its very earliest stage. Might not perhaps other trace catalysts also have caused too early chain transfer, in our former unsuccessful experiments to extend the growth reaction into the region of a true polyethylene ? Thus Holzkamp and I started, together with Breil, a systematic search for possible substances having effects similar to nickel. The result was the discovery of the new, extremely active polymerization catalysts (*33*) to which my name has been associated through the politeness of my colleague Natta, (*48*).

X

At this point the chemistry of organometallic compounds and of macromolecules coalesced in a new, surprising and unexpected phenomenon. What we actually did was nothing more than to add small amounts of compounds, including halides of transition metals, to triethylaluminum in order to see what happened to ethylene in the presence of these mixtures. We expected that in some cases butene would be formed, in others our normal "growth products." The most striking result of this series of experiments was when we found for the first time, instead of one of the expected results, an autoclave filled with a solid cake of snowwhite polyethylene, originating from a mixture of ethylene, zirconium triacetylacetonate, and triethylaluminum. The same catalyst tested the next day with propylene did not give a corresponding result. However, polypropylene was discovered a little later after the chlorides of titanium had been recognized as components for much more powerful polymerization catalysts. Catalysts of this type polymerized ethylene at atmospheric pressure and even below. Very soon my institute in Mülheim-Ruhr was no longer alone in this field, with its knowledge of new polymerization catalysts. There was a rush (*9*) of others into this area which today, more than 10 years later, seems not yet to be entirely finished.

During the past decade a great number of papers and some books have been published on our catalysts, and on the new polymers now available by this new extremely varied aid to macromolecular chemistry. It will be sufficient here to mention some of the more impressive facts.

(1) *Catalyst Components.* The components for the "organometallic mixed catalysts"[1] are suitable compounds of practically any transition metal of Groups IV to VIII, on the one hand, and compounds with at least one C—M bond, M being a metal of Groups I–III (especially aluminum!) and some others, on the other hand. Instead of organometallic compounds some other products can be used, for instance, hydrides. In such cases true metal alkyls are very probably formed during the polymerization process. Since not only the special combination of the two components but also their

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[1] This is a literal translation for my original designation in my language "Metallorganische Mischkatalysatoren"; the expression "organometallic complex catalysts" is younger and was suggested by others after our discovery.

ratio, the solvent used, and many other factors influence the activity of the catalysts, the direction of the polymerization and the average length of the polymer chain, it was indeed an extremely wide field which was opened up by that Mülheim discovery in 1953/54. Of course, the discoverer of such a new province of polymer chemistry cannot expect, and did not expect, that all imaginable combinations of such components would work in every case and for all monomers, but certainly he has the right to claim the conception of the rule: Take any organometallic, combine it with a compound of a transition metal, and you will have a good chance of finding a suitable catalyst for your special polymerization problem. This instruction has resulted in a considerable narrowing of the necessary research of subsequent workers.

(2) *Monomers and Products of their Polymerization.* The most important discovery was no doubt that of the "isotaxy" (ataxy, syndiotaxy, or quite generally speaking stereospecificity) of the poly[mono-substituted ethylenes] by Natta (*13*). Isotactic polypropylene, poly-α-butene, and poly[4-methyl-1-pentene] are plastics of growing importance, with combinations of special properties never attained by any former plastic. Other subsequent developments were those of the ethylene-propylene copolymers and the ethylene-propylene terpolymers, manufactured with vanadium halide organoaluminum catalysts. The former, a high-grade rubber of entirely saturated character, the latter a similar product, but with copolymerized small quantities of diolefins like dicyclopentadiene; 1,6-octadiene; 1,5-cyclooctadiene; and 4,7,8,9-tetrahydroindene; and containing some residual double bonds in the molecules facilitating the vulcanization of the materials. This list may be completed by mentioning the stereospecific polymerization of the conjugated dienes, especially poly[*cis*-1,4-butadiene] (in Germany "Stereokautschuk"), poly[*cis*-1,4-isoprene] (synthetic "natural" rubber) and the corresponding poly-*trans*-1,4- and poly-1,2-products. Here recent developments have quite obviously transgressed far beyond organometallic chemistry, properly speaking, and have moved over entirely to the plastic and rubber specialists.[2]

XI

Let us return from these more industrial applications of the new group of catalysts containing metal–carbon bonds to more specific organometallic

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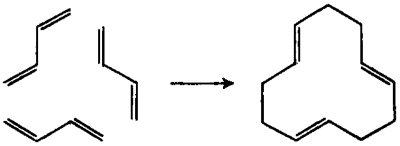
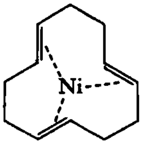
[2] The existing literature is too extensive to be cited here. Some citations will be found in Ziegler (*31*, *33–35*).

compounds. Without any doubt the discovery of the new polymerization catalysts had constituted a kind of breakthrough in a rather continuous development of organometallic chemistry. In the light of modern valence theories all that I had found up to this breakthrough can be condensed into the single letter σ or word "sigma." In all reactions metal–carbon "sigma bonds" exclusively were involved. In other words: I always stayed on the level of quite "normal," conventional, or—let us even say—antiquated chemistry. Of course I knew quite well that since 1950 with the discovery of ferrocene a new ,"modern" organometallic chemistry was rapidly growing up, characterized by the presence of pi-bonds in the molecules. To bring the problem to its most condensed form I would like to say: the breakthrough in my work was the bringing together of the "sigma" and the "pi". This means that in my opinion both sigma and pi bonds between carbon and metal atoms play most important and decisive roles in the mechanisms of the new polymerization processes, in one case predominantly the one type, in another case the other type, or even both. I will not go into details; many other authors have already done so; see f.i. (*6*).[3] More recently, a series of remarkable new findings in the chemistry of organometallic π-compounds has arisen under the leadership of Günther Wilke, at the institute at which the author of this article has now spent nearly 25 years of his life.

The starting point of this development was the discovery by Wilke (*18*) of the synthesis of cyclododecatriene-1,5,9 from butadiene using typical organometallic mixed catalysts.



This new hydrocarbon itself gave a very interesting typical new π-complex with nickel (*19*), which was crystalline and volatile.



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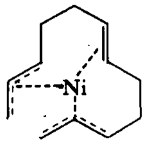
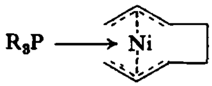
[3] See articles in previous volumes of this series: G. N. Schrauzer (Vol. 2); Heck (Vol. 4); Aguiló (Vol. 5); and Chalk and Harrod, this volume, p. 119.

The elucidation of the mechanisms (*21*) of the cyclotrimerization and the corresponding cyclodimerization led to other crystalline and well-defined intermediates of formulas A and B



(A)

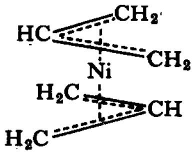


(B)

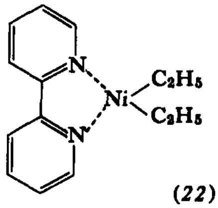
demonstrating the importance of metal π-complexes as intermediates of reactions catalyzed by transition metals.

The substance (A) was the first compound of a transition metal in which exclusively π-allyl groups were attached to the metal atom in addition to one double bond.

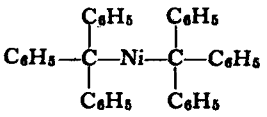
The second compound of this type was the very simple one, bis(π-allyl)-nickel (*20*).



The discovery of bis(π-allyl)nickel led to the recognition that most of the transition metals form such complexes in which exclusively allyl groups are attached to the central metal atom (*24*).[4] Further investigation demonstrated very clearly that in the transition allyl metal compounds both types of metal–carbon bonds, σ and π, play important roles, and that even differences in the participation of the two types of bonds are possible. By a rather peculiar



(*22*)



$C_6H_5-\overset{C_6H_5}{\underset{C_6H_5}{C}}-Ni-\overset{C_6H_5}{\underset{C_6H_5}{C}}-C_6H_5$

(*23*)

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[4] Partial allyl compounds like π-allylpalladium chloride (*15*), or π-allylcobalt tricarbonyl (7) had been discovered earlier by other authors not related to the author's institute.

development the study of such π-complexes finally also led to the discovery of some new compounds with typical transition metal–carbon sigma bonds—usually believed to be unstable—for instance the two last formulas on the opposite page.

XII

I began this article with a single experiment of my own and was led to discuss in my essay, some results which I cannot count as my own personal chemistry. My fictitious interviewer may now ask: "Is that your whole story, or is there anything else of some importance omitted, and in what field are you still active now?"

There were some additional observations in the field of the complex compounds of the aluminum alkyls, for instance, the discovery of $Na[AlEt_3F]$ and $NaF \cdot 2AlEt_3$ and many others, together with Köster and Lehmkuhl (*44*), and since these saltlike compounds have rather good electrolytical conductivities we came to study several electrolytical processes, using such complexes as electrolytes. Our first aim was to make extremely pure aluminum (*45*), an investigation which later has been continued by Doetzer (*3*) and extended to very pure gallium and indium. Our next aim was the electrolytical synthesis of metal alkyls. One leading idea was the attempt to extend the direct synthesis of aluminum alkyls by combining aluminum, olefins, and hydrogen to other metals. This direct synthesis proved to be a singular property of aluminum. But combined with an electrolysis such as

$$NaF \cdot 2\ AlEt_3 + \tfrac{3}{4}\ Pb + 3\ \text{faraday} = Al + NaF \cdot AlEt_3 + \tfrac{3}{4}\ PbEt_4$$

we would also have a similar synthesis of tetraethyllead, since then hydrogen and ethylene can be added to the aluminum to give triethylaluminum. This simple process did not work very successfully, and therefore all later efforts have been devoted to complexes like $NaAlEt_4$, which on electrolysis behave like a solution of sodium ethyl in triethylaluminum, according to an old idea of Hein *et al.* (*8*). The resynthesis of the ethylsodium aluminate is possible by adding sodium hydride and ethylene to the aluminum triethyl.

$$AlEt_3 + NaH + C_2H_4 = NaAlEt_4$$

Using electrolytes containing (besides other substances) this system, and using a mercury cathode for protecting the metal alkyls obtained at the anodes against the very active sodium, rather nicely working new electrolytical processes for making alkyl compounds of lead and other metals have been developed, essentially in collaboration with Lehmkuhl, Eisenbach, and Schäfer (*11*, *32*).

The essential problem for such applications of organoaluminum complex compounds in electrolytical processes is the recovery of sodium (or potassium) from their respective amalgams, or even for an electrolytical purification of these two metals themselves, if there would be any need for such processes. This question is more an economic than a chemical one, and therefore the author is often being asked what "success" he would expect from his intensive work in the electrochemical field. Here this essay touches, at its end, the personal philosophy of the author. What does "success" mean for a scientist? If you have had some success in any desirable direction, should you not allow yourself some work which perhaps is more a personal hobby than the beginning of a prospective new field? There were many difficulties to be overcome in the electrolytical work and finally we overcame them all. "We," that means the author together with H. Lehmkuhl, W. Grimme, E. Hüther, E. Lindner, H. Dislich, W.-R. Larbig, and E. Blanck. By no means have all our results yet been published, and normally a scientist should publish or be silent. But you will remember: I imagine myself confronted with a fictitious interviewer, and against the inquisitiveness of an interviewer there is no defense!

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Aliphatic Organopolysilanes

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I

INTRODUCTION

The organopolysilanes are those compounds containing at least one silicon–silicon bond and one silicon–carbon linkage. This review is mainly concerned with the chemistry of aliphatic derivatives of polysilanes. Consideration of aromatic organopolysilanes is excluded from this review except as far as they are used as intermediates for synthesis and their properties correlate with the aliphatic silicon–silicon compounds, because the aromatic organopolysilanes have recently been well reviewed elsewhere (*31*, *51*, *73*, *76a*, *212*). Physical properties of the polysilanes also are excluded from consideration except for spectral properties of ultraviolet absorption and nuclear magnetic resonance, since they are well summarized in earlier excellent reviews and texts (*8*, *34*, *35*, *51*, *131*, *132*).

The first member of this class of compounds, $(C_2H_5)_3SiSi(C_2H_5)_3$, was prepared by Friedel and Ladenburg in 1869 (*40*). Since then, until recently, only a limited number of alkyl derivatives of polysilanes (mostly hexaalkyldisilanes) have been synthesized and studied. The reason for this lack of interest for a long time seems to be 2-fold. First, the synthesis of well-defined organopolysilanes was not an easy task; starting materials, such as $Cl_3SiSiCl_3$ and, especially, higher perchloropolysilanes (*191*), were not readily available in large quantities, and convenient preparative methods of organopolysilanes other than hexaalkyldisilanes had not been established. Second, unlike the organopolysiloxanes, the organopolysilanes were not of practical interest because they lacked properties desirable for useful polymeric materials, including thermal and chemical stability (*141*).

During the past decade, however, significant advances have been made in the preparation and chemistry of aliphatic organopolysilanes. A large number of silicon–silicon compounds of various types (peralkylated, silicon-functional, and carbon-functional) have been prepared, and mechanisms of some of their reactions elucidated. It is hoped that this review will demonstrate how the chemistry of aliphatic organopolysilanes is unique as well as similar to that of organomonosilanes.

II

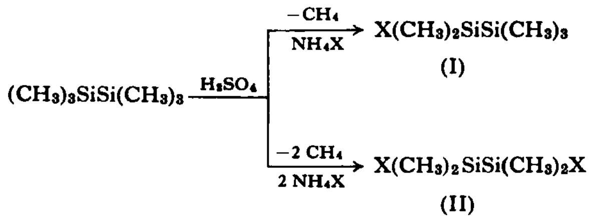
SILICON-FUNCTIONAL ORGANOPOLYSILANES

A. Silicon–Halogen Compounds

1. *Synthesis*

a. *Halogenodealkylation of Alkyl (mostly methyl) polysilanes.* This reaction is most conveniently used and is extensively applicable to preparation of various types of methylchloro- and/or methylfluoropolysilanes. It is subdivided into two types of reaction: (1) demethylation of methylpolysilanes with concentrated sulfuric acid followed by treatment with an ammonium halide, and (2) halogenodealkylation of alkylpolysilanes by hydrogen chloride, acyl chlorides, or alkyl bromides in the presence of anhydrous aluminum chloride.

The halogenodemethylation with sulfuric acid and ammonium chloride (or fluoride or, better, hydrogen fluoride) is most successfully applied to synthesis of chloro(or fluoro)pentamethyldisilane (I) and 1,2-dichloro(or difluoro)tetramethyldisilane (II) (*126*). The reaction of concentrated sulfuric acid with hexamethyldisilane at room temperature proceeds in two distinct steps: first, a heterogeneous but fast step, and second, a homogeneous but slow one. The first step corresponds to cleavage of one methyl from one silicon, while the second involves cleavage of the second methyl from another silicon. Therefore, treatment of the resulting sulfuric acid solution with an ammonium halide at the point either of the first or of the second end of methane evolution gives almost exclusively (I) or (II), respectively. Only a small percentage of the reaction gives cleavage of the silicon–silicon bond.



$$(CH_3)_3SiSi(CH_3)_3 \xrightarrow{H_2SO_4} \begin{cases} \xrightarrow[NH_4X]{-CH_4} X(CH_3)_2SiSi(CH_3)_3 \quad \text{(I)} \\ \xrightarrow[2\,NH_4X]{-2\,CH_4} X(CH_3)_2SiSi(CH_3)_2X \quad \text{(II)} \end{cases}$$

X = Cl or F

Demethylation by sulfuric acid can be successfully extended to certain organofunctional methyldisilanes. For instance, (chloromethyl)pentamethyldisilane easily undergoes demethylation under similar conditions to give 1-(chloromethyl)-2-chloro(or fluoro)tetramethyldisilane upon treatment with an ammonium halide, in good yield (*120*). Moreover, this method is still satisfactory for synthesis of 1,3-dichloro(or difluoro-)hexamethyltrisilane (III), which is obtainable in 40% (or 55%) yield from octamethyltrisilane (in this case, demethylation occurs concurrently at both the 1- and 3-silicon atoms, unlike the demethylation of hexamethyldisilane) (*102*, *106*, *107*).

$$(CH_3)_3SiSi(CH_3)_2Si(CH_3)_3 \xrightarrow[2.\ NH_4X]{1.\ H_2SO_4} X(CH_3)_2SiSi(CH_3)_2Si(CH_3)_2X$$

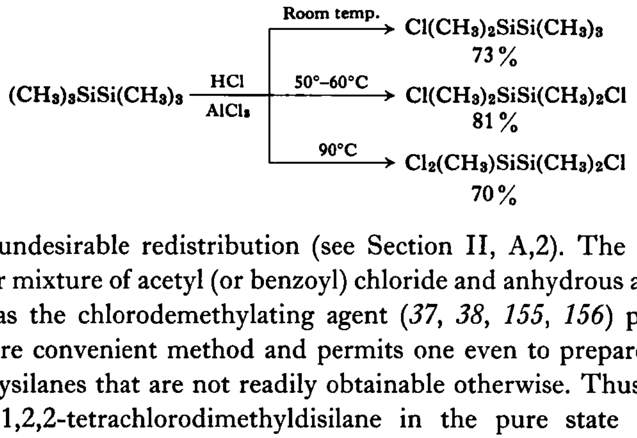
(III)

X = Cl or F

However, the method is no longer satisfactorily applicable to synthesis of higher polysilane derivatives because extensive cleavage of the silicon–silicon bond occurs and a mixture of isomeric halopolysilane derivatives that are inseparable by distillation is formed. For example, the reaction of decamethyltetrasilane with sulfuric acid and treatment with ammonium hydrogen fluoride leads to the formation of several fluoro derivatives of lower silanes in addition to a mixture of two isomeric difluorooctamethyltetrasilanes, $F[(CH_3)_2Si]_4F$ and $F(CH_3)_2SiSi(CH_3)_2Si(CH_3)(F)Si(CH_3)_3$, in approximately 1:1 ratio (*106*).

Highly branched, permethylated polysilanes are sometimes quite resistant to concentrated sulfuric acid. Thus, tetrakis(trimethylsilyl)silane does not undergo any change up to 100° C. At higher temperature, explosive oxidative cleavage of the silicon–silicon bond has been observed to occur (*49*).

The chlorodemethylation with anhydrous hydrogen chloride or with acetyl (or benzoyl) chloride in the presence of anhydrous aluminum chloride affords another widely applicable method for preparation of methylchlorodisilanes and polysilanes. Thus, by bubbling dry hydrogen chloride through hexamethyldisilane containing a catalytic amount of anhydrous aluminum chloride, chloropentamethyldisilane, 1,2-dichlorotetramethyldisilane, or 1,1,2-trichlorotrimethyldisilane can be obtained selectively, depending upon the reaction conditions (*155*, *156*). Deactivation of the catalyst by adding acetone is necessary before isolation of the products by distillation in order to avoid undesirable redistribution (see Section II, A,2). The use of an equimolar mixture of acetyl (or benzoyl) chloride and anhydrous aluminum chloride as the chlorodemethylating agent (*37*, *38*, *155*, *156*) provides a much more convenient method and permits one even to prepare methylchloropolysilanes that are not readily obtainable otherwise. Thus, one can obtain 1,1,2,2-tetrachlorodimethyldisilane in the pure state from the "disilane fraction,"[1] 1-chloroheptamethyltrisilane, 1,3-dichlorohexamethyltrisilane, and 1,2,3-trichloropentamethyltrisilane in good yield from octamethyltrisilane, and tetrakis(chlorodimethylsilyl)silane from the corresponding permethylated derivative (*155*, *156*).



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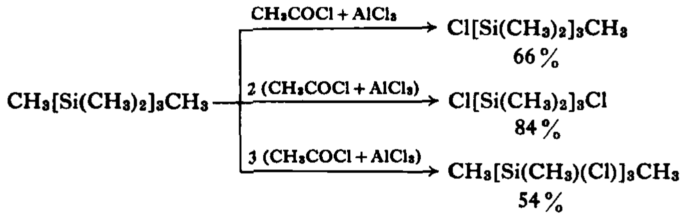
[1] The disilane fraction refers to a fraction boiling over the range of about 150°–160° C which is obtained by fractionation of the higher boiling fraction of methylchlorosilanes produced by the so-called "direct synthesis" (*141*, *214*). It is composed mainly of 1,1,2-trichlorotrimethyldisilane and 1,1,2,2-tetrachlorodimethyldisilane, somewhat contaminated by siloxanes (*6*, *22*, *27*, *114*, *125*, *126*, *134*).



$$CH_3[Si(CH_3)_2]_3CH_3 \xrightarrow{CH_3COCl + AlCl_3} Cl[Si(CH_3)_2]_3CH_3 \quad 66\%$$

$$CH_3[Si(CH_3)_2]_3CH_3 \xrightarrow{2\,(CH_3COCl + AlCl_3)} Cl[Si(CH_3)_2]_3Cl \quad 84\%$$

$$CH_3[Si(CH_3)_2]_3CH_3 \xrightarrow{3\,(CH_3COCl + AlCl_3)} CH_3[Si(CH_3)(Cl)]_3CH_3 \quad 54\%$$

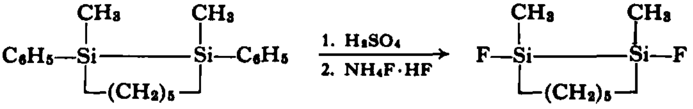
$$[(CH_3)_3Si]_4Si \xrightarrow{\text{Excess } CH_3COCl + AlCl_3} [Cl(CH_3)_2Si]_4Si$$

One example has been reported of aluminum chloride-catalyzed bromodeethylation using isopropyl bromide (*197*). By this method, bromopentaethyldisilane is obtained in 72% yield from hexaethyldisilane.

b. *Halogenodephenylation of Phenylmethylpolysilanes.* Because the phenyl–silicon linkage is much more susceptible to cleavage by electrophilic reagents, halogenodephenylation of phenylmethylpolysilanes proceeds smoothly under mild conditions where demethylation does not occur. This method, therefore, is often useful for synthesis of certain chloro(or fluoro)-methylpolysilanes that are not obtainable by the method described above. It also involves the use of either a combination of concentrated sulfuric acid and ammonium chloride (or ammonium hydrogen fluoride) or anhydrous hydrogen chloride with aluminum chloride catalyst.

Thus, the action of sulfuric acid on 1,1-diphenyltetramethyldisilane below 10° C followed by treatment with ammonium chloride gives 1,1-dichlorotetramethyldisilane in 60% yield (*116*). Similarly, dephenylation by sulfuric acid of 1,2-diphenyl-1,2-dimethyl-1,2-disilacycloheptane gives, after treatment with ammonium hydrogen fluoride, 1,2-difluoro-1,2-dimethyl-1,2-disilacycloheptane in 81% yield (*112*, *124*), whereas this product can not advantageously be obtained from the 1,1,2,2-tetramethyl compound (see Section III, C,4).

$$(C_6H_5)_2(CH_3)SiSi(CH_3)_3 \xrightarrow[2.\ NH_4Cl]{1.\ H_2SO_4} Cl_2(CH_3)SiSi(CH_3)_3$$

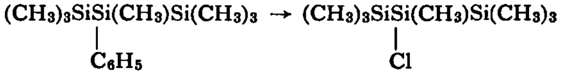


$$C_6H_5\!-\!\overset{CH_3}{Si}\!-\!\overset{CH_3}{Si}\!-\!C_6H_5\ \text{with}\ (CH_2)_5 \xrightarrow[2.\ NH_4F\cdot HF]{1.\ H_2SO_4} F\!-\!\overset{CH_3}{Si}\!-\!\overset{CH_3}{Si}\!-\!F\ \text{with}\ (CH_2)_5$$

Chlorodephenylation with hydrogen chloride in the presence of aluminum chloride is carried out at room temperature either in chloroform or in benzene solution. The reaction in chloroform proceeds with cleavage of only one phenyl from each silicon atom even if it bears more than one phenyl group (*116*). By means of this method, 1- and 2-chloroheptamethyltrisilane, 1,4-dichlorooctamethyltetrasilane, and 1,5-dichlorodecamethylpentasilane are prepared from the corresponding phenyl derivatives, and 1-chloro-1-phenyltetramethyldisilane is obtained from 1,1-diphenyltetramethyldisilane.

$$(C_6H_5)(CH_3)_2SiSi(CH_3)_2Si(CH_3)_3 \rightarrow Cl(CH_3)_2SiSi(CH_3)_2Si(CH_3)_3$$

53% (*107*)



$$(CH_3)_3Si\underset{\displaystyle C_6H_5}{\underset{|}{Si}}(CH_3)Si(CH_3)_3 \rightarrow (CH_3)_3Si\underset{\displaystyle Cl}{\underset{|}{Si}}(CH_3)Si(CH_3)_3$$

76% (*107*)

$$C_6H_5[Si(CH_3)_2]_nC_6H_5 \rightarrow Cl[Si(CH_3)_2]_nCl$$

$n=4$, 76% (*107*)
$n=5$, 69% (*115*)

$$(C_6H_5)_2(CH_3)SiSi(CH_3)_3 \xrightarrow[\text{inCHCl}_3]{\text{HCl, AlCl}_3} Cl(C_6H_5)(CH_3)SiSi(CH_3)_3$$

59% (*116*)

On the other hand, chlorodephenylation in benzene solution affords completely dephenylated products. Thus, 1,1-dichlorotetramethyldisilane and 1,1,1-trichlorotrimethyldisilane are obtained from the corresponding phenyldisilanes (*116*).

$$(C_6H_5)_n(CH_3)_{3-n}SiSi(CH_3)_3 \xrightarrow[\text{in } C_6H_6]{\text{HCl, AlCl}_3} Cl_n(CH_3)_{3-n}SiSi(CH_3)_3$$

$n=2$, 60%
$n=3$, 60%

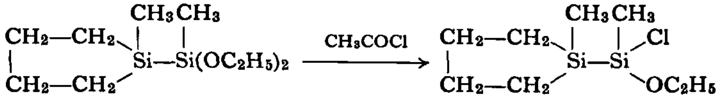
c. *Halogenodealkoxylation of Methylalkoxypolysilanes.* As is the case with monosilane compounds, alkoxy derivatives of polysilanes are converted to the corresponding chloro- and fluoropolysilanes by treatment with acetyl (or benzoyl) chloride and 48% aqueous hydrogen fluoride (or concentrated sulfuric acid, then ammonium hydrogen fluoride), respectively. In general, yields are satisfactory.

$$(CH_3)_3SiSi(CH_3)_2OC_2H_5 \xrightarrow{CH_3COCl} (CH_3)_3SiSi(CH_3)_2Cl$$

80% (*126*)

$$C_2H_5O(CH_3)_2SiSi(CH_3)_2OC_2H_5 \xrightarrow{C_6H_5COCl} Cl(CH_3)_2SiSi(CH_3)_2Cl$$

64% (*126*)



77% (*112*)

$$(CH_3)_3SiSi(CH_3)_2OC_2H_5 \xrightarrow{\text{HF aq.}} (CH_3)_3SiSi(CH_3)_2F$$

65% (*126*)

$$C_2H_5O(CH_3)_2SiSi(CH_3)_2OC_2H_5 \xrightarrow{\text{HF aq.}} F(CH_3)_2SiSi(CH_3)_2F$$

61% (*126*)

$$(C_2H_5O)_2(CH_3)SiSi(CH_3)_2OC_2H_5 \xrightarrow[\text{2. } NH_4F\cdot HF]{\text{1. } H_2SO_4} F_2(CH_3)SiSi(CH_3)_2F$$

59% (*112*)

d. *Cleavage of Permethylated Polysilanes by Halogens or Halides.* This method also affords a useful approach to synthesis of certain methylhalopolysilanes. The reaction of bromine with a mixture of permethylated polysilanes (readily prepared from sodium condensation of dimethyldichlorosilane in the presence of a small amount of trimethylchlorosilane used as chain stopper) in ethyl bromide, chloroform, or carbon tetrachloride at −50° C or so gives 1,2-dibromotetramethyldisilane in 60% yield (*109*), while a similar reaction with decamethyltetrasilane affords bromopentamethyldisilane in 57% yield and 1-bromoheptamethyltrisilane in 43% yield (*106*, *178*) (Section III, C, 3,a).

$$CH_3[Si(CH_3)_2]_nCH_3 \xrightarrow{Br_2} (CH_3)_3SiBr + Br(CH_3)_2SiSi(CH_3)_2Br$$

The cleavage of dodecamethylcyclohexasilane by phosphorus pentachloride in *sym*-tetrachloroethane (*66*), anhydrous hydrogen chloride or *tert*-butyl chloride (*56*) (see Section II, C, 1,c) provides a convenient approach to synthesis of certain α,ω-dichloro permethylated polysilanes.

$$[(CH_3)_2Si]_6 \xrightarrow[\substack{Cl_2CHCHCl_2 \\ \text{reflux}}]{PCl_5} \begin{array}{l} Cl[Si(CH_3)_2]_nCl \\ n=3,\ 16.7\% \\ n=4,\ 24.3\% \\ n=6,\ 24.3\% \end{array}$$

Cleavage with iodine yields 1,6-diiodododecamethylhexasilane (*177*).

e. *Halogenation of Organopolysilanes Containing Silicon–Hydrogen Bonds.* Under appropriate conditions, the silicon–hydrogen bond can be halogenated with the silicon–silicon bond intact. Thus, iodopentamethyldisilane is prepared in 78.5% yield by the interaction of iodine and pentamethyldisilane in chloroform at room temperature over a 3-day period (*178*).

Tris(trimethylsilyl)chlorosilane is obtained in 50% and 80–90% yield when the corresponding hydride is treated with phosphorus pentachloride and carbon tetrachloride, respectively, while tris(trimethylsilyl)bromosilane is produced in 79% yield when the hydride is allowed to react with 1-bromobutane (*59*).

$$\begin{tikzcd}
 & {[(CH_3)_3Si]_3SiCl} \\
{[(CH_3)_3Si]_3SiH} \arrow[ur, "PCl_5", "or\ CCl_4"'] \arrow[dr, "C_4H_9Br"] & \\
 & {[(CH_3)_3Si]_3SiBr}
\end{tikzcd}$$

f. *Partial Alkylation of Hexachlorodisilane.* The synthesis of ethylpentachloro- and diethyltetrachlorodisilane by the action of ethylmagnesium bromide on hexachlorodisilane has been reported (*208*). The method involving partial alkylation of halopolysilanes, however, appears to be of limited applicability because the products are often inseparable from one another by conventional fractional distillation. Partial phenylation of certain chloropolysilanes, on the other hand, proceeds as desired (*107, 112, 115*). Thus, the action of phenylmagnesium chloride on 1,1,2,2-tetrachlorodimethyldisilane and 1,4-dichlorooctamethyltetrasilane in tetrahydrofuran gives, respectively, 1,2-dichloro-1,2-diphenyl-1,2-dimethyldisilane in 50% yield (*112*) and 1-chloro-4-phenyloctamethyltetrasilane in 51% yield (*115*).

g. *Miscellaneous.* By treatment of bis(pentamethyldisilanyl) ether and of bis(pentamethyldisilanyl)amine with boron trifluoride, fluoropentamethyldisilane is prepared in good yield (*188*).

$$[(CH_3)_5Si_2]_2Y + BF_3 \rightarrow 2(CH_3)_5Si_2F$$
$$Y = O,\ 81\%;\quad Y = NH,\ 66\%$$

2. *Chemical Properties*

The organohalopolysilanes are capable of undergoing many of the reactions that are common to the related monosilane derivatives, with the silicon–silicon bond intact. Since a number of examples are encountered in succeeding sections, we will not give them here.

Under certain conditions, alkylchlorodisilanes undergo cleavage of their silicon–silicon bond or disproportionation. Thus, when the mixed vapor of chloropentamethyldisilane and hydrogen chloride in the molar ratio of 1:1

is passed into a quartz tube heated to 500° C, dimethylchlorosilane and trimethylchlorosilane are produced in 36% and 53% yield, respectively (*165*).

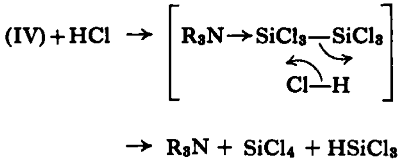
$$Cl(CH_3)_2SiSi(CH_3)_3 + HCl \xrightarrow{500^\circ C} (CH_3)_2SiHCl + (CH_3)_3SiCl$$

With hexamethyldisilane, the cleavage occurs at lower temperatures, giving a 1:1 mixture of $(CH_3)_3SiH$ and $(CH_3)_3SiCl$ in 15% yield at 350° C and in 54% yield at 450° C. Similar reaction using the "disilane fraction" and hydrogen chloride at 450°–700° C yields a mixture of CH_3SiCl_3, $(CH_3)_2SiCl_2$, and CH_3SiHCl_2, along with other minor products (*6*). Although mechanistic studies on hydrogen chloride cleavage of the disilanes at elevated temperatures have not yet been made, in view of the fact that the hexamethyldisilane itself appears to be stable up to about 500° C and the cleavage of chloropentamethyldisilane gives rise to the preferential formation of $(CH_3)_2SiHCl$ and $(CH_3)_3SiCl$, a mechanism involving heterolytic rather than homolytic scission of the silicon–silicon bond is probable.

Certain tertiary organic amines and suitable salts thereof are known to act as effective catalysts for hydrogen chloride cleavage of the "disilane fraction" (*10b*, *28*, *47a*). With these, it is satisfactorily converted to a mixture of methylchloromonosilanes at temperatures of the order of 75°–100° C. A closely related reaction involves the cleavage of the silicon–silicon bond in ethylchlorodisilanes by ammonium halides and by trimethylamine hydrochloride at 120°–130° C (*208*). The ease of cleavage in this reaction decreases in the order $Cl_3SiSiCl_3 > C_2H_5Si_2Cl_5 > (C_2H_5)_2Si_2Cl_4 \gg (C_2H_5)_6Si_2$, which is apparently reverse to the order in the uncatalyzed cleavage of methylchlorodisilanes by hydrogen chloride. In view of the fact that certain perchloropolysilanes are capable of forming relatively stable amine complexes under suitable conditions (*91*, *191*), the cleavage of the disilanes containing higher chlorine content by ammonium chloride or hydrogen chloride in the presence of amines probably proceeds by the mechanisms involving the formation of an amine complex intermediate (IV), wherein susceptibility of the silicon–silicon bond to attack by hydrogen chloride must be enhanced. The more chlorine atoms there are on silicon, the easier the formation of (IV) must be.

$$R_3N + Cl_3SiSiCl_3 \rightarrow R_3\overset{+}{N} \rightarrow \overset{-}{Si}Cl_3{—}SiCl_3$$

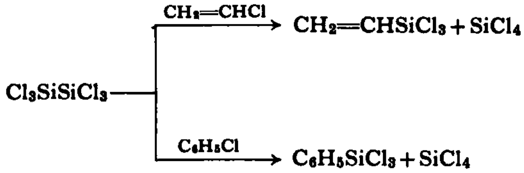
(IV)



$$(\mathrm{IV}) + HCl \rightarrow \left[\begin{array}{c} R_3N \rightarrow SiCl_3\text{—}SiCl_3 \\ Cl\text{—}H \end{array}\right] \rightarrow R_3N + SiCl_4 + HSiCl_3$$

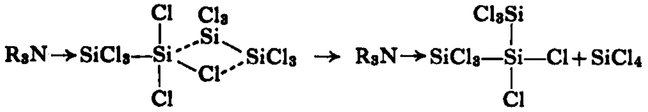
On the other hand, in the uncatalyzed cleavage by hydrogen chloride, electrophilic attack of a proton on the silicon–silicon bond may play an important role in the four-centered transition state.

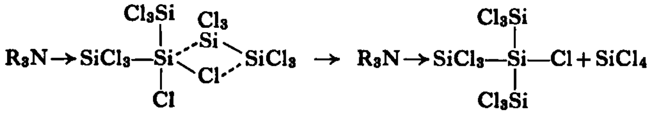
The action of vinyl chloride or chlorobenzene on hexachlorodisilane at 600° C produces vinyltrichlorosilane (20% yield) or phenyltrichlorosilane (30% yield), respectively (*24*).

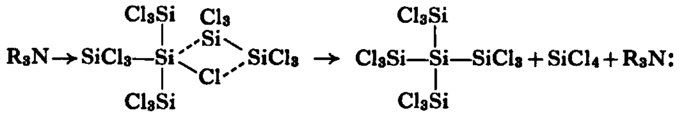


Similar reactions using $(CH_3)_3SiSi(CH_3)_3$, $Cl(CH_3)_2SiSi(CH_3)_3$, or $Cl(CH_3)_2SiSi(CH_3)_2Cl$ in place of $Cl_3SiSiCl_3$ represent more complex patterns involving intramolecular rearrangement of the disilanes (see Section III, C, 1). Here, a free radical mechanism has been suggested (*24*).

A most interesting chemical behavior of halopolysilanes (and also other polysilane derivatives) is the disproportionation of the silicon–silicon bond. This is closely related to the cleavage reaction because both often occur concurrently and are similar in mechanisms. Ammonium halides, tertiary organic amines, quaternary ammonium or phosphonium halides, or silver cyanide act as catalysts in the disproportionation of hexachlorodisilane (or octachlorotrisilane) (*90–93*, *138*, *191*) or methylchlorodisilanes (*28*, *189*). Thus, a catalytic amount of trimethylamine brings about the disproportionation of hexachlorodisilane to silicon tetrachloride and dodecachloropentasilane, $(Cl_3Si)_4Si$, or tetradecachlorohexasilane, $(Cl_3Si)_3SiSi_2Cl_5$, depending upon the conditions under which the reaction is effected. The following mechanism has been suggested (*191*) for the formation of $(Cl_3Si)_4Si$:







The mechanism obviously can be applied also to the disproportionation of alkylchlorodisilanes of higher chlorine content (*28*).

If silver cyanide is used as the "catalyst," chloropentamethyldisilane as well as the "disilane fraction" undergoes disproportionation, although in this case good conversions require employment of relatively large quantities of silver cyanide (*187*).

$$n(CH_3)_3SiSi(CH_3)_2Cl \xrightarrow[200^\circ C]{AgCN} (n-1)(CH_3)_3SiCl + (CH_3)_3Si[Si(CH_3)_2]_nCl$$

This gives an average value of 5.5 for *n*. In view of the disproportionation observed with $(CH_3)_3SiSi(CH_3)_2(CN)$ (Section II, E, 2), it appears likely that the catalytic effect of the silver cyanide is due to the transient formation of the (cyano)methylpolysilanes.

Another striking chemical feature that methylchlorodisilanes and -polysilanes display is their ability to undergo the aluminum chloride-catalyzed redistribution reaction much more rapidly than do the related methylchloromonosilanes. Thus, when an equimolar mixture of 1,2-dichlorotetramethyldisilane and hexamethyldisilane is stirred at room temperature in the presence of a catalytic amount of anhydrous aluminum chloride, equilibrium is established between chloropentamethyldisilane and its original components within 1.5 hours (*154a*).

$$Cl(CH_3)_2SiSi(CH_3)_2Cl + (CH_3)_3SiSi(CH_3)_3 \overset{AlCl_3}{\rightleftarrows} 2\,Cl(CH_3)_2SiSi(CH_3)_3$$

The apparent equilibrium constant,

$$K = \frac{[C_5H_{15}Si_2Cl]^2}{[C_4H_{12}Si_2Cl_2][C_6H_{18}Si_2]}$$

was found to be 82.6 in benzene solution. In chloroform, however, a reaction of this type is not observed to proceed even after 1 week at room temperature.

Similar rapid equilibrium is established among 1,3-dichlorohexamethyltrisilane, octamethyltrisilane, and 1-chloroheptamethyltrisilane, with the equilibrium being to the side of the last compound (*156*).

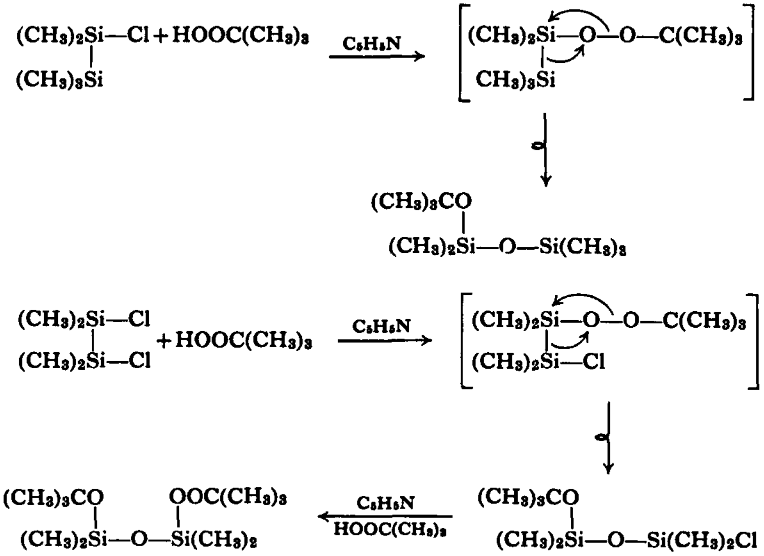
$$Cl[Si(CH_3)_2]_3Cl + CH_3[Si(CH_3)_2]_3CH_3 \overset{AlCl_3}{\rightleftarrows} 2\ Cl[Si(CH_3)_2]_3CH_3$$

By using a combination of chloromethylpolysilanes and aluminum chloride catalyst, a new type of electrophilic aromatic substitution can successfully be achieved, as indicated by the equation that follows (*154a*).

$$C_6H_5Si(CH_3)_3 + Cl{-}Si(CH_3)_2Si(CH_3)_3 \xrightarrow{AlCl_3} C_6H_5Si(CH_3)_2Si(CH_3)_3 + Cl{-}Si(CH_3)_3$$

The electrophilic nature of the reaction is demonstrated by the fact that phenyltrimethylsilane undergoes the reaction faster than *p*-chlorophenyltrimethylsilane and slower than *p*-methylphenyltrimethylsilane, the apparent relative rates at an early stage of the reaction being $k_{p\text{-Cl}}/k_H = 0.2$ and $k_{p\text{-CH}_3}/k_H = 2.0$.

The action of *tert*-butyl hydroperoxide on chloropentamethyldisilane and on 1,2-dichlorotetramethyldisilane in the presence of pyridine leads not to the expected peroxydisilanes but exclusively to *tert*-butoxypentamethyldisiloxane and 1-*tert*-butoxy-3-*tert*-butylperoxytetramethyldisiloxane, respectively. Both of these are products from intramolecular rearrangement



involving migration of the substituted silyl groups from silicon to oxygen (*95*).

A number of examples of intramolecular rearrangements of organometallic and organometalloidal peroxides are well known, and there are several instances indicating a strong tendency for substituted silyl groups to undergo 1,2-shift from silicon to carbon under certain conditions (see Section III, C, 1, and Section IV, A, 2,a,e; B, 2,a).

B. Silicon–Alkoxy Compounds

1. *Synthesis*

Almost all the known methods for synthesis of alkoxy-substituted monosilanes can be applied to the synthesis of organoalkoxypolysilanes. Typical processes are alcoholysis of the corresponding chloro- or hydropolysilanes, and partial alkylation of alkoxypolysilanes, as shown by the following equations:

$$Cl(CH_3)_2SiSi(CH_3)_2Cl + 2\ C_2H_5OH \xrightarrow{NH_3} (C_2H_5O)(CH_3)_2SiSi(CH_3)_2(OC_2H_5)$$

66% (*109*)

$$\underset{\text{Disilane fraction}}{(CH_3)_nSi_2Cl_{6-n}} + (6-n)\ C_2H_5OH \xrightarrow{NH_3} (C_2H_5O)(CH_3)_2SiSi(CH_3)(OC_2H_5)_2 + (C_2H_5O)_2(CH_3)SiSi(CH_3)(OC_2H_5)_2$$

(*114, 126*)

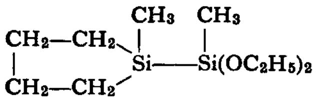
$$\underset{n=2\text{–}4}{H[Si(CH_3)_2]_nH} + 2\ CH_3OH \xrightarrow{LiOCH_3\ (\text{catalyst})} CH_3O[Si(CH_3)_2]_nOCH_3 + 2\ H_2$$

(*5*)

$$[(C_2H_5O)_2(CH_3)Si]_2 + 2\ CH_3MgBr \xrightarrow{\text{Ether}} [(C_2H_5O)(CH_3)_2Si]_2$$

(*114, 126*)

$$[(C_2H_5O)_2(CH_3)Si]_2 + BrMg(CH_2)_4MgBr \xrightarrow{\text{Ether}}$$



(V) (*112*)

As indicated by the last equation, the action of $BrMg(CH_2)_4MgBr$ on 1,1,2,2-tetraethoxydimethyldisilane in ethyl ether leads exclusively to the formation of compound (V), which contains a silacyclopentane ring, but not a 1,2-disilacyclohexane one, and keeps two ethoxy groups intact (see also Section III, B).

Another important method for synthesis involves the disproportionation of methoxy-substituted disilanes, which will be discussed in the next section.

2. *Chemical Properties*

Alkoxyorganopolysilanes undergo cleavage and disproportionation under certain conditions, as well as many of the reactions common to the related alkoxy-substituted monosilanes.

The cleavage of the silicon–silicon bond by alkaline reagents, such as alcoholic alkali and wet piperidine, with the evolution of an equivalent of hydrogen for each silicon–silicon bond has long been recognized and often employed for the quantitative determination of the number of such bonds.

$$\mathrm{R_3Si{-}SiR_3 + 2\,ROH \xrightarrow{RO^-} 2\,R_3SiOR + H_2}$$

However this is invalid for hexaalkyldisilanes because they are quite stable toward alcoholic alkali (*184*). A study of the reaction kinetics of the cleavage of a series of ethoxymethyldisilanes with sodium ethoxide in ethanol indicates that the reaction is second order, first both in disilane and ethoxide ion, and that substitution of ethoxy groups by methyl on the disilane linkage considerably reduces the rate of cleavage. Since the rate of hydrogen evolution from the $\mathrm{R_3SiH}$ compound is much greater than that from the corresponding disilane $\mathrm{R_3SiSiR_3}$, e.g., $\mathrm{(CH_3)_2SiH(OC_2H_5)}$ is about 10^4 times more reactive than $\mathrm{[(C_2H_5O)(CH_3)_2Si]_2}$, the step of nucleophilic cleavage of the silicon–silicon bond by ethoxide ion is rate-determining.

$$\mathrm{R_3Si{-}SiR_3 + EtO^- + EtOH \xrightarrow{Slow} R_3SiOEt + [R_3SiH] + EtO^-}$$

$$\mathrm{[R_3SiH] + EtO^- + EtOH \xrightarrow{Fast} R_3SiOEt + H_2 + EtO^-}$$

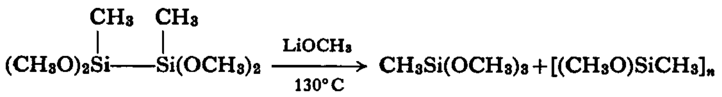
Methoxy-substituted methylpolysilanes of the formulas $\mathrm{CH_3O[Si(CH_3)_2]_\mathit{n}OCH_3}$ and $\mathrm{CH_3O[Si(CH_3)(OCH_3)]_\mathit{n}OCH_3}$, where $n \geqslant 2$, readily undergo both the base-catalyzed disproportionation, and thermal disproportionation in the absence of added base ($\mathrm{Si{-}Si/Si{-}OCH_3}$ redistribution) (*4*, *5*, *143*). Thus, heating 1,2-dimethoxytetramethyldisilane to 100° C with lithium methoxide over a 10-hour period gives dimethyldimethoxysilane, and 1,3-dimethoxyhexamethyltrisilane in 55–60% yield, along with a small amount of 1,4-dimethoxyoctamethyltetrasilane (*5*).

$$\begin{aligned}\mathrm{2\,CH_3O[Si(CH_3)_2]_2OCH_3} &\xrightarrow[100^\circ\,\mathrm{C}]{\mathrm{LiOCH_3}} \mathrm{(CH_3)_2Si(OCH_3)_2} + \\ &\qquad \mathrm{CH_3O[Si(CH_3)_2]_3OCH_3 + CH_3O[Si(CH_3)_2]_4OCH_3}\end{aligned}$$

When 1,3-dimethoxyhexamethyltrisilane is heated at 185° C in the presence of lithium methoxide, the major product is 1,5-dimethoxydecamethylpentasilane (40–50% yield), and the 1,4-dimethoxytetrasilane is again formed as a minor product. This suggests that the predominant reaction path is represented by the equation

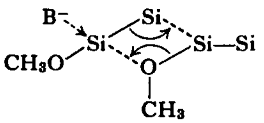
$$2\ CH_3O[Si(CH_3)_2]_3OCH_3 \xrightarrow[185^\circ C]{LiOCH_3} (CH_3)_2Si(OCH_3)_2 + CH_3O[Si(CH_3)_2]_5OCH_3$$

The lithium methoxide-catalyzed disproportionation of 1,1,2,2-tetramethoxydimethyldisilane is extremely rapid at 130° C, and within 5 minutes produces 98% of the theoretical amount of methyltrimethoxysilane and a mixture of higher polysilanes.

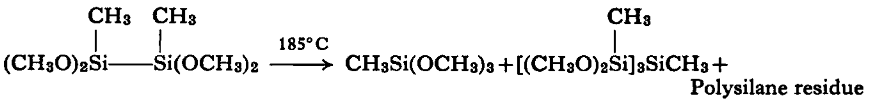


$$(CH_3O)_2\overset{CH_3}{\overset{|}{Si}}-\overset{CH_3}{\overset{|}{Si}}(OCH_3)_2 \xrightarrow[130^\circ C]{LiOCH_3} CH_3Si(OCH_3)_3 + [(CH_3O)SiCH_3]_n$$

In view of the facts that the reactivity of the series $CH_3O[Si(CH_3)_2]_nOCH_3$ for the base-catalyzed $SiSi/SiOCH_3$ redistribution decreases rather dramatically with increasing chain length, and that the ease of redistribution increases with increasing methoxy substitution (methoxypentamethyldisilane does not undergo the reaction of this type), a possible reaction mechanism would involve nucleophilic assistance in a four-centered transition state (*5*), which is analogous to that proposed for the amine-catalyzed disproportionation of halopolysilanes (Section II, A, 2).



Thermal disproportionation in the absence of added base takes place when 1,1,2,2-tetramethoxydimethyldisilane is heated at 185° C for 40 hours, giving methyltrimethoxysilane, tris(methyldimethoxysilyl)methylsilane and a viscous nonvolatile polysilane residue (*4*).



$$(CH_3O)_2\overset{CH_3}{\overset{|}{Si}}-\overset{CH_3}{\overset{|}{Si}}(OCH_3)_2 \xrightarrow{185^\circ C} CH_3Si(OCH_3)_3 + [(CH_3O)_2Si]_3\overset{CH_3}{\overset{|}{Si}}CH_3 + \text{Polysilane residue}$$

Both 1,2-dimethoxytetramethyldisilane and 1,3-dimethoxyhexamethyltrisilane also undergo thermolysis at higher temperatures (225° and 175° C, respectively) to give dimethyldimethoxysilane and the homologous series of α,ω-dimethoxypermethylated polysilanes. In contrast to the base-catalyzed disproportionation, thermolysis characteristically produces a more random distribution of the series.

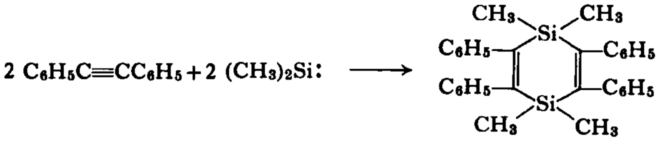
$$CH_3O[Si(CH_3)_2]_2OCH_3 \xrightarrow{\text{Heat}} (CH_3)_2Si(OCH_3)_2 + \underset{n=3\text{–}5}{CH_3O[Si(CH_3)_2]_nOCH_3}$$

A mechanism involving the formation of a divalent silicon (silene) intermediate from an α-elimination of the alkoxy-substituted di- or trisilanes, followed by a series of insertion reactions has been proposed (*4*). For instance, the thermolysis of 1,2-dimethoxytetramethyldisilane may proceed as follows:

$$CH_3O[Si(CH_3)_2]_2OCH_3 \rightarrow (CH_3)_2Si(OCH_3)_2 + (CH_3)_2Si:$$

$$(n-2)\,(CH_3)_2Si: + CH_3O[Si(CH_3)_2]_2OCH_3 \rightarrow CH_3O[Si(CH_3)_2]_nOCH_3$$

This mechanism is supported by an observation that when 1,2-dimethoxytetramethyldisilane is heated at 225° C in the presence of excess diphenylacetylene, 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexadiene is produced in 49% yield. The formation of this compound has previously been reported from reactions believed to involve dimethylsilylene.



C. Silicon–Hydrogen Compounds

1. *Synthesis*

a. ***Reduction of Halopolysilanes or Alkoxypolysilanes with Lithium Aluminum Hydride.*** This is the most generally applicable method for preparing the silicon–hydrogen compounds (*3, 10a, 107, 190*). Yields are very high with highly alkylated polysilanes, but they are strongly dependent upon the conditions under which the reaction is effected when a halo- or alkoxypolysilane to be reduced is highly substituted by the negative groups. In the latter case, the presence of a large excess of lithium aluminum hydride in the reaction system should be avoided because otherwise extensive cleavage of the silicon–silicon bond occurs.

An extreme example is given by the reduction of hexachlorodisilane (*10a*). Whereas disilane, Si_2H_6, can be obtained in 87% yield when 15% excess of a solution of lithium aluminum hydride in ether is added to the chlorodisilane, the product is exclusively monosilane, SiH_4, when a solution of the chlorodisilane is added to a solution of lithium aluminum hydride so that an excess of the latter is always present.

b. *Coupling of Alkylhalosilanes with Metals, and Related Reactions.* The Wurtz-type reaction that is used frequently to prepare peralkylated (or arylated) di- and polysilanes can be applied to synthesis of silicon–hydrogen polysilanes. Thus, a homologous series of α,ω-dihydropermethylpolysilanes, $H[(CH_3)_2Si]_nH$, can successfully be prepared from a mixed sodium coupling of $(CH_3)_2HSiCl$ and $(CH_3)_2SiCl_2$(*5*), and tetrakis(dimethylsilyl)-silane, $[H(CH_3)_2Si]_4Si$, can be obtained by lithium condensation of $(CH_3)_2HSiCl$ and $SiCl_4$ (*63*).

The use of magnesium in tetrahydrofuran as the condensing agent has been reported to be much more satisfactory than the use of alkali metals for preparing a class of symmetrical disilanes of the general formula (C_6H_5)-$RHSiSiHR(C_6H_5)$, where R may be alkyl or aryl, from the corresponding halosilanes (*175*).

A variation of the above methods involves the use of liquid sodium amalgam as the condensing agent (*29*, *207*). By permitting CH_3SiH_2I or $(CH_3)_2SiHBr$ to react with the amalgam at room temperature, the synthesis of 1,2-dimethyldisilane or the homologous series of α,ω-dihydropermethylpolysilanes, respectively, is attained.

$$CH_3SiH_2I \xrightarrow{Na/Hg} \underset{49.7\%}{H_2(CH_3)SiSi(CH_3)H_2} + \underset{25.5\%}{CH_3SiH_3} \quad (29)$$

$$(CH_3)_2SiHBr \xrightarrow{Na/Hg} \underset{n=2\text{–}5}{H[(CH_3)_2Si]_nH} + (CH_3)_2SiH_2 \quad (207)$$

Doubtless, in these reactions unstable intermediate silylmercury compounds such as $[H_2(CH_3)Si]_2Hg$ and $[H(CH_3)_2Si]_2Hg$ are first produced which then undergo decomposition. The formation of the trisilane and higher polysilanes from the reaction of $(CH_3)_2SiHBr$ with Na/Hg may be rationalized by the insertion into $[H(CH_3)_2Si]_2Hg$ of dimethylsilylene, $(CH_3)_2Si{:}$, which is probably produced during the reaction through decomposition of an unstable intermediate species $(CH_3)_2SiHg$, followed by decomposition of the adducts. The generation of dimethylsilylene and its insertion into the

Si—H bond to produce pentamethyldisilane has been reported recently (*171*).

$$(CH_3)_2SiCl_2 + 2\ Na/K \xrightarrow{260°\text{–}280°\ C} (CH_3)_2Si: + 2\ KCl$$

$$(CH_3)_2Si: + (CH_3)_3Si\text{—}H \rightarrow (CH_3)_3SiSi(CH_3)_2H \quad (30\%)$$

Certain reactions of silyl–alkali metal compounds, such as coupling of $(CH_3)_n(C_6H_5)_{3-n}SiLi$ with appropriate chlorosilanes (*51*) and hydrolysis of $[(CH_3)_3Si]_3SiLi$ (*63*), lead to the formation of organopolysilanes with the silicon–hydrogen bond. There have been few reports of such synthesis.

$$3\ (CH_3)_2(C_6H_5)SiLi + Cl_3SiH \rightarrow [(CH_3)_2(C_6H_5)Si]_3SiH$$

$$[(CH_3)_3Si]_3SiLi \xrightarrow{H_2O,\ H^+} [(CH_3)_3Si]_3SiH$$

c. *Hydrohalogenation of* $[(CH_3)_2Si]_6$. Dodecamethylcyclohexasilane is much more susceptible to cleavage by hydrogen chloride than the linear polysilanes (see Section II, A, 2), and can be converted to a mixture of two types of homologous series, α-chloro-ω-hydropermethylpolysilanes, $H[(CH_3)_2Si]_nCl$ and α,ω-dichloropermethylpolysilanes, $Cl[(CH_3)_2Si]_nCl$, where $n = 1\text{–}6$, by treatment with anhydrous hydrogen chloride in boiling dichloromethane, xylene, or *o*-dichlorobenzene, or in a stainless steel autoclave at pressures of 400 to 600 psi and temperatures of 50° to 70° C. *tert*-Butyl chloride also brings about the formation of the same products in an autoclave at 140°–150° C and 140 psi. The ratio of products formed depends upon the amount of hydrogen chloride or *tert*-butyl chloride used (*56*).

d. *Mercury* $6(^3P_1)$ *Sensitized Decomposition of Methylsilanes.* The mercury $6(^3P_1)$ photosensitization of methylsilanes containing silicon–hydrogen bonds leads to the formation of methyldisilanes and a trisilane by way of initial loss of a hydrogen atom or atoms from the silicon–hydrogen bonds followed by recombination of the resulting silyl or silene radicals (*135*).

$$(CH_3)_2SiH_2 \rightarrow [H(CH_3)_2Si\text{—}]_2 + H[Si(CH_3)_2]_3H + H_2$$

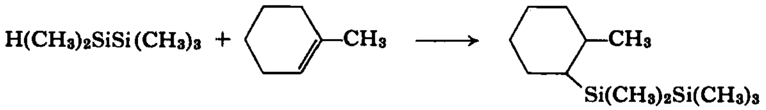
$$CH_3SiH_3 \rightarrow [H_2(CH_3)Si\text{—}]_2 + H_2$$

2. *Chemical Properties*

Under suitable conditions, alkylpolysilanes containing the silicon–hydrogen bond are capable of undergoing many of the reactions common to the related monosilanes without cleavage of the silicon–silicon bond. Thus, $H(CH_3)_2SiSi(CH_3)_3$ is successfully converted to $I(CH_3)_2SiSi(CH_3)_3$ (Section II, A, 1,e), and $H[Si(CH_3)_2]_nH$ to $CH_3O[Si(CH_3)_2]_nOCH_3$ in good yield (Section II, B, 1). Reaction of a disilane with diethylmercury gives a compound with an SiSi—Hg linkage (Section II, E, 5).

The addition of pentamethyldisilane, $H(CH_3)_2SiSi(CH_3)_3$, and 1,1,2,2-tetramethyldisilane $H(CH_3)_2SiSi(CH_3)_2H$, to some olefins (so-called hydrosilation) under free radical conditions proceeds in the normal way (*190*). Thus, pentamethyldisilane adds to 1-octene to give *n*-octylpentamethyldisilane in the presence of di-*tert*-butyl peroxide in 78% yield. It also reacts with 1-methylcyclohexene to give 1-methyl-2-(pentamethyldisilanyl)cyclohexane in the presence of the same catalyst in 80–90% yield, upon irradiation with ultraviolet light in fair yield, but in poor yield upon heating to 300° C in the absence of a catalyst.

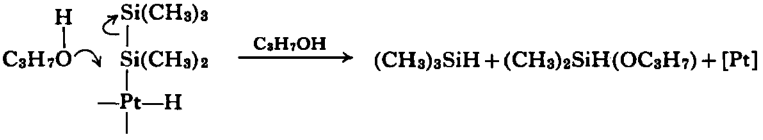
$$H(CH_3)_2SiSi(CH_3)_3 + C_6H_{13}CH{=}CH_2 \rightarrow (n\text{-}C_8H_{17})(CH_3)_2SiSi(CH_3)_3$$



(possibly *trans*)

On the other hand, chloroplatinic acid-catalyzed reaction of pentamethyldisilane with olefins results in much cleavage of the silicon–silicon bond and yields only traces of the expected product; the principal products are trimethylsilane and isopropoxysilicon compounds.

Although the mechanism of the platinum-catalyzed hydrosilation is poorly understood, it seems probable that an intermediate with a platinum–silicon bond is formed, with which the olefin and hydrogen may also be complexed. The cleavage of pentamethyldisilane may be rationalized by considering nucleophilic attack of isopropyl alcohol, which is used for preparing the catalyst solution, on the silicon atom that has become attached to platinum and thus vulnerable to the attack by any Lewis base (see also Section IV, A, 2,f; B, 2,b).



$$\overset{H}{\overset{|}{C_3H_7O}}\ \ \underset{\overset{|}{-Pt-H}}{\overset{Si(CH_3)_3}{\overset{|}{Si(CH_3)_2}}} \xrightarrow{C_3H_7OH} (CH_3)_3SiH + (CH_3)_2SiH(OC_3H_7) + [Pt]$$

This mechanism for cleavage may be supported by the fact that the addition of pentamethyldisilane to olefins in the presence of a platinum catalyst free from any protic solvent proceeds smoothly (Section IV, A, 1,c).

D. *Silanols and Siloxanes*

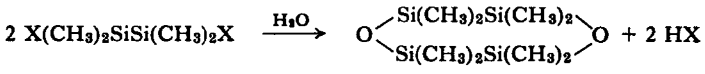
1. *Silanols*

Aliphatic silanols containing the silicon–silicon bond are liable to dehydration condensation to siloxanes unless highly sterically hindered. Thus, pentamethyldisilanol was prepared in 40% yield by careful hydrolysis of bromopentamethyldisilane under strictly neutral conditions, but underwent dehydration to the dimer $[(CH_3)_3SiSi(CH_3)_2]_2O$ in a short time (*178*). All attempts to prepare tetramethyldisilane-1,2-diol have failed (*126*); the product is always its dehydration cyclic dimer, $[—(CH_3)_2SiSi(CH_3)_2O—]_2$. This much stronger tendency for organodisilanols to undergo dehydration condensation as compared with the related monosilanols may be understood in terms of the increased availability of vacant silicon 3*d* oribtals at the silicon–silicon bond which favors an interaction between molecules.

Some highly sterically hindered silanols such as tetracyclohexyldisilane-1,2-diol (*139*) and tris(trimethylsilyl)silanol (*59*) are readily obtainable and resistant to dehydration.

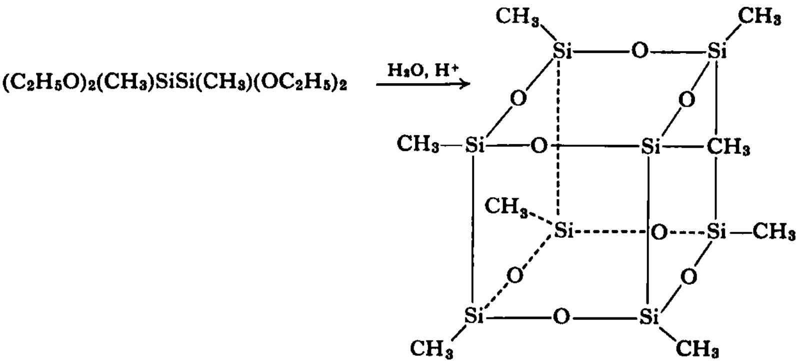
$$2\ (CH_3)_3SiSi(CH_3)_2X \xrightarrow{H_2O} [(CH_3)_3SiSi(CH_3)_2—]_2O + 2\ HX$$

(VI)



$$2\ X(CH_3)_2SiSi(CH_3)_2X \xrightarrow{H_2O} O\begin{matrix} \diagup Si(CH_3)_2Si(CH_3)_2 \diagdown \\ \diagdown Si(CH_3)_2Si(CH_3)_2 \diagup \end{matrix}O + 2\ HX$$

(VII)



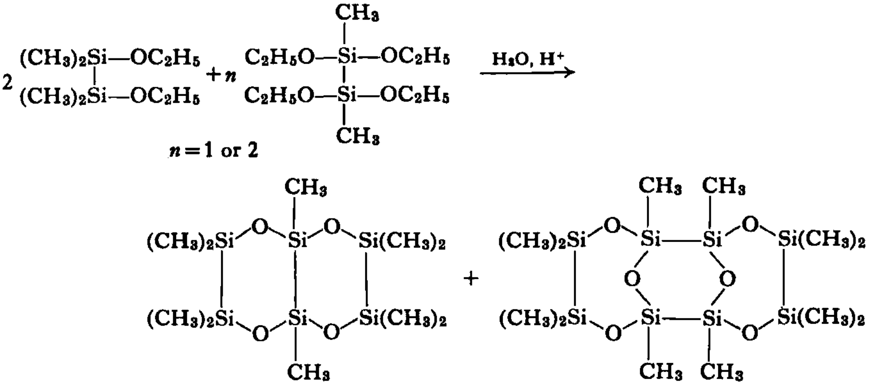
$$(C_2H_5O)_2(CH_3)SiSi(CH_3)(OC_2H_5)_2 \xrightarrow{H_2O,\ H^+}$$

(VIII)

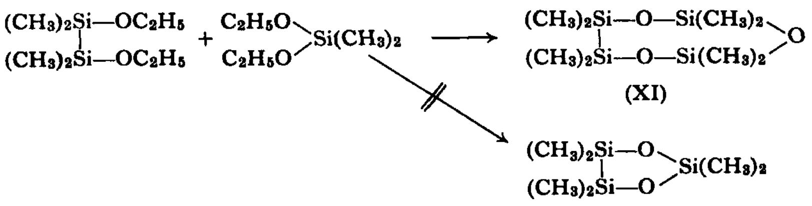
2. *Siloxanes*

a. *Synthesis.* Any silicon-functional organopolysilanes are readily converted to siloxanes, such as (VI)–(VIII) (see p. 38), upon hydrolysis (*109, 126*). Surprisingly enough, acid hydrolysis of tetraethoxy-1,2-dimethyldisilane gives a cagelike dehydration tetramer (VIII) of 1,2-dimethyldisilanetetraol in over 40% yield.

Cohydrolysis of 1,2-dichlorotetramethyldisilane with trimethylchlorosilane leads to a homologous series of linear siloxanes with trimethylsiloxy end groups of the formula $(CH_3)_3SiO[Si(CH_3)_2Si(CH_3)_2O]_nSi(CH_3)_3$. Cohydrolysis of 1,1,2,2-tetraethoxydimethyldisilane with 1,2-diethoxytetramethyldisilane under acidic conditions gives two fused-ring siloxanes; one contains two fused rings (IX), the other three fused rings (X) (*83, 109*).

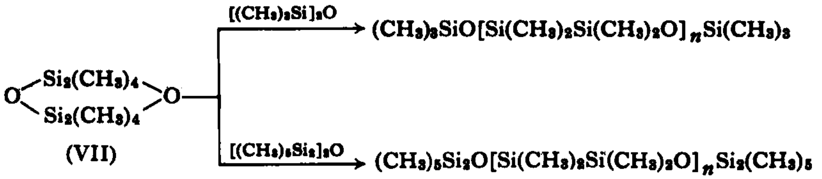

(IX) (X)

Cohydrolysis of 1,2-diethoxytetramethyldisilane with dimethyldiethoxysilane yields as the major product a seven-membered cyclic compound (XI) in which two dimethylsiloxy units are incorporated, but no traces of a five-membered product (XII) (*109*).


(XI)

(XII)

The procedure involving catalytic rearrangement of the siloxane bond, so-called catalytic equilibration, can also be applied to synthesis of the homologous series of linear disilanylenesiloxanes. Thus, by stirring a mixture of octamethyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane (VII) with hexamethyldisiloxane or with bis(pentamethyldisilanyl) ether (VI) in the presence of sulfuric acid as catalyst at room temperature, one can obtain the homologous series of linear disilanylenesiloxanes containing trimethylsiloxy or pentamethyldisilanoxy end groups, respectively (*109*).



(VII)

b. *Structures of Cyclic, Fused-Ring, and Cagelike Systems.* The crystal and molecular structures of the cyclic, fused-ring, and cagelike methyldisilanylenesiloxanes have recently been determined by X-ray diffraction.

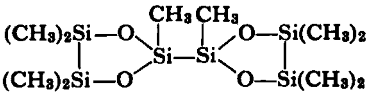
Octamethyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane (VII) crystallizes in the monoclinic space group C_{2h}^5–$P2_{1/c}$ with four molecules in the unit cell. The unit cell constants are $a = 7.67 \pm 0.02$ Å, $b = 6.64 \pm 0.02$Å, $c = 17.39 \pm 0.03$ Å, and $\beta = 111.0 \pm 0.2°$. The six-membered ring of a molecule has a chair form close to a plane (*182*).

The dehydrated tetramer of 1,2-dimethyldisilanetetraol (VIII) crystallizes in the tetragonal space group $P4/nnc$ with four molecules per unit cell. The unit cell constants are $a = 11.73 \pm 0.02$ Å, and $c = 17.17 \pm 0.02$ Å. The skeleton of a molecule consists of two crown-shaped $(\text{—Si—O—})_4$ rings which are crystallographically independent of each other and are connected by four Si—Si bonds along the *c* axis. The four six-membered $(\text{—Si—Si—O})_2$ rings have boat forms. Hence, the molecule forms a cagelike conformation with an approximate symmetry of $4/mm$. Each molecule in the unit cell is surrounded by four adjacent molecules related to centers of symmetry; these molecules form, in a sense, a layer perpendicular to the *c* axis (*82*).

The three-fused-ring system (X) crystallizes in the triclinic space group $P\bar{1}$ with one molecule in the unit cell. The unit cell constants are $a = 7.71 \pm 0.02$ Å, $b = 10.17 \pm 0.02$ Å, $c = 10.17 \pm 0.02$ Å, $\alpha = 106.7 \pm 0.2°$, $\beta = 109.6 \pm$

0.2°, and $\gamma = 78.1 \pm 2°$. The skeleton of a molecule[2] is composed of two seven-membered siloxane rings and one six-membered siloxane ring in the chair conformation with a center of symmetry. The seven-membered ring is nearly planar, except for the one oxygen atom. The dihedral angle between the seven-membered and six-membered rings is about 109°. The whole molecule, approximately, has a noncrystallographic mirror plane perpendicular to the line connecting the midpoints of two Si—Si bonds in the six-membered ring. The Si—Si bond length and the Si—O—Si bond angle are, respectively, 2.38 ± 0.01 Å and 148° for the seven-membered ring, and 2.36 ± 0.01 Å and 133° for the six-membered ring (*83*).

The compound with the formula $(CH_3)_{10}O_4Si_6$ that is obtained as one of the products from cohydrolysis of $[(C_2H_5O)_2(CH_3)Si—]_2$ and $[(C_2H_5O)(CH_3)_2Si—]_2$ has a structure in which two six-membered rings are fused together as described above (IX), and not a structure containing two isolated five-membered rings as shown below. It crystallizes in the monoclinic space group C_{2h}^5–$P2_{1/n}$ with four molecules in the unit cell. The unit cell constants



are $a = 14.00$ Å, $b = 22.53$ Å, $c = 7.87$ Å, $\alpha = \sim 90°$, $\beta = 99.0°$, and $\gamma = \sim 90°$ (*84*).

E. Miscellaneous Compounds

1. *Silicon–Nitrogen Compounds*

The chemistry of silicon–nitrogen compounds has been the subject of considerable study, but little interest has been shown in organopolysilane derivatives of such type. Only a limited number of compounds have been

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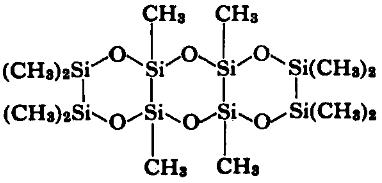
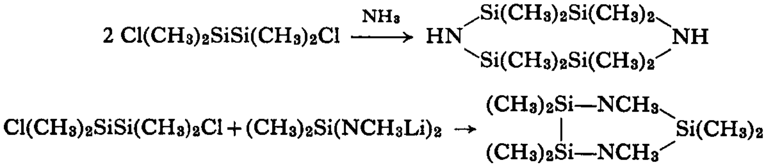
[2] Originally, a structure was proposed in which three six-membered rings are fused together in a linear manner, as shown below (*109*).



reported so far. Bis(pentamethyldisilanyl)amine (*188*) and 2,2,3,3,5,5,6,6-octamethyl-1,4-diaza-2,3,5,6-tetrasilacyclohexane (*203*) are prepared from the reaction of ammonia with chloropentamethyldisilane and 1,2-dichlorotetramethyldisilane, respectively, in ether, and octamethyl-1,3-diaza-2,4,5-trisilacyclopentane (*202*) is made by the action of bis(*N*-lithiomethylamino)dimethylsilane on the 1,2-dichlorodisilane.

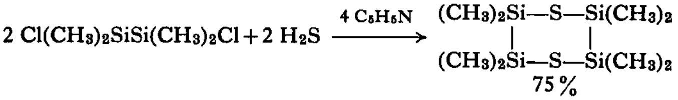
$$2\ (CH_3)_3SiSi(CH_3)_2Cl \xrightarrow{NH_3} [(CH_3)_3SiSi(CH_3)_2]_2NH$$



Liquid bis(pentamethyldisilanyl)amine is considerably associated as compared with bis(trimethylsilyl)amine, as indicated by the respective values of Trouton's constant, 28.1 and 23.5. This is probably due to the increased availability of vacant silicon 3*d* orbitals at the silicon–silicon bond which might favor an interaction between two molecules (*1*, *188*).

2. *Silicon–Sulfur Compounds*

The only known compound of such type is octamethyl-1,4-dithia-2,3,5,6-tetrasilacyclohexane, which has been prepared by the reaction of 1,2-dichlorotetramethyldisilane with hydrogen sulfide in the presence of pyridine (*204*).



Although this crystalline product is not hygroscopic, it appears to undergo hydrolysis in the air as evidenced by the fact that it smells of hydrogen sulfide.

3. *Silicon Pseudohalides*

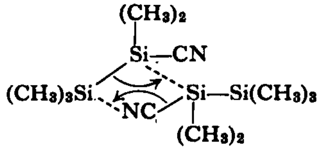
a. *Si—(CN) Compounds.* (Iso)cyanopentamethyldisilane [pentamethyldisilanyl (iso)cyanide] is prepared in good yield from chloropentamethyldisilane and silver cyanide (*30*, *187*). Like trimethyl(iso)cyanosilane, this compound may be a mixture of the normal cyanide and the isocyanide. The infrared spectrum shows two maxima at 4.58 and 4.76μ, the relative intensities being in the ratio of about 3.2:1, perhaps due to the normal cyanide and the isocyanide stretching frequency, respectively.

(Iso)cyanopentamethyldisilane readily undergoes disproportionation on heating at 175°–180° C to give trimethyl(iso)cyanosilane and the homologous series of 1-(iso)cyano permethylated polysilanes. 1-(Iso)cyanoheptamethyltrisilane thus obtained also undergoes reaction of the same type but less readily (*187*).

$$n(CH_3)_3SiSi(CH_3)_2(CN) \xrightarrow[7\text{ hr}]{175^\circ\text{C}} (n-1)(CH_3)_3Si(CN) + CH_3[Si(CH_3)_2]_{n+1}(CN)$$

$$n\,CH_3[Si(CH_3)_2]_3(CN) \xrightarrow[60\text{hr}]{175^\circ\text{–}195^\circ\text{C}} (n-1)(CH_3)_3Si(CN) + CH_3[Si(CH_3)_2]_{2n+1}(CN)$$

A mechanism for the disproportionation reaction has been suggested which involves the formation of an intermediate species (or transition state) in which a lone pair of electrons from the cyanide group of one molecule interacts with vacant silicon 3*d* orbitals of an adjacent molecule (or more probably, partly with a *d* orbital of each silicon atom simultaneously), the silicon–silicon bond being thereby weakened.



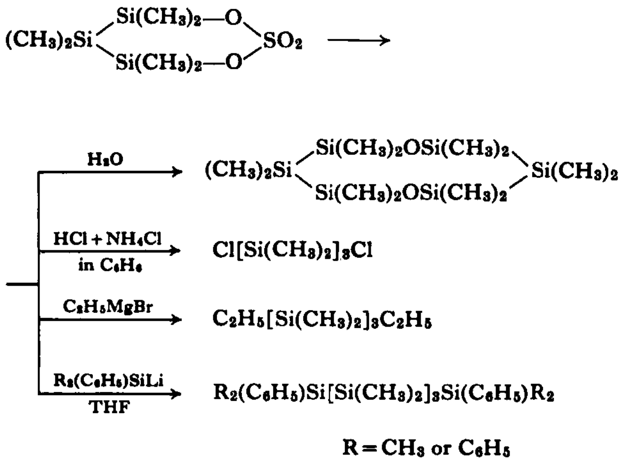
b. *Si—NCO Compounds.* Isocyanatopentamethyldisilane (pentamethyldisilanyl isocyanate), $(CH_3)_5Si_2NCO$, is prepared in about 50% yield by the reaction of chloropentamethyldisilane with silver cyanate (*188*). Evidence for the isocyanate structure of the compound is afforded by a close resemblance of its infrared spectrum to that of isocyanatotrimethylsilane and silicon tetraisocyanate. The spectrum displays the symmetrical NCO stretching vibration at 1427 cm^{-1} [1435 cm^{-1} for $(CH_3)_3SiNCO$ and 1482 cm^{-1} for $Si(NCO)_4$] and the antisymmetrical at 2280 cm^{-1} [2282 cm^{-1} for $(CH_3)_3SiNCO$ and 2284 cm^{-1} for $Si(NCO)_4$], but no normal cyanate absorption in the vicinity of 1200 and 2250 cm^{-1} and no Si—O—C in the 1050–1090 cm^{-1} region.

c. *Si—N_3 Compounds.* Pentamethyldisilanyl azide, $(CH_3)_5Si_2N_3$, has been prepared by the interaction of chloropentamethyldisilane and a metal azide MN_3, where M is lithium, sodium, potassium or silver (*185*).

4. *Silicon Sulfates and Sulfonates*

Four organopolysilicon sulfates have been prepared and studied recently (*115*). A most convenient preparative method involves the reaction of an appropriate chloropolysilane with a theoretical amount of 100% sulfuric acid, which usually is employed for synthesis of the monosilicon sulfates. No appreciable cleavage of the silicon–silicon bond occurs. In general, organopolysilicon sulfates are relatively stable to heat and can be isolated by distillation under reduced pressure. Yields are very high (about 80–95%). These sulfates sometimes are also obtained from the residue of distillation of the organic layer resulting from halogenodemethylation of permethylated polysilanes (Section II, A, 1,a). Whereas hexamethyltrisilanylene sulfate is a monomeric (by mass spectrometry) crystalline solid, readily soluble in most inert organic solvents, tetramethyldisilanylene sulfate is an insoluble powder and hence probably polymeric.

All of these sulfates are extremely hygroscopic, and undergo many of the reactions that are known to the monosilicon sulfates without cleavage of the silicon–silicon bond. Typical examples of reactions of hexamethyltrisilanylene sulfate are illustrated by the following equations:



The reaction with excess $R_2(C_6H_5)SiLi$ reagents in tetrahydrofuran for a prolonged period of time leads to considerable formation of dodecamethylcyclohexasilane, $[(CH_3)_2Si]_6$, and $R_2(C_6H_5)SiSi(C_6H_5)R_2$ (see Section III, C, 7).

By an interesting reaction involving trimethylsilyl chlorosulfonate and hexamethyldisilane, two methanesulfonates containing the silicon–silicon bond have recently been prepared (*13*).

$$(CH_3)_3SiSO_3Cl + (CH_3)_6Si_2 \xrightarrow{-(CH_3)_3SiCl} CH_3SO_3Si_2(CH_3)_5 \xrightarrow{(CH_3)_3SiSO_3Cl} [CH_3SO_3Si(CH_3)_2\text{—}]_2$$

5. *Silicon–Metal Compounds*

The chemistry of a class of organometallic compounds that contain a linkage between two different metallic and/or metalloidal elements has recently been the subject of considerable study (*195*, *207*), but only very little interest has been shown in such compounds with the silicon–silicon–metal bond. Only a few derivatives of mercury and alkali metals are known.

(Pentaethyldisilanyl)ethylmercury, bis(pentaethyldisilanyl)mercury and (pentaethyldisilanyl)triethylgermylmercury are prepared by means of reactions indicated by the following equations (*198*).

$$(C_2H_5)_3SiSi(C_2H_5)_2H + (C_2H_5)_2Hg \xrightarrow[-C_2H_6]{160°C} \underset{19.5\%}{(C_2H_5)_3SiSi(C_2H_5)_2HgC_2H_5} + \underset{8.1\%}{[(C_2H_5)_3SiSi(C_2H_5)_2]_2Hg}$$

$$(C_2H_5)_3SiSi(C_2H_5)_2HgC_2H_5 + (C_2H_5)_3GeH \rightarrow \underset{50.4\%}{(C_2H_5)_3SiSi(C_2H_5)_2HgGe(C_2H_5)_3}$$

Interestingly, as compared with usual unsymmetrically substituted diorganomercurials, these mercury derivatives are thermally stable enough to be distilled under reduced pressure without undergoing decomposition or disproportionation.

Certain organopolysilanyl alkali metal compounds are formed as reactive intermediates under appropriate conditions. They will be described in some detail in Section III, C, 7.

III

PERALKYLATED POLYSILANES

In this section, for convenience, we first deal with the synthesis and some physical properties of permethylated polysilanes, and then synthesis of other peralkylated and partially phenylated methyl polysilanes. Finally, chemical reactions of all such types of compounds will be discussed together.

A. Permethylated Polysilanes

The three types of compounds to be considered here are a homologous series of linear polysilanes with the general formula $CH_3[Si(CH_3)_2]_nCH_3$, where n equals 2 through 12; a few branched-chain compounds; and three cyclic polysilanes of the formula $[(CH_3)_2Si]_n$, n being 5, 6, and 7.

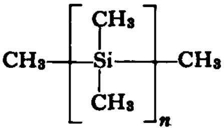
1. *Synthesis*

a. *Alkali Metal Condensation of Methylhalosilanes.* The most convenient and generally applicable method for synthesis involves condensation of methylhalosilanes (usually the chlorosilanes) by treatment with sodium, potassium, sodium-potassium alloy, or lithium. The reaction is carried out under a variety of conditions, depending upon the nature of halosilanes and metals used.

The synthesis of hexamethyldisilane is most conveniently accomplished by the coupling of trimethylchlorosilane using sodium-potassium alloy as the condensing agent. Here, the reaction smoothly proceeds under ordinary pressure in the absence (75% yield) (*178*) as well as in the presence of an inert solvent such as xylene (69% yield) (*209*) and tetrahydrofuran (*178*). No special techniques are required. The use of potassium alone also permits one to obtain the disilane from trimethylchlorosilane in good yield either in the absence (92%) (*16*) or in the presence of solvent [in tetrahydrofuran, 50% (*16*); in ethylene glycol dimethyl ether, 59% (*16*); in hexamethyldisilane, 85% yield (*180*)]. However, if sodium is used for the coupling of trimethylchlorosilane, it is necessary to shake the reagents with a catalytic amount of ethyl acetate at 200°–230° C for a long period of time in an autoclave (40–60% yield) (*102*) or to stir the reactants with an anhydrous aluminum chloride catalyst vigorously by means of a high-speed agitator (10^4 rpm) at 160°–180° C in decalin (75% yield) (*180, 181*). On the other hand, trimethyliodosilane readily undergoes coupling to hexamethyldisilane with the aid of sodium (*194*).

The action of liquid sodium amalgam on trimethylchlorosilane (*34a, 34b*) or -bromosilane (*207*) at room temperature results in the exclusive formation of bis(trimethylsilyl)mercury, $[(CH_3)_3Si]_2Hg$, which is relatively stable to heat. This compound, however, undergoes decomposition on heating at 100°–160° C for a day to give hexamethyldisilane in quantitative yield (*9, 34a, 34b, 207*).

The homologous series of linear polysilanes with the formula (XIII) are prepared by treating appropriate methylchlorosilanes with sodium–potassium alloy in an inert solvent such as xylene, tetrahydrofuran, benzene–ligroin, or benzene–*n*-heptane (*102*, *108*, *176*, *209*). In the preparation of polysilanes higher than tetrasilane, it is desirable to choose two chlorosilanes employed so that the polysilanes to be produced may differ at least by two silicon atoms from each other in order to facilitate the separation of products by fractional distillation.



$$CH_3-\left[\begin{array}{c} CH_3 \\ | \\ -Si- \\ | \\ CH_3 \end{array}\right]_n-CH_3$$

(XIII)

$$2\ (CH_3)_3SiCl + Cl(CH_3)_2SiSi(CH_3)_3 \rightarrow (XIII),\ n=3$$

$$2\ Cl(CH_3)_2SiSi(CH_3)_3 \rightarrow (XIII),\ n=4$$

$$2\ (CH_3)_3SiSi(CH_3)_2Cl + x\ Cl(CH_3)_2SiSi(CH_3)_2Cl \rightarrow (XIII),\ n=4, 6, 8, 10, 12$$

$$2\ CH_3[Si(CH_3)_2]_3Cl + x\ Cl[Si(CH_3)_2]_3Cl \rightarrow (XIII),\ n=6, 9, 12$$

$$2\ (CH_3)_3SiCl + x\ Cl[Si(CH_3)_2]_3Cl \rightarrow (XIII),\ n=5, 8, 11$$

$$2\ (CH_3)_3SiSi(CH_3)_2Cl + x\ Cl[Si(CH_3)_2]_3Cl \rightarrow (XIII),\ n=7$$

A variation of the preparative method for octamethyltrisilane (XIII; $n = 3$) involves the reaction of dimethyldichlorosilane with lithium in the presence of a large excess of trimethylchlorosilane in tetrahydrofuran (*60*). The yields of the trisilane are good (~65%), and small amounts of the next two higher homologs also are obtained. An advantage claimed for this procedure is that it is a one-step synthesis employing commercially available materials.

$$2\ (CH_3)_3SiCl + (CH_3)_2SiCl_2 + 4\ Li \xrightarrow{THF} \underset{n=3\text{–}5}{CH_3[Si(CH_3)_2]_nCH_3}$$

When a smaller ratio of $(CH_3)_3SiCl$ to $(CH_3)_2SiCl_2$ is used, the series of compounds $CH_3[Si(CH_3)_2]_nCH_3$ with $n = 3$–8 and 10 is obtained along with some dodecamethylcyclohexasilane.

A highly branched-chain permethylated polysilane, tetrakis(trimethylsilyl)silane, can be prepared in 70% yield by a mixed lithium coupling of trimethylchlorosilane (20% molar excess) and silicon tetrachloride in tetrahydrofuran (*63*).

$$4\,(CH_3)_3SiCl + SiCl_4 + 5\,Li \xrightarrow{THF} [(CH_3)_3Si]_4Si$$

Tris(trimethylsilyl)silyllithium, which is readily formed upon treatment of tetrakis(trimethylsilyl)silane with methyllithium or triphenylsilyllithium in ether–tetrahydrofuran (*63*), is useful as the reagent for construction of molecules of an interesting class of highly sterically hindered methylpolysilanes. The synthesis of hexakis(trimethylsilyl)disilane gives an example (*59*).

$$[(CH_3)_3Si]_3SiLi + ClSi[Si(CH_3)_3]_3 \rightarrow [(CH_3)_3Si]_3SiSi[Si(CH_3)_3]_3 + LiCl$$

Three permethylated cyclosilanes of the formula $[(CH_3)_2Si]_n$ with $n = 5$–7 are prepared by allowing dimethyldichlorosilane to react with sodium–potassium alloy in tetrahydrofuran. From this reaction, an insoluble polymeric mass and a crystalline solid are produced (*21*, *177*). The latter consists, for the most part, of dodecamethylcyclohexasilane but it also contains decamethylcyclopentasilane and tetradecamethylcycloheptasilane in small quantities. The amounts of both five- and seven-membered cyclosilanes are much increased if the reaction is worked up immediately after the addition of the dichlorosilane is completed with little or no refluxing. The three cyclosilanes can be separated by preparative gas chromatography (*21*).

The coupling of dimethyldichlorosilane by treatment with lithium in tetrahydrofuran in the presence of a catalytic amount of triphenylsilyllithium affords another convenient method for synthesis of dodecamethylcyclohexasilane. The yields are in the range of 60–70% (*76*).

$$6\,(CH_3)_2SiCl_2 + 12\,Li \xrightarrow[THF]{(C_6H_5)_3SiLi} [(CH_3)_2Si]_6 + 12\,LiCl$$

Possible mechanisms of catalysis of triphenylsilyllithium will be considered in Section III, C, 8.

b. *Methylation of Halopolysilanes with Organometallic Reagents*. The use of reactions of organometallic compounds, such as a methyl Grignard reagent (*19*, *132a*) and dimethylzinc (*14*), with hexahalodisilanes (mostly Si_2Cl_6) constitutes a classical method for synthesis of hexamethyldisilane. A variation of this method which involves the utilization of the "disilane fraction" in place of hexahalodisilane provides a most convenient and inexpensive route to hexamethyldisilane (*125*, *126*, *129*).

$$\underset{\text{Disilane fraction}}{(CH_3)_nSi_2Cl_{6-n}} + (6-n)\,CH_3MgX \rightarrow (CH_3)_6Si_2 + (6-n)\,MgClX$$

No attempts have been made to prepare permethylated polysilanes higher than the disilane by means of a similar reaction with perhalopolysilanes except for preparation of $[(CH_3)_2Si]_x$ of indefinite structure from $[SiBr_2]_x$ obtainable through reduction of $SiBr_4$ with silicon at 1200° C (*160*). Such an approach appears to be unpromising in view of an observation that the action of phenylmagnesium bromide on octachlorotrisilane exclusively results in cleavage of the silicon–silicon bond giving hexaphenyldisilane and tetraphenylsilane, and yields no traces of the expected octaphenyltrisilane (*161*). On the other hand, silicon–silicon cleavage is slight, if any, when partially methylated chloropolysilanes are further methylated with the Grignard reagent.

$$Cl[Si(CH_3)Cl]_nCl + (n+2)\,CH_3MgBr \rightarrow CH_3[Si(CH_3)_2]_nCH_3$$

(*187*)

$$[Cl_2(CH_3)Si]_3SiCH_3 + CH_3MgBr \rightarrow [(CH_3)_3Si]_3SiCH_3$$

(*4*)

c. *Miscellaneous*. The mercury $6(^3P_1)$ photosensitization of trimethylsilane gives rise to the formation of hexamethyldisilane (*135*). Hexamethyldisilane is also produced along with many other compounds from the condensation of tetramethylsilane by an electrical discharge (*78*). The thermal decomposition of diethylsilane, $(C_2H_5)_2SiH_2$, at 460° C gives solid polymeric material containing silicon–silicon bonds, $(SiCH_3)_x$, in addition to other products (*43–45*). The pyrolysis at 300°–400° C in a nitrogen atmosphere of high-molecular-weight insoluble permethylpolysilane, obtained by lithium condensation of dimethyldichlorosilane in tetrahydrofuran, yields dodecamethylcyclohexasilane (*136*). In the presence of alkali metal compounds, such rearrangement of the silicon–silicon bond can be effected under much milder conditions, which will be described in some detail in this Section, C, 7.

2. *Some Physical Properties*

Permethylated linear polysilanes (XIII) are stable colorless liquids or white crystalline substances. Their melting points are plotted against the number of silicon atoms in Fig. 1. It is seen that the alternating effect of odd and even numbered structures on the melting point exists up to the octasilane, but afterward the melting points display a regular progression as the molecular weight increases (*108*). In Fig. 2 is plotted the variation in viscosity with the number of silicon atoms of the permethylated linear

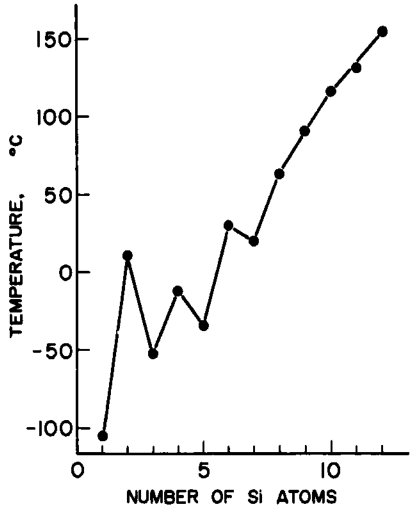


FIG. 1. Variation of melting point with the number of silicon atoms in the case of permethylated linear polysilanes.

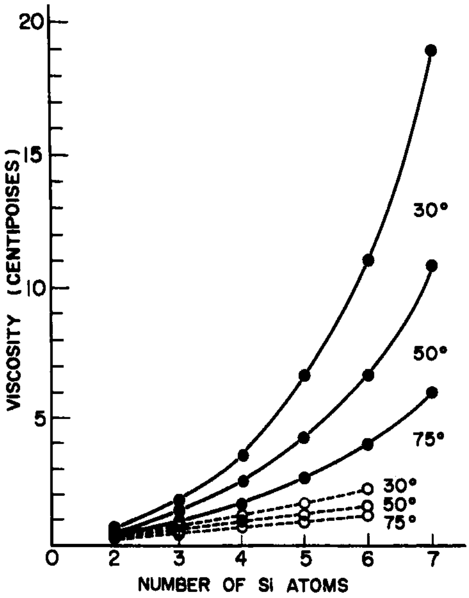


FIG. 2. Viscosities of permethylated polysilanes and polysiloxanes at different temperatures: ●, polysilanes; ○ polysiloxanes.

polysilanes (*106*) and polysiloxanes (*85*). The figure shows that both the viscosities of the polysilanes and their change with temperature are considerably greater than those of the analogous polysiloxanes. Energies of activation of viscous flow, E_{vis}, for the polysilanes and polysiloxanes are

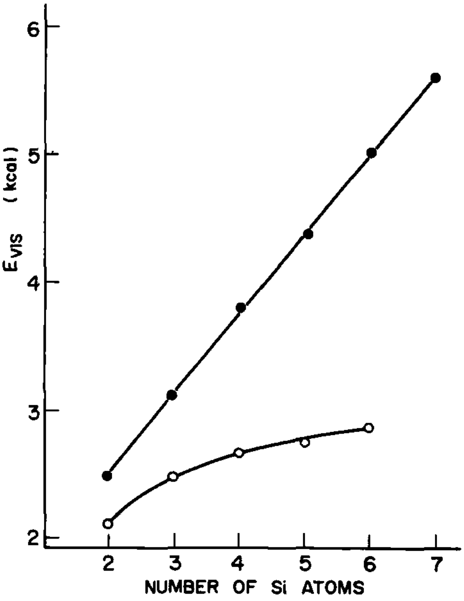


FIG. 3. Relation between E_{vis} and the number of silicon atoms in the permethylated linear polysilanes and polysiloxanes; ●, polysilanes; ○, polysiloxanes.

plotted against the number of silicon atoms in Fig. 3. For the polysilanes, the value of E_{vis} increases as a linear function of the number of silicon atoms. The pronounced difference in physical properties, including viscosity and its temperature coefficient for viscous flow, between the polysilanes and polysiloxanes has been discussed in the literature (*205*).

Both highly branched and cyclic permethylated polysilanes are snow-white crystalline solids with relatively high melting points.

B. Other Peralkylated Polysilanes

The synthesis of both symmetrically and unsymmetrically substituted organopolysilanes is achieved in analogous fashion to that of permethylated polysilanes. Some examples are given below.

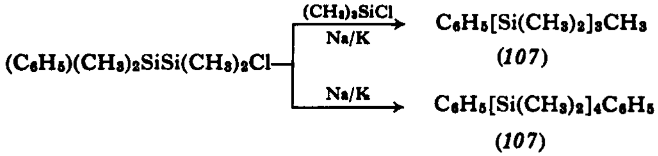
$$2\,R_3SiX + 2\,Na \rightarrow R_3SiSiR_3 + 2\,NaX$$
$R = C_2H_5;\ X = Cl$ (*64*)
$R = C_2H_5,\ n\text{-}C_3H_7,\ n\text{-}C_4H_9,\ \text{iso-}C_5H_{11},\ n\text{-}C_6H_{13};\ X = I$ (*194*)

$$2\,R(C_2H_5)(n\text{-}C_3H_7)SiCl + 2\,Na \rightarrow [R(C_2H_5)(n\text{-}C_3H_7)Si\text{—}]_2 + 2\,NaCl$$
$R = C_6H_5,\ C_6H_5CH_2$ (*97*)

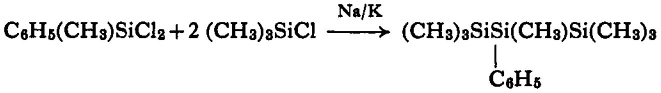
$$(C_2H_5)_3SiSi(C_2H_5)_2Br + 2\,Na \rightarrow C_2H_5[Si(C_2H_5)_2]_4C_2H_5$$
(*140*)

$$I_3SiSiI_3 + 3(C_2H_5)_2Zn \rightarrow (C_2H_5)_3SiSi(C_2H_5)_3 + 3\,ZnI_2$$
(*41*)

$$(SiBr_2)_x + 2x\,RMgX \rightarrow (SiR_2)_x + 2x\,MgXBr$$
$R = C_2H_5,\ C_3H_7,\ C_4H_9$ (*160*)



$$(C_6H_5)(CH_3)_2SiSi(CH_3)_2Cl \xrightarrow[Na/K]{(CH_3)_3SiCl} C_6H_5[Si(CH_3)_2]_3CH_3 \quad (107)$$
$$(C_6H_5)(CH_3)_2SiSi(CH_3)_2Cl \xrightarrow{Na/K} C_6H_5[Si(CH_3)_2]_4C_6H_5 \quad (107)$$



$$C_6H_5(CH_3)SiCl_2 + 2\,(CH_3)_3SiCl \xrightarrow{Na/K} (CH_3)_3SiSi(CH_3)(C_6H_5)Si(CH_3)_3$$

(*107*)

Hexaalkyldisilanes, along with other products, are formed when tetraalkylsilanes are heated with hydrogen at high temperatures and pressures (*33*, *87*).

$$2\,RSiR'_3 + H_2 \xrightarrow[100\ \text{atm}]{360^\circ C} 2\,RH + R'_3\,SiSiR'_3$$
$R = C_2H_5,\ C_6H_5,\ R' = CH_3;$
$R = C_2H_5,\ C_3H_7,\ \text{iso-}C_4H_9,\ \text{iso-}C_5H_{11},\ R' = C_2H_5$

The formation of hexaethyldisilane, along with other products, is also encountered when a mixture of triethylsilane and diethylzinc is heated at 160° C for 8 hours (*199*).

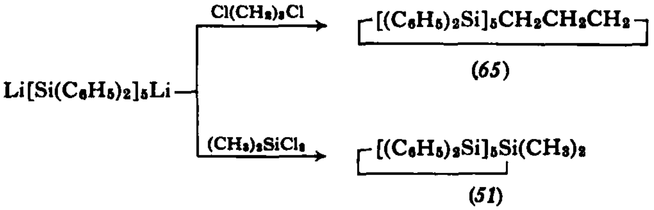
Various types of partially arylated alkylpolysilanes are most conveniently obtainable by use of the silyl metallic reagents. Since a number of examples of the synthesis of such a class of compounds have been given in recent reviews (*48*, *51*, *73*, *76a*, *212*), only a few are illustrated below.

$$(+)\text{-neo-}C_5H_{11}(C_6H_5)(CH_3)Si^{*}Cl + (C_6H_5)_2(CH_3)SiLi \rightarrow (-)\text{-neo-}C_5H_{11}(C_6H_5)(CH_3)Si^{*}Si(CH_3)(C_6H_5)_2$$
(*172*)

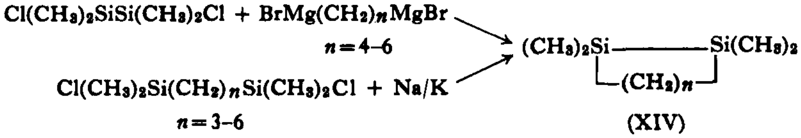
$$2\,(C_6H_5)_3SiLi + Cl[Si(CH_3)_2]_nCl \xrightarrow{THF} (C_6H_5)_3Si[Si(CH_3)_2]_nSi(C_6H_5)_3$$
$n = 1\text{–}5$ (*115*)

$$\mathrm{Li[Si(C_6H_5)_2]_nLi} \xrightarrow{(\mathrm{CH_3})_3\mathrm{PO_4}} \mathrm{CH_3[Si(C_6H_5)_2]_nCH_3}$$

$n = 4$ and 5 (*88*)

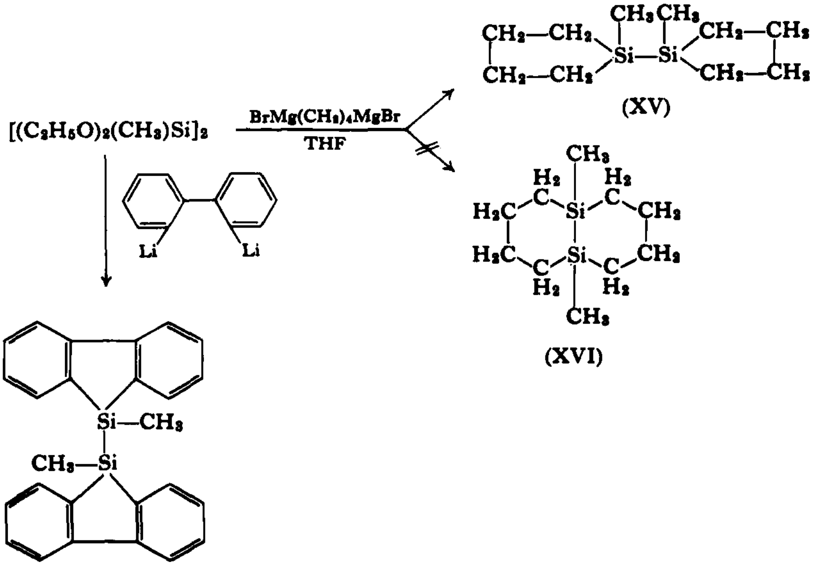


A class of compounds of the general formula (XIV) can be prepared by two types of reaction: the action of the polymethylenedimagnesium dibromide on 1,2-dichlorotetramethyldisilane in tetrahydrofuran, and sodium–potassium condensation of α,ω-bis (chlorodimethylsilyl)alkanes in benzene–n-heptane solution (*124*).



(XIV)

Yields of the disilacylclopentane (XIV, $n=3$), hexane (XIV; $n=4$) and heptane (XIV; $n=5$) are satisfactory, whereas those of the disilacyclooctane



(XV)

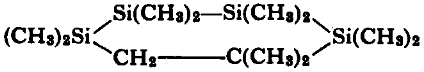
(XVI)

(XIV; $n = 6$) are extremely low (0–5%) in either method. This is doubtless due to the severely increased steric interaction of nonbonded groups attached to the ring, i.e., an axial methyl group and three axial hydrogen atoms on either side of the ring, in addition to a lowering of the probability of intramolecular collision of the two reactive atoms at the chain ends.

When tetraethoxy-1,2-dimethyldisilane is treated with tetramethylenedimagnesium dibromide in tetrahydrofuran, bis(1-methyl-1-silacyclopentyl) (XV), and not its isomeric bicyclodisilane (XVI), is formed in 62% yield (*110*). Analogously, the reaction with 2,2′-dilithiodiphenyl produces 5,5′-dimethyl-5,5′-bis(dibenzosilole) (*127*).

An interesting silacycloalkane containing silicon–silicon bonds in the ring (XVII) has been obtained by introducing isobutylene into a reaction mixture of dimethyldichlorosilane and lithium metal in tetrahydrofuran at 0°–10° C (*137*).

$$(CH_3)_2SiCl_2 + 2\,Li \xrightarrow{-2\,LiCl} [(CH_3)_2Si\!:] \xrightarrow{(CH_3)_2C{=}CH_2}$$



(XVII)

C. Chemical Properties

1. *Thermolysis*

Hexamethyldisilane appears to be stable up to about 500° C, but undergoes isomerization when passed in a quartz tube heated at 600° C to give trimethylsilane and trimethyl(dimethylsilylmethyl)silane in the molar ratio of approximately 1:4, along with the unchanged disilane (*151*, *164*).

$$(CH_3)_3SiSi(CH_3)_3 \xrightarrow{600^\circ C} (CH_3)_3SiCH_2Si(CH_3)_2H + (CH_3)_3SiH$$

This process may well be understood in terms of intramolecular rearrangement of the disilane by a free radical chain mechanism, the average kinetic chain length being about 4.

$$(CH_3)_3SiSi(CH_3)_3 \rightarrow 2\,(CH_3)_3Si\cdot$$

$$(CH_3)_3Si\cdot + (CH_3)_3SiSi(CH_3)_3 \rightarrow (CH_3)_3SiH + (CH_3)_3SiSi(CH_3)_2CH_2\cdot$$

$$(CH_3)_3SiSi(CH_3)_2CH_2\cdot \rightarrow (CH_3)_3SiCH_2Si(CH_3)_2\cdot$$

$$(CH_3)_3SiCH_2Si(CH_3)_2\cdot + (CH_3)_3SiSi(CH_3)_3 \rightarrow (CH_3)_3SiCH_2Si(CH_3)_2H + (CH_3)_3SiSi(CH_3)_2CH_2\cdot$$

In contrast, 1,2-diphenyltetramethyldisilane does not undergo thermolysis at 600° C, and is recovered unchanged. This apparently indicates that substitution by phenyl groups on silicon strengthens the silicon–silicon bond (*151*).

2. *Reaction with Benzoyl and Di-tert-butyl Peroxides*

Decomposition of benzoyl peroxide in hexamethyldisilane at 80° C gives, as major products, benzene, benzoic acid, 1,2-bis(pentamethyldisilanyl)-ethane and benzylpentamethyldisilane (*151*). The reaction of hexamethyldisilane in carbon tetrachloride with benzoyl peroxide (at reflux temperature) and with di-*tert*-butyl peroxide (in a sealed tube at 129° C) gives (chloromethyl)pentamethyldisilane as the main product arising from the silane (*150*). In no case are rearrangement products formed. Therefore, in solution at relatively low temperature, the pentamethyldisilanylmethyl radical does not undergo rearrangement as in the thermolysis. The main fate of this free radical is dimerization in the absence of solvent or chlorine atom abstraction when carbon tetrachloride is present.

$$2\,(CH_3)_3SiSi(CH_3)_2CH_2\cdot \rightarrow [(CH_3)_3SiSi(CH_3)_2CH_2\text{—}]_2$$

$$(CH_3)_3SiSi(CH_3)_2CH_2\cdot + CCl_4 \rightarrow CCl_3\cdot + (CH_3)_3SiSi(CH_3)_2CH_2Cl$$

Analogous results have been observed with the decomposition of benzoyl peroxide and di-*tert*-butyl peroxide in hexaethyldisilane (*196*).

These facts suggest that intramolecular rearrangement of the disilanylmethyl radical must require a high activation energy.

3. *Cleavage by Halogens and Halides*

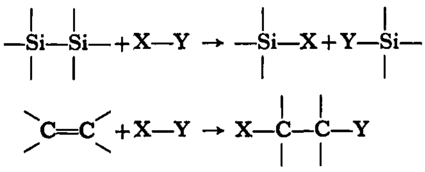
a. *By Halogens.* Hexaalkyldisilanes and alkylchlorodisilanes of lower chlorine content are easily cleaved by halogens (*64*, *121*, *178*),

$$R_3SiSiR_3 + X_2 \rightarrow 2\,R_3SiX$$
$$X = Cl,\ Br,\ \text{and}\ I$$

whereas hexaaryldisilanes and alkylchlorodisilanes of higher chlorine content such as $(CH_3)_3Si_2Cl_3$ and $(CH_3)_2Si_2Cl_4$ are only slowly attacked or highly resistant to cleavage (*103*, *120*, *183*). The relative reactivity of halogens for cleavage of a given silicon–silicon bond decreases in the order chlorine > bromine ≫ iodine (*183*). Thus, the cleavage of 1,2-dichlorotetramethyldisilane by bromine occurs quantitatively at room temperature, but that by iodine only to some 20% extent after 48 hours, although the latter is brought to completion if aluminum iodide is added (*178*).

$$\mathrm{Cl(CH_3)_2SiSi(CH_3)_2Cl} \begin{cases} \xrightarrow{\mathrm{Br_2}} 2\ \mathrm{(CH_3)_2SiClBr} \\ \xrightarrow{\mathrm{I_2\ (AlI_3)}} 2\ \mathrm{(CH_3)_2SiClI} \end{cases}$$

A study of kinetics of the cleavage of several alkyldisilanes by iodine and by bromine indicates that the reaction is second order, first order in each reactant, and that the substitution of methyl groups by chlorine on the silicon–silicon linkage considerably reduces the rate of cleavage (*183*). The cleavage of the silicon–silicon bond by halogens thus appears to resemble the electrophilic addition of halogens to the carbon–carbon double bond, the rates of which are also decreased by electron-withdrawing substituents. Examples indicating some parallelism between cleavage of the silicon–silicon bond and electrophilic addition reactions to the carbon–carbon double bond are often encountered.



$$\mathrm{{-}Si{-}Si{-}} + \mathrm{X{-}Y} \rightarrow \mathrm{{-}Si{-}X} + \mathrm{Y{-}Si{-}}$$

$$\mathrm{{>}C{=}C{<}} + \mathrm{X{-}Y} \rightarrow \mathrm{X{-}C{-}C{-}Y}$$

The stabilization of the silicon–silicon bond by negative substituents is also indicated in the reaction of one molar equivalent of bromine with octamethyltrisilane and with decamethyltetrasilane in chloroform at −40° C, which proceeds entirely as indicated by the following equations, and constitutes a most convenient method for synthesis of the bromodisilane and -trisilane (Section II, A, 1,d) (*178*).

$$\mathrm{(CH_3)_3SiSi(CH_3)_2Si(CH_3)_3 + Br_2 \rightarrow (CH_3)_3SiBr + (CH_3)_3SiSi(CH_3)_2Br}$$

$$\mathrm{(CH_3)_3SiSi(CH_3)_2Si(CH_3)_2Si(CH_3)_3 + Br_2}$$

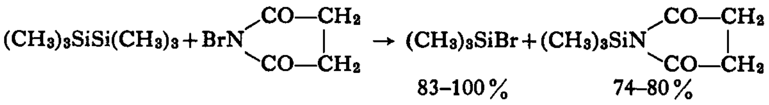
$$\begin{cases} \rightarrow 2\ \mathrm{(CH_3)_3SiSi(CH_3)_2Br} \quad 57\% \\ \rightarrow \mathrm{(CH_3)_3SiBr + (CH_3)_3SiSi(CH_3)_2Si(CH_3)_2Br} \quad 43\% \end{cases}$$

Complete cleavage of the silicon–silicon bond in permethylated polysilanes is effected by the action of excess bromine in carbon tetrachloride at room temperature.

$$CH_3[Si(CH_3)_2]_nCH_3 + (n-1)\,Br_2 \rightarrow 2\,(CH_3)_3SiBr + (n-2)\,(CH_3)_2SiBr_2$$

This reaction can be employed for quantitative determination of the silicon–silicon bond in such and related types of compounds (*178*).

b. *By* N-*Bromosuccinimide.* *N*-Bromosuccinimide immediately reacts with hexamethyldisilane in chloroform and in carbon tetrachloride in the cold to give trimethylbromosilane and *N*-trimethylsilylsuccinimide in high yield (*20*, *148*). Similar results are also obtained in the presence of benzoyl peroxide at 80° C. No traces of (bromomethyl)pentamethyldisilane are formed.



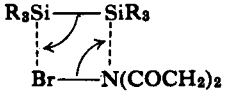
$$(CH_3)_3SiSi(CH_3)_3 + BrN\begin{matrix}CO—CH_2\\ |\\ CO—CH_2\end{matrix} \rightarrow \underset{83\text{–}100\%}{(CH_3)_3SiBr} + \underset{74\text{–}80\%}{(CH_3)_3SiN\begin{matrix}CO—CH_2\\ |\\ CO—CH_2\end{matrix}}$$

Similarly, the action of *N*-bromosuccinimide on 1,2-dimethyltetraethyldisilane (*20*) 1,2–dipenyltetramethyldisilane (*148*) exclusively leads to the cleavage of the silicon–silicon bond, although a gentle supply of heat is necessary to keep the reaction with the phenyl-substituted disilanes proceeding.

$$[C_6H_5(CH_3)_2Si—]_2 + BrN(COCH_2)_2 \rightarrow C_6H_5(CH_3)_2SiBr + \text{Other products}$$

$$C_6H_5(CH_3)_2SiSi(CH_3)_3 + BrN(COCH_2)_2 \rightarrow \underset{12.3\%}{C_6H_5(CH_3)_2SiBr} + \underset{67.4\%}{(CH_3)_3SiBr} + \text{Other products}$$

In view of the facts described above, a possible reaction mechanism seems to involve a four-centered transition state with electrophilic attack of bromine on one silicon assisted by nucleophilic attack of nitrogen on another.



c. *By Other Halides.* Hexamethyldisilane undergoes extensive cleavage of the silicon–silicon bond under conditions of peroxide-initiated chlorination with sulfuryl chloride and with *tert*-butyl hypochlorite (Section IV, A, 1,a). This bond is also very susceptible to oxidative cleavage by various salts of heavy metals (*20*, *166*). Thus, the reaction of hexamethyldisilane with tin(IV), copper(II) and nickel(II) chloride at elevated temperature (~150°–200° C) gives trimethylchlorosilane (44–86% yield) with formation of tin(II) and copper(I) chloride and metallic nickel, respectively. Similarly, 1,2-dimethyltetraethyldisilane reacts with nickel(II) bromide at 190°–200° C to give methyldiethylbromosilane in 44% yield along with reduced nickel (*20*). If this type of cleavage reaction is applied to an alkoxy-substituted disilane, the corresponding chloroalkoxymonosilane that is otherwise obtainable with difficulty can easily be prepared in good yield (*20*).

$$[CH_3(CH_3O)_2Si\text{—}]_2 + CuCl_2 \rightarrow \underset{87\%}{2\ CH_3Si(OCH_3)_2Cl} + Cu$$

Reaction of dodecamethylcyclohexasilane with phosphorus pentachloride (Section II, A, 1,d), hydrogen chloride, and *tert*-butyl chloride (Section II, C, 1,c), and reaction of hexamethyldisilane with hydrogen chloride at elevated temperature (Section II, A, 2) provide further examples of cleavage by halides.

4. *Cleavage by Sulfuric Acid*

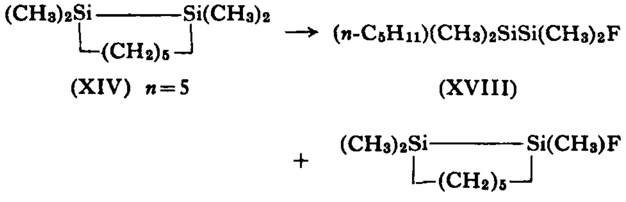
As mentioned earlier (Section II, A, 1,a), although the silicon–silicon bond in hexamethyldisilane is fairly resistant to oxidative cleavage by concentrated sulfuric acid, this bond in higher homologs of the series $CH_3[Si(CH_3)_2]_nCH_3$ becomes more reactive toward the acid with increasing chain length.

The behavior of 1,1,2,2-tetramethyl-1,2-disilacycloalkanes (XIV) toward concentrated sulfuric acid is dependent upon their ring size (*124*). Thus, both the disilacyclopentane (XIV; $n = 3$) and -hexane (XIV; $n = 4$) vigorously react with the acid at 17°–20° C and exclusively undergo cleavage of the silicon–silicon bond to give, after treatment with ammonium hydrogen fluoride, the corresponding α,ω-bis(fluorodimethylsilyl)alkanes in almost quantitative yield.

$$\underbrace{(CH_3)_2Si\text{———}Si(CH_3)_2}_{(CH_2)_n} \xrightarrow[2.\ NH_4F\cdot HF]{1.\ H_2SO_4} F(CH_3)_2Si(CH_2)_nSi(CH_3)_2F$$

(XIV) $n = 3$ and 4

On the other hand, reaction of the disilacycloheptane (XIV; $n = 5$) with sulfuric acid is not so energetic as that of the lower homologs and gives two major products with the silicon–silicon bond intact, (XVIII) and (XIX), in the ratio of about 1 : 1, along with three minor ones, (XX), (XXI), and (XXII). Only the last compound is a product arising from cleavage of the silicon–silicon bond.

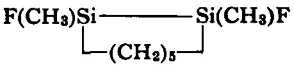


(XIV) $n=5$ (XVIII) (XIX)

$$\underbrace{(CH_3)_2Si\text{———}Si(CH_3)_2}_{(CH_2)_5} \longrightarrow (n\text{-}C_5H_{11})(CH_3)_2SiSi(CH_3)_2F + \underbrace{(CH_3)_2Si\text{———}Si(CH_3)F}_{(CH_2)_5}$$

$F(n\text{-}C_5H_{11})(CH_3)SiSi(CH_3)_2F$

(XX)



$$\underbrace{F(CH_3)Si\text{———}Si(CH_3)F}_{(CH_2)_5}$$

(XXI)

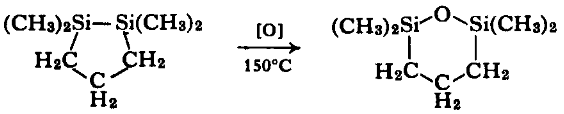
$F(CH_3)_2Si(CH_2)_5Si(CH_3)_2F$

(XXII)

The selective cleavage of the silicon–silicon bond in the disilacyclopentane and -hexane is probably due to the concentration of internal angular strain at this bond in such smaller polygonal molecules. In case of the disilacycloheptane, however, it seems likely that the strain is smaller and uniformly distributed all over the ring, and hence cleavage occurs preferentially at the silicon–carbon bond by the accepted mechanism involving both an electrophilic attack on carbon and nucleophilic attack on silicon by the sulfuric acid molecule(s) (*169*).

5. *Oxidation by Oxygen, Perbenzoic Acid, and Other Substances*

Acyclic peralkylated polysilanes are sufficiently stable to air oxidation to be handled at moderate to relatively high temperature without specific precautions. On the other hand, five-membered ring compounds are easily attacked by molecular oxygen and converted to siloxanes (*21*, *115*, *122*).



$$[(CH_3)_2Si]_5 \xrightarrow[\text{Room temp.}]{[O]} \text{Siloxanes}$$

Although organodisilanes are quite stable to oxidation by alkaline hydrogen peroxide (*101*), they are quantitatively oxidized to the corresponding siloxanes by perbenzoic acid (*149*). Thus, hexamethyldisilane is converted to hexamethyldisiloxane, and phenylpentamethyldisilane to phenylpentamethyldisiloxane, in almost quantitative yield. In the latter case, neither a symmetrical disiloxane (hexamethyl- or diphenyltetramethyldisiloxane) nor a compound arising from phenyl–silicon cleavage is formed.

$$\mathrm{R(CH_3)_2SiSi(CH_3)_3 + C_6H_5CO_3H \rightarrow R(CH_3)_2SiOSi(CH_3)_3 + C_6H_5CO_2H}$$
$$\mathrm{R = CH_3 \text{ or } C_6H_5}$$

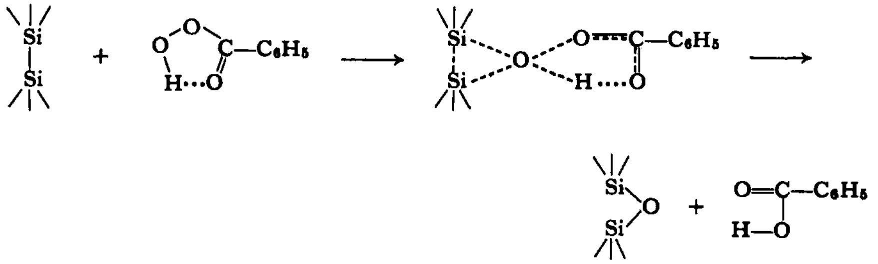
A kinetic study of the reaction of hexamethyldisilane and several ring-substituted phenylpentamethyldisilanes with perbenzoic acid in benzene indicates that the reaction is second order, first in each reactant. Table I lists second-order rate constants at 45° C and activation parameters for the reaction. It can be seen that the substitution of one methyl group by phenyl reduces the reactivity. The plots of logarithms of the rate constants against the Brown–Okamoto σ^+ values for the phenyl-substituted disilanes give a fairly good linear relationship with negative ρ values. This suggests that electron-donating substituents on the benzene ring of the disilane are capable of resonance interaction with the silicon atom, possibly through p_π–d_π conjugation, to make the silicon–silicon bond more reactive to the electrophilic cleavage. These features of this reaction are qualitatively parallel to those of the epoxidation of substituted ethylenes. However, for the peracid oxidation of disilanes, the entropy of activation is a controlling factor.

TABLE I

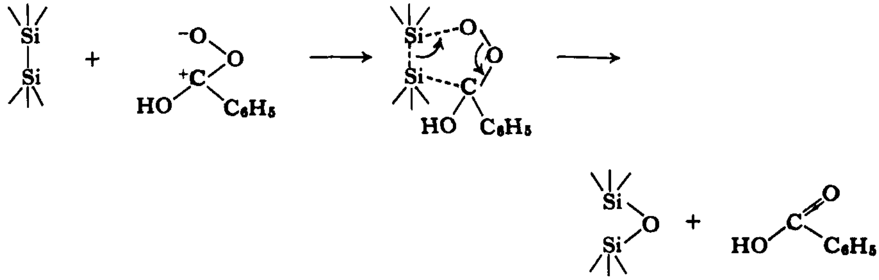
SECOND ORDER RATE CONSTANTS AT 45° C AND ACTIVATION PARAMETERS FOR OXIDATION REACTION OF DISILANES WITH PERBENZOIC ACID IN BENZENE

Disilane	$k_2 \times 10^4$(45° C) (liter/mole sec)	$\Delta H^{\ddagger}$ (kcal/mole)	$-\Delta S^{\ddagger}$ (e.u.)
$\mathrm{(CH_3)_3SiSi(CH_3)_3}$	11.7	13.7	27.3
p-$\mathrm{CH_3OC_6H_4Si(CH_3)_2Si(CH_3)_3}$	11.9	14.2	27.4
p-$\mathrm{CH_3C_6H_4Si(CH_3)_2Si(CH_3)_3}$	8.79	14.0	28.7
m-$\mathrm{CH_3C_6H_4Si(CH_3)_2Si(CH_3)_3}$	7.44	13.8	29.6
$\mathrm{C_6H_5Si(CH_3)_2Si(CH_3)_3}$	6.93	13.4	31.1
p-$\mathrm{ClC_6H_4Si(CH_3)_2Si(CH_3)_3}$	6.46	13.2	31.6
m-$\mathrm{ClC_6H_4Si(CH_3)_2Si(CH_3)_3}$	6.55	14.2	29.6
$\mathrm{C_6H_5Si(CH_3)_2Si(CH_3)_2C_6H_5}$	3.89	17.7	18.6

By analogy with the "molecular" mechanism proposed for epoxidation of olefins (7), a mechanism for the present reaction has been suggested which involves direct insertion of an oxygen atom by the electrophilic attack of a cyclic hydrogen-bonded form of the peracid on the silicon–silicon bond.



However, in view of the more recent data on kinetics of the reaction with 1,2-di(substituted phenyl)tetramethyldisilane (*158*) and the newly proposed epoxidation mechanism involving the 1,3-dipolar form of the peracid (*130*), the mechanism that follows also appears to be worth due consideration.



Oxidative cleavage of the organodisilanes also occurs with various other sorts of oxidizing agents, including nitrogen dioxide (*173*), 70% as well as fuming nitric acid, chromium trioxide in sulfuric acid, potassium permanganate in aqueous sulfuric acid (*167*), potassium dichromate in acetic acid (*51*), silver nitrate, mercuric acetate, and vanadium pentoxide (*20*).

$$(CH_3)_3SiSi(CH_3)_3 + 2\,HNO_3 \rightarrow (CH_3)_3SiOSi(CH_3)_3 + 2\,NO_2 + H_2O$$

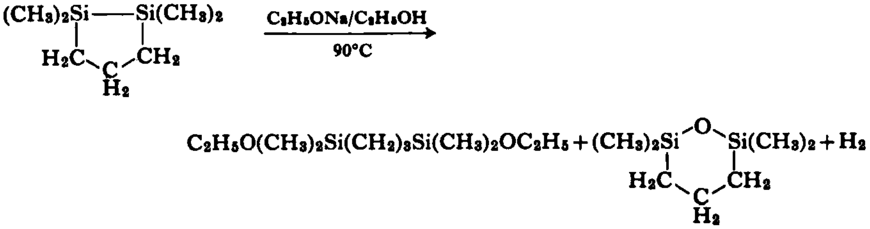
$$[(CH_3)_2Si]_6 \xrightarrow{[O]} \underset{n=3\text{–}8}{[(CH_3)_2SiO]_n}$$

$$(CH_3)_3SiSi(C_6H_5)_3 + AgNO_3 \rightarrow \text{Siloxanes} + Ag + NO$$

$$(CH_3)_3SiSi(CH_3)_3 + Hg(O_2CCH_3)_2 \xrightarrow[\text{reflux}]{[C_2H_5OCH_2CH_2]_2O} \underset{70\%}{2\,(CH_3)_3SiO_2CCH_3} + \underset{95\%}{Hg}$$

6. *Cleavage by Alcoholic Alkali*

Hexaorganodisilanes are quite resistant to alcoholic alkali (Section II, B, 2). However, 1,1,2,2-tetramethyl-1,2-disilacyclopentane undergoes cleavage exclusively at the silicon–silicon bond with evolution of an almost theoretical volume of hydrogen when heated at 90° C with 0.6 *N* sodium ethoxide in ethanol over an 80-hour period, giving products as depicted by the following equation (*124*).



In marked contrast, the next higher homolog, disilacyclohexane, is completely inert under the same conditions as above. These results indicate that the five-membered disilane is much more highly strained than the six-membered one.

7. *Reactions with Alkali Metals and Their Derivatives*

The preparation of organosilylmetallic compounds by cleaving aryl-substituted disilanes with alkali metals in an appropriate solvent, and their applications in organometallic syntheses, have recently been the subject of considerable study and are thoroughly reviewed elsewhere (*48*, *51*, *73*, *76a*, *212*). Incidentally, a recent study on the stereochemistry of lithium metal cleavage of the silicon–silicon bond in an optically active disilane, (−)-neo-$C_5H_{11}(C_6H_5)(CH_3)Si^*Si(CH_3)(C_6H_5)_2$, has revealed that the reaction proceeds with retention of configuration of silicon, and a possible mechanism has been proposed which involves a quasi-cyclic four-centered transition state (*172*). More recently, however, this mechanism has been criticized (*200*).

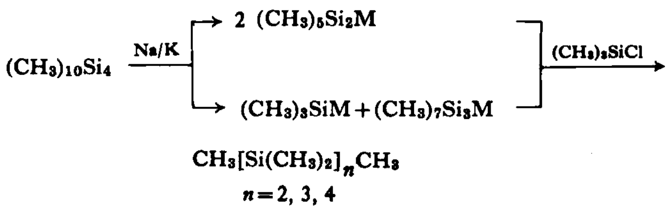
Unlike aryl-substituted disilanes, hexaalkyldisilanes are known not to undergo such cleavage.

Permethylated polysilanes higher than the disilane, on the other hand, do undergo cleavage by sodium–potassium alloy in tetrahydrofuran; the longer the chain, the easier the cleavage is (*177*, *179*). In a polysilyl anion, the negative charge can be distributed over several silicon atoms and this may greatly stabilize the anion.

$$(CH_3)_3Si{-}\overset{\ominus}{Si}R_2 \leftrightarrow (CH_3)_3\overset{\ominus}{Si}{=}SiR_2$$

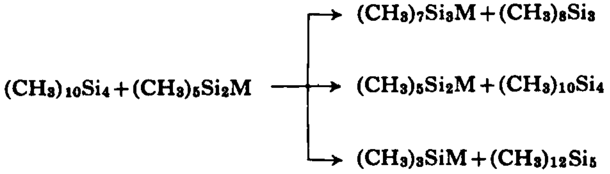
In agreement with this hypothesis, tetrakis(trimethylsilyl)silane gives tris(trimethylsilyl)silyllithium when treated with methyllithium or triphenylsilyllithium in tetrahydrofuran (*63*).

The cleavage of decamethyltetrasilane by sodium–potassium alloy followed by coupling with trimethylchlorosilane gives several lower homologs of methylpolysilanes of both linear and cyclic type (*179*). Although the formation of linear polysilanes up to the tetrasilane is understood in terms

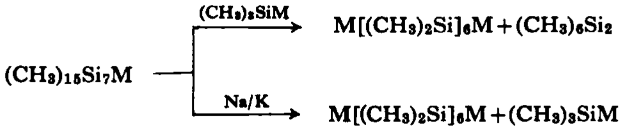


$$(CH_3)_{10}Si_4 \xrightarrow{Na/K} \left[\begin{array}{l} 2\ (CH_3)_5Si_2M \\ (CH_3)_3SiM + (CH_3)_7Si_3M \end{array}\right] \xrightarrow{(CH_3)_3SiCl} CH_3[Si(CH_3)_2]_nCH_3 \quad n = 2, 3, 4$$

of the simple cleavage of the tetrasilane, it is necessary to take into account further modes of cleavage in order to explain the formation of higher and cyclic derivatives. The following have been suggested:



$$(CH_3)_{10}Si_4 + (CH_3)_5Si_2M \rightarrow \begin{cases} (CH_3)_7Si_3M + (CH_3)_8Si_3 \\ (CH_3)_5Si_2M + (CH_3)_{10}Si_4 \\ (CH_3)_3SiM + (CH_3)_{12}Si_5 \end{cases}$$



$$(CH_3)_{15}Si_7M \rightarrow \begin{cases} \xrightarrow{(CH_3)_3SiM} M[(CH_3)_2Si]_6M + (CH_3)_6Si_2 \\ \xrightarrow{Na/K} M[(CH_3)_2Si]_6M + (CH_3)_3SiM \end{cases}$$

$$M[(CH_3)_2Si]_6M + (CH_3)_3SiCl \rightarrow M[(CH_3)_2Si]_6Cl + (CH_3)_3SiM$$

$$\xrightarrow{-MCl} [(CH_3)_2Si]_6$$

Of these equations, the first two illustrate SiSi/SiM redistribution, while the last indicates metal–chlorine exchange followed by intramolecular coupling.

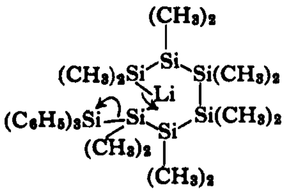
The mechanistic pathway for the preparation of dodecamethylcyclohexasilane by lithium coupling of dimethyldichlorosilane in the presence of triphenylsilyllithium (Section III, A, 1,a) is illustrated analogously in the following equations (*76*):

$$(C_6H_5)_3SiLi + ClSi(CH_3)_2R \longrightarrow (C_6H_5)_3SiSi(CH_3)_2R \xrightarrow{2\,Li} (C_6H_5)_3SiLi + LiSi(CH_3)_2R$$

$$(C_6H_5)_3SiSi(CH_3)_2R + LiSi(CH_3)_2R \rightarrow (C_6H_5)_3SiLi + R(CH_3)_2SiSi(CH_3)_2R$$

$$R = Cl,\ Si(C_6H_5)_3,\ \text{or}\ [Si(CH_3)_2]_nR$$

$$(C_6H_5)_3Si[Si(CH_3)_2]_6Si(C_6H_5)_3 \xrightarrow[-(C_6H_5)_3SiLi]{2\,Li}$$

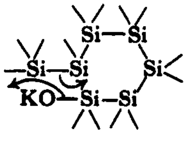


$$\xrightarrow{-(C_6H_5)_3SiLi} [(CH_3)_2Si]_6$$

Recently, polysilanes of formula $(C_6H_5)_3Si[Si(CH_3)_2]_nSi(C_6H_5)_3$ with $n = 1\text{–}5$ have been found to be converted to dodecamethylcyclohexasilane in good yield by treatment with a small amount of triphenylsilyllithium alone in tetrahydrofuran (*115*). Interestingly enough, when $(C_6H_5)_3SiSi(CH_3)_2\text{-}Si(C_6H_5)_3$ is treated with the silyllithium reagent, the five-membered cyclic compound is obtained in a higher yield than the six-membered one. Under similar conditions, a compound in which two silicon–silicon bonds are linked by a methylene bridge, $(C_6H_5)_3SiSi(CH_3)_2CH_2Si(CH_3)_2Si(C_6H_5)_3$, does not undergo cyclization to $[—Si(CH_3)_2CH_2Si(CH_3)_2—]_2$.

$$\cdots\ —[—(CH_3)_2Si—]_xOH \xrightarrow{KOH} \cdots\ —[(CH_3)_2Si—]_xOK$$

$$\longrightarrow \cdots$$



$$\longrightarrow \cdots\ \overset{|}{\underset{|}{Si}}—OK + [(CH_3)_2Si]_6$$

Dodecamethylcyclohexasilane can also be obtained in about 60% yield when the insoluble solid polydimethylsilane is heated for a few minutes with a catalytic amount of potassium hydroxide or sodium-naphthalene in tetrahydrofuran or better in diglyme (*168*). A possible mechanism is illustrated on p. 64.

8. *Formation of the Radical Anion* $[Si(CH_3)_2]_6^{\cdot-}$

Dodecamethylcyclohexasilane gives a radical anion when treated with sodium–potassium alloy in dimethoxyethane–tetrahydrofuran at −95° C (*86*). By ESR analysis, it was concluded that the unpaired electron is delocalized equally over all six silicon atoms and so contacts equally all of the protons on the 12 methyl groups of the molecule. Recently, similar radical anions $[Si(CH_3)_2]_5^{\cdot-}$ and $[Si(CH_3)_2]_7^{\cdot-}$ have been obtained from the five- and seven-membered ring cyclopolysilanes (*21, 205a*).

IV

CARBON-FUNCTIONAL ORGANOPOLYSILANES

The carbon-functional organopolysilanes are those organopolysilanes which contain at least one heteroatom or nonbenzenoid unsaturated linkage attached to silicon through carbon (*34, 47*). In spite of a vast number of carbon-functional monosilane derivatives of various types, such organopolysilanes so far prepared are limited both in number and in type. Some of the general methods for preparation of carbon-functional monosilanes are applicable to polysilanes, but others are not because the silicon–silicon bond in general is highly sensitive to cleavage by oxidizing agents.

A. Compounds Containing Heteroatoms in the Organic Portion

1. *Synthesis*

a. *Chlorination of Methyl Groups.* Photochemical chlorination of the "disilane fraction" [a mixture consisting mainly of $(CH_3)_2Si_2Cl_4$ and $(CH_3)_3Si_2Cl_3$] gives the mono- and dichlorinated products, which are most conveniently separated after exhaustive methylation of the silicon–chlorine bonds. Thus, (chloromethyl)pentamethyldisilane (XXIII) and (dichloromethyl)pentamethyldisilane (XXIV) are readily obtained in the pure state (*103, 120*).

$$(CH_3)_nSi_2Cl_{6-n} \xrightarrow[\text{UV light}]{Cl_2} (ClCH_2)(CH_3)_{n-1}Si_2Cl_{6-n} + (Cl_2CH)(CH_3)_{n-1}Si_2Cl_{6-n}$$

$$\xrightarrow{CH_3MgBr} \underset{\text{(XXIII)}}{(ClCH_2)(CH_3)_5Si_2} + \underset{\text{(XXIV)}}{(Cl_2CH)(CH_3)_5Si_2}$$

Although direct chlorination cannot be applied to methylchlorodisilanes of lower chlorine content as well as permethylated polysilanes because they are highly sensitive to cleavage, peroxide-initiated chlorination with sulfuryl chloride is fairly satisfactory for them. Thus, hexamethyldisilane (*120*) and 1,2-dichlorotetramethyldisilane (*110*) are converted to the corresponding monochloromethyl derivatives, although extensive cleavage of the silicon–silicon bond also occurs.

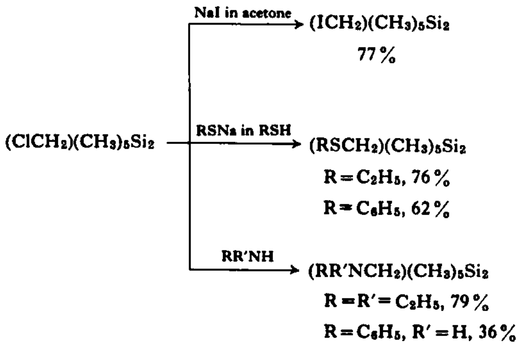
$$R(CH_3)_2SiSi(CH_3)_2R + SO_2Cl_2 \xrightarrow{(C_6H_5CO_2)_2} \underset{42\%}{(ClCH_2)(R)(CH_3)SiSi(CH_3)_2R} + R(CH_3)_2SiCl$$

$$R = CH_3 \text{ or } Cl$$

Hexamethyldisilane is converted to (chloromethyl-) and (dichloromethyl)pentamethyldisilane in lower yield by treatment with *tert*-butyl hypochlorite under ultraviolet irradiation (*166*). This process is accompanied by the significant formation of products arising from cleavage of the silicon–silicon bond and subsequent reactions.

Neither chlorination of alkyl groups higher than methyl nor bromination of any alkyls including methyl has been reported as yet.

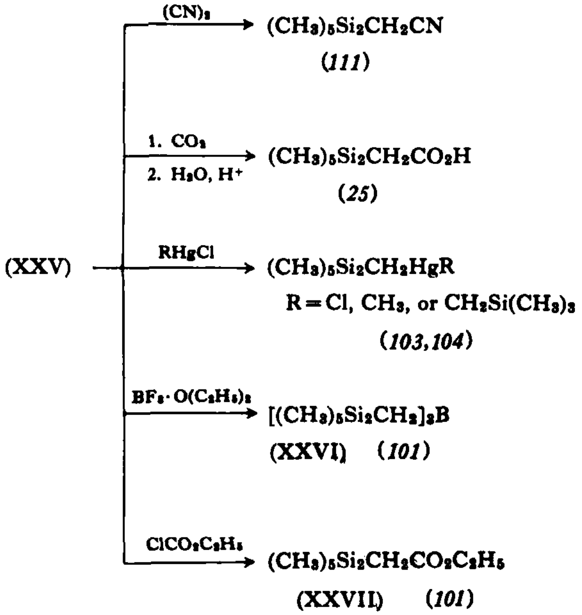
b. *Conversion of the Chloromethyl Group to Others.* (Chloromethyl)-pentamethyldisilane can be transformed into other (heteroatom-substituted methyl)pentamethyldisilanes in high yield by treatment with certain kinds of nucleophilic reagents. Examples are given below (*103*, *111*).



With any alkoxide, however, no corresponding (alkoxymethyl)disilane is produced. Intramolecular rearrangement exclusively occurs to give the $(CH_3)_3SiCH_2Si(CH_3)_2OR$ compounds (see this Section, A, 2,a).

The (chloromethyl)disilane readily forms a Grignard reagent (XXV), which undergoes many reactions in the normal way to produce certain carbon-functional disilanes that can not be prepared by nucleophilic substitution (*25*, *104*, *111*).

$$(CH_3)_5Si_2CH_2Cl + Mg \xrightarrow{\text{Ether}} \underset{\text{(XXV)}}{(CH_3)_5Si_2CH_2MgCl}$$



Oxidation of the tris(pentamethyldisilanylmethyl)borane (XXVI) by alkaline hydrogen peroxide leads to the (hydroxymethyl)disilane, while reduction of the ethyl (pentamethyldisilanylmethyl)acetate (XXVII) with lithium aluminum hydride yields the (β-hydroxyethyl)disilane.

$$\underset{\text{(XXVI)}}{[(CH_3)_5Si_2CH_2]_3B} \xrightarrow[\text{OH}^-]{H_2O_2} (CH_3)_5Si_2CH_2OH$$

$$\underset{\text{(XXVII)}}{(CH_3)_5Si_2CH_2CO_2C_2H_5} \xrightarrow{LiAlH_4} (CH_3)_5Si_2CH_2CH_2OH$$

These alcohols can be further transformed into other compounds by known processes. For example,

$$\begin{tikzcd} & (CH_3)_5Si_2CH_2O_2CCH_3 \quad 71\%\ (111) \\ (CH_3)_5Si_2CH_2OH \arrow[ur, "(CH_3CO)_2O"] \arrow[dr, "CH_2{=}CHCN", "\text{Triton B}"'] & \\ & (CH_3)_5Si_2CH_2OCH_2CH_2CN \quad 70\%\ (127) \end{tikzcd}$$

c. *Addition to Multiple Bonds.* Vinylpentamethyldisilane (XXVIII) readily undergoes hydroboration. Subsequent oxidation with alkaline hydrogen peroxide gives (α-hydroxyethyl)- and (β-hydroxyethyl)pentamethyldisilane in the molar ratio of 25:75, in 65% overall yield (*101*).

$$\begin{tikzcd} & (CH_3)_5Si_2CH(CH_3)OH \\ \underset{\text{(XXVIII)}}{(CH_3)_5Si_2CH{=}CH_2} \arrow[ur, "1.\ {[BH_3]}"] \arrow[dr, "2.\ H_2O_2,\ OH^-"'] & \\ & (CH_3)_5Si_2CH_2CH_2OH \end{tikzcd}$$

The vinyldisilane (XXVIII) undergoes chloroplatinic acid-catalyzed hydrosilation with trimethylsilane with great ease at 40° C to give (β-trimethylsilylethyl)pentamethyldisilane in 93% yield, which can also be obtained in 80% yield by the addition of pentamethyldisilane to vinyltrimethylsilane in the presence of *trans*-dichloro(ethylene)(pyridine)-platinum(II) as catalyst in benzene at 45° C (*128*).

$$\begin{tikzcd} \underset{\text{(XXVIII)}}{(CH_3)_5Si_2CH{=}CH_2 + HSi(CH_3)_3} \arrow[dr, "H_2PtCl_6"] & \\ & (CH_3)_5Si_2CH_2CH_2Si(CH_3)_3 \\ (CH_3)_5Si_2H + CH_2{=}CHSi(CH_3)_3 \arrow[ur, "trans\text{-}(C_2H_4)(C_5H_5N)PtCl_2"'] & \end{tikzcd}$$

Peroxide-initiated addition of pentamethyldisilane to vinylpentamethyldisilane gives 1,2-bis(pentamethyldisilanyl)ethane in 80% yield (*155*).

$$(CH_3)_5Si_2H + CH_2{=}CHSi_2(CH_3)_5 \xrightarrow{(tert\text{-}C_4H_9O)_2} (CH_3)_5Si_2CH_2CH_2Si_2(CH_3)_5$$

Addition of bromotrichloromethane to the vinyldisilane (XXVIII) in the presence of benzoyl peroxide at 80° C gives α-bromo-γ,γ,γ-trichloropropylpentamethyldisilane in 80% yield (*147*).

$$\underset{\text{(XXVIII)}}{(CH_3)_5Si_2CH{=}CH_2 + BrCCl_3} \rightarrow (CH_3)_5Si_2CHBrCH_2CCl_3$$

d. *Attachment of Carbon-Functional Groups to Silicon with Organometallic Reagents.* The use of organolithium reagents in which lithium and chlorine are attached to the same carbon permits one to prepare organopolysilanes with a group such as dichloromethyl (*158*).

$$CH_2Cl_2 + n\text{-}C_4H_9Li \xrightarrow[-78^\circ C]{\text{THF-ether}} Cl_2CHLi$$

$$Cl_2CHLi + Cl[Si(CH_3)_2]_nCH_3 \rightarrow Cl_2CH[Si(CH_3)_2]_nCH_3$$

$$n = 1,\ 63\%;\ n = 2,\ 35\%$$

Methoxymethyl derivatives of polysilanes, which cannot be obtained from the corresponding chloromethyl compounds by nucleophilic substitution because of intramolecular rearrangement, are prepared successfully by the reaction of chloropolysilanes with monochloromethyl ether in the presence of magnesium in tetrahydrofuran.

$$CH_3OCH_2Cl + Mg + ClSi_2(CH_3)_5 \rightarrow CH_3OCH_2Si_2(CH_3)_5 \quad 44\%\ (\mathit{111})$$

$$2\ CH_3OCH_2Cl + 2\ Mg + Cl[Si(CH_3)_2]_2Cl \rightarrow [(CH_3OCH_2)(CH_3)_2Si{-}]_2 \quad 50\%\ (\mathit{122})$$

Functionally substituted phenyl groups also are directly introduced by the use of Grignard or organolithium reagents.

$$p\text{-}YC_6H_4MgBr + ClSi_2(CH_3)_5 \rightarrow p\text{-}YC_6H_4Si_2(CH_3)_5$$

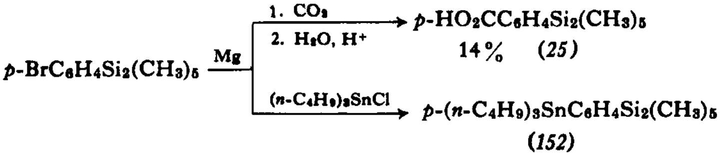
$Y = Cl$ (*25, 149*); $Y = Br$, 12% (*25*); $Y = CH_3O$, 43% (*149*);
$Y = (CH_3)_2N$, 50% (*25*); $Y = (CH_3)_3SiO$, 32% (*145*)

$$2\ YC_6H_4MgCl + Cl[Si(CH_3)_2]_2Cl \rightarrow [(YC_6H_4)(CH_3)_2Si{-}]_2$$

$Y = p\text{-}CH_3O$, 44% (*157, 158*); $Y = m\text{-}Cl$, 23% (*147*)

$$p\text{-}CH_3OC_6H_4Li + Cl[Si(CH_3)_2]_2C_6H_4CH_3\text{-}p \rightarrow p\text{-}CH_3OC_6H_4[Si(CH_3)_2]_2C_6H_4CH_3\text{-}p \quad 50\%\ (\mathit{157, 158})$$

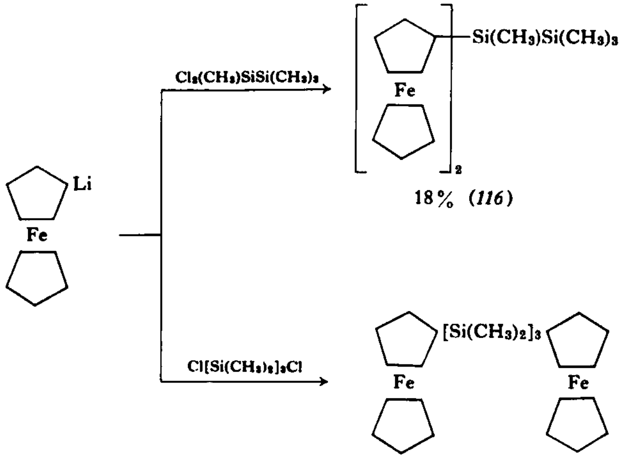
Some of these products can be further transformed into other functionally substituted phenyl derivatives.



$$\begin{tikzcd} & p\text{-}HO_2CC_6H_4Si_2(CH_3)_5 \quad 14\%\ (\mathit{25}) \\ p\text{-}BrC_6H_4Si_2(CH_3)_5 \arrow[ur, "1.\ CO_2"', "2.\ H_2O,\ H^+"] \arrow[dr, "(n\text{-}C_4H_9)_3SnCl"'] \arrow[r, phantom, "Mg"] & \\ & p\text{-}(n\text{-}C_4H_9)_3SnC_6H_4Si_2(CH_3)_5 \quad (\mathit{152}) \end{tikzcd}$$

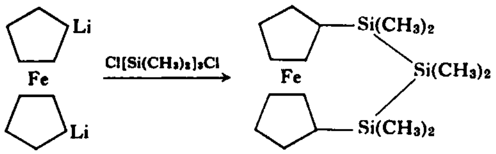
$$p\text{-}(CH_3)_3SiOC_6H_4Si_2(CH_3)_5 \xrightarrow[NH_3]{C_2H_5OH} p\text{-}HOC_6H_4Si_2(CH_3)_5 \quad 41\%\ (\mathit{145})$$

Ferrocenes substituted with silicon–silicon groupings are prepared by (1) the reaction of lithiated ferrocenes with an appropriate chloropolysilane and/or (2) lithiation of a cyclopentadienyldisilane followed by treatment with ferrous chloride. The following give examples (*116*, *117*):

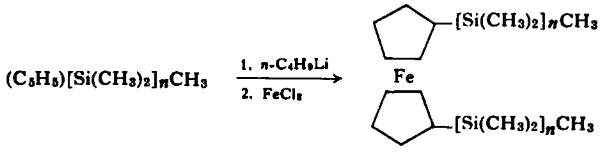


18% (*116*)

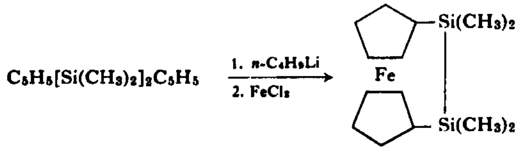
4% (*116*)



12% (*116*)



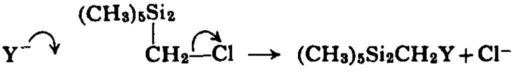
$n = 2$, 65% (*117*); $n = 3$, 58% (*116*)



23% (*116*)

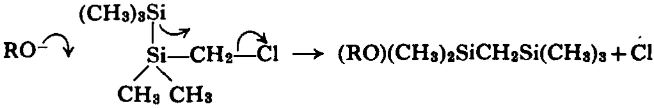
2. *Chemical Properties*

a. *Reactions of (Chloromethyl)pentamethyldisilane and Related Compounds.* As mentioned in part in the preceding section, (chloromethyl)pentamethyldisilane selectively undergoes three types of nucleophilic reactions, depending upon the nature of the reagent used. Thus, substitution of the chlorine atom exclusively takes place by sodium iodide in acetone, by sodium mercaptides in mercaptans, or by amines; only intramolecular rearrangement proceeds with sodium alkoxides in alcohols; while only silicon–carbon cleavage occurs with sodium (or potassium) cyanide in alcohols (*103*, *111*).



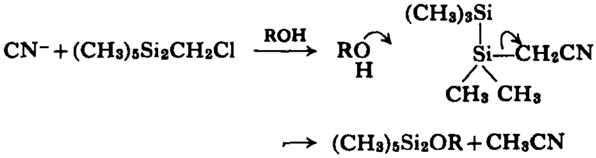
$$Y^- + (CH_3)_5Si_2CH_2{-}Cl \longrightarrow (CH_3)_5Si_2CH_2Y + Cl^-$$

$Y = I, C_2H_5S, C_6H_5S, (C_2H_5)_2N, C_6H_5NH$



$$RO^- + (CH_3)_3Si{-}Si(CH_3)_2{-}CH_2{-}Cl \longrightarrow (RO)(CH_3)_2SiCH_2Si(CH_3)_3 + Cl^-$$

$R = CH_3, C_2H_5, iso\text{-}C_3H_7, C_6H_5$



$$CN^- + (CH_3)_5Si_2CH_2Cl \xrightarrow{ROH} \underset{H}{RO} \quad (CH_3)_3Si{-}Si(CH_3)_2{-}CH_2CN \longrightarrow (CH_3)_5Si_2OR + CH_3CN$$

The reaction with acetate in acetic acid proceeds in two steps; first, substitution leading to the (acetoxymethyl)disilane; second, intramolecular rearrangement to a compound with two silyl groups linked by a methylene bridge.

$$CH_3CO_2^- + (CH_3)_5Si_2CH_2Cl \xrightarrow{CH_3CO_2H}$$

$$(CH_3)_5Si_2CH_2O_2CCH_3 \xrightarrow{\Delta} (CH_3CO_2)(CH_3)_2SiCH_2Si(CH_3)_3$$

In fact, the (acetoxymethyl)disilane, prepared through an alternative route (see this Section, A, 1,b), undergoes complete rearrangement on heating to reflux for 6 hours.

In marked contrast to the acetate, (methoxymethyl)pentamethyldisilane, once prepared by an alternative method (see this Section, A, 1,d), is quite stable to any change upon refluxing with alkoxide ion in alcohols as well as on heating to 240° C for 8 hours in a sealed tube. Therefore, it seems likely that the intramolecular rearrangement by alkoxide ion is synchronous with the detachment of the chlorine atom.

(Cyanomethyl)pentamethyldisilane, prepared through the Grignard reaction (see this Section, A, 1,b), is stable in refluxing pure ethanol, but undergoes complete cleavage of the cyanomethyl–silicon bond when refluxed in ethanol containing a catalytic amount of cyanide ion. Doubtless, this ease of cleavage is due to the highly electronegative nature of the cyanomethyl group.

(Chloromethyl)pentamethyldisilane itself undergoes complete intramolecular rearrangement at 240° C within 8 hours to give a disilylmethane derivative (*105*). Anhydrous aluminum chloride acts as the catalyst for the rearrangement, making it proceed vigorously at or below room temperature (*120*).

$$(CH_3)_3SiSi(CH_3)_2CH_2Cl \xrightarrow{\Delta} Cl(CH_3)_2SiCH_2Si(CH_3)_3$$

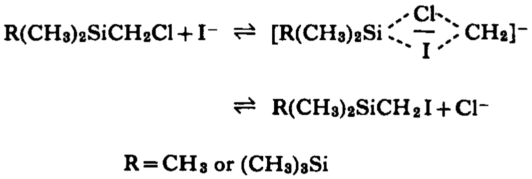
An analogous rearrangement is observed in the action of boron trichloride on (methoxymethyl)pentamethyldisilane at a temperature near 0° C (*122*). The only isolable product is $Cl(CH_3)_2SiCH_2Si(CH_3)_3$.

b. *The Electrical Effect of the* $(CH_3)_5Si_2$ *Group.* Although evidence is not as clear as one would wish, the pentamethyldisilanyl group appears to be somewhat more electron-releasing by an inductive (+I) effect than the trimethylsilyl group. The apparent dissociation constants in 50% aqueous ethanol at 25° C of the acids $(CH_3)_5Si_2CH_2COOH$ and $(CH_3)_3SiCH_2COOH$ are 0.106×10^{-6} and 0.25×10^{-6}, respectively (*25*).

On the other hand, the $(CH_3)_5Si_2$ group seems to be slightly more electron-withdrawing by a −T effect than the $(CH_3)_3Si$; this implies the possibility of p_π–d_π–d_π conjugation for a grouping $C(sp^2)$—Si—Si. The dissociation constants in 60% aqueous ethanol at 25° C of the acids p-$(CH_3)_5Si_2C_6H_4COOH$, p-$(CH_3)_3SiC_6H_4COOH$, and C_6H_5COOH are reported to be 1.20×10^{-6}, 1.17×10^{-6}, and 1.12×10^{-6}, respectively (*25*).

Data from other studies, including the infrared spectroscopy of vinyl-substituted polysilanes (*154*), copolymerization of some vinylpolysilanes with styrene and with acrylonitrile (*154*), and kinetics of the reaction of organosilylacetylenes with ethylmagnesium bromide (*213*), are consistent with the above sequence.

c. *Reactivity of (Chloromethyl)pentamethyldisilane toward Iodide Ion.* The chlorine atom of (chloromethyl)pentamethyldisilane is somewhat more readily displaced (2.25 times faster at 20° C) by iodide ion in acetone than is the chlorine of (chloromethyl)trimethylsilane (*123*), which in turn is some 16 times more reactive than *n*-butyl chloride at 50° C (*12*). This relatively high reactivity of the disilane, in spite of the slightly more electron-releasing nature of the pentamethyldisilanyl group relative to trimethylsilyl, appears to be consistent with the "bridging" mechanism proposed for nucleophilic substitutions of $(CH_3)_3MCH_2Cl$ compounds, where M is silicon, germanium, and tin (*12*), because in the case of the disilane the partial negative charge in the transition state would be distributed over two silicon atoms rather than one (*1*, *192*).



$$R(CH_3)_2SiCH_2Cl + I^- \rightleftharpoons [R(CH_3)_2Si \overset{Cl}{\underset{I}{-}} CH_2]^-$$

$$\rightleftharpoons R(CH_3)_2SiCH_2I + Cl^-$$

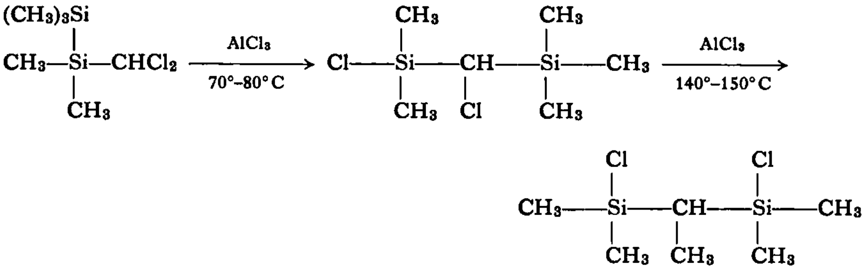
$$R = CH_3 \text{ or } (CH_3)_3Si$$

d. *Hydrogen Chloride Cleavage of Silicon-Substituted Diorganomercurials.* A study of the cleavage reaction of some unsymmetrical silicon-substituted diorganomercurials by hydrogen chloride in ethanol (*104*) reveals that the ease of cleavage of the groups studied decreases in the order: $(CH_3)_3SiCH_2 >$ $(CH_3)_3SiSi(CH_3)_2CH_2 > (C_2H_5)(CH_3)_2SiSi(CH_3)_2CH_2 > (CH_3)_3CSi$ $(CH_3)_2CH_2 \sim [(CH_3)_3Si]_2CH > CH_3$. This order seems to be understood in terms of both positive inductive and steric effects of organosilicon substituents on the carbon atom linked to mercury. The slightly lesser ease of cleavage of the $(CH_3)_5Si_2CH_2$ as compared with $(CH_3)_3SiCH_2$ in spite of the somewhat stronger electron-releasing nature of the $(CH_3)_5Si_2$ group relative to that of the $(CH_3)_3Si$ seems to be due to the larger steric effect of the disilanyl group.

e. *Reactions of Dichloromethyl Derivatives.* As is the case with monosilane derivatives, a dichloromethyl group attached to silicon in polysilanes is replaced by an alkoxy group with great ease. Thus, the action of sodium ethoxide in ethanol on (dichloromethyl)pentamethyldisilane gives ethoxypentamethyldisilane in 57% and bis(pentamethyldisilanyl) ether in 22% yield, along with methylene chloride in 72% yield. This reaction affords structure proof of this dichloro compound (*103*).

$$(Cl_2CH)Si_2(CH_3)_5 \xrightarrow[C_2H_5OH]{C_2H_5O^-} C_2H_5OSi_2(CH_3)_5 + [(CH_3)_5Si_2\text{—}]_2O + CH_2Cl_2$$

The (dichloromethyl)disilane undergoes two successive and discrete intramolecular rearrangements with anhydrous aluminum chloride (*103*). Under mild conditions, only migration of the trimethylsilyl group from silicon to carbon takes place to give (trimethylsilyl)(chlorodimethylsilyl)-chloromethane in 83% yield. At a higher temperature and with a larger amount of the catalyst, the second intramolecular rearrangement, which involves the migration of a methyl from silicon to carbon, occurs to give 1,1-bis(chlorodimethylsilyl)ethane in 70% overall yield.



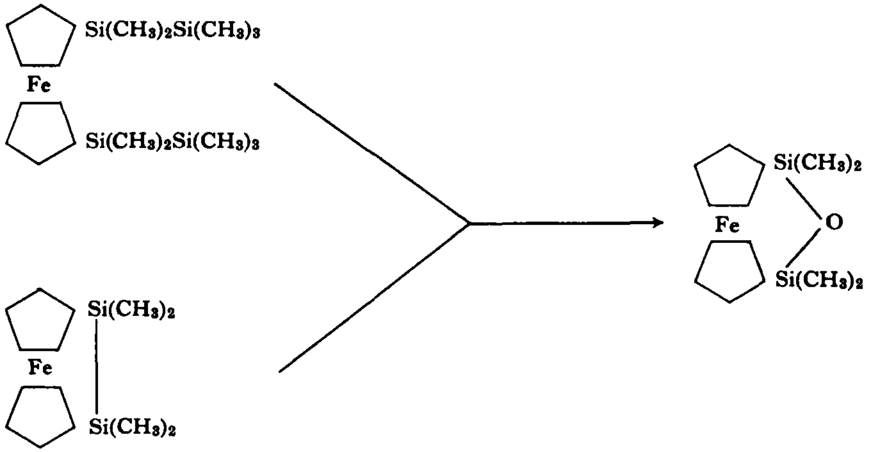
$$CH_3\text{—}\overset{(CH_3)_3Si}{\underset{CH_3}{Si}}\text{—}CHCl_2 \xrightarrow[70°\text{–}80°C]{AlCl_3} Cl\text{—}\overset{CH_3}{\underset{CH_3}{Si}}\text{—}\underset{Cl}{CH}\text{—}\overset{CH_3}{\underset{CH_3}{Si}}\text{—}CH_3 \xrightarrow[140°\text{–}150°C]{AlCl_3} CH_3\text{—}\overset{Cl}{\underset{CH_3}{Si}}\text{—}\underset{CH_3}{CH}\text{—}\overset{Cl}{\underset{CH_3}{Si}}\text{—}CH_3$$

When the (dichloromethyl)disilane is heated at 200° C for 8 hours in the absence of added catalyst, it also undergoes intramolecular rearrangement to give (trimethylsilyl)(chlorodimethylsilyl)chloromethane as a single product (*105*).

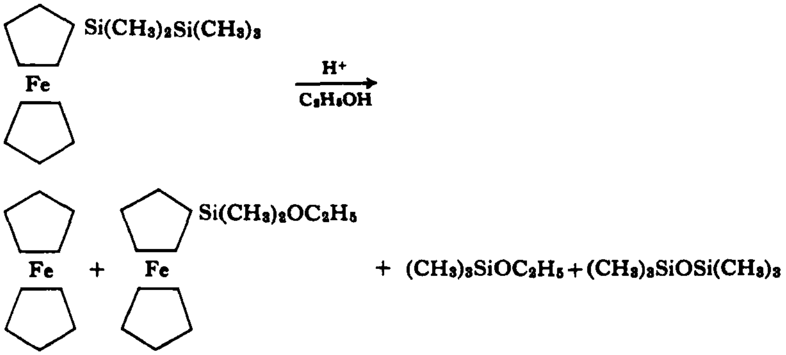
Aluminum chloride-catalyzed intramolecular rearrangement of 1-(dichloromethyl)heptamethyltrisilane followed by methylation gives tris-(trimethylsilyl)methane in 72% overall yield (*158*).

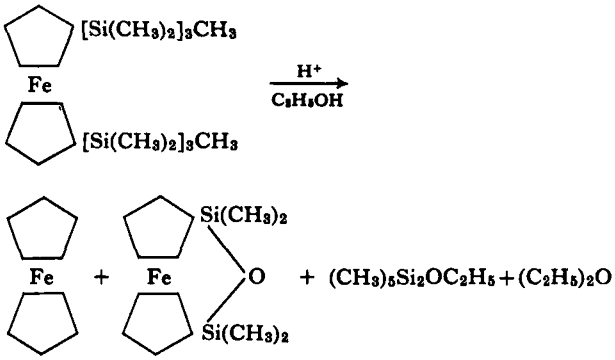
$$(Cl_2CH)[Si(CH_3)_2]_3CH_3 \xrightarrow{AlCl_3} \underset{X=CH_3 \text{ or } Cl}{\text{Mixture of } [X(CH_3)_2Si]_3CH} \xrightarrow{CH_3MgBr} [(CH_3)_3Si]_3CH$$

f. *Cleavage of Silicon–Silicon Bond Adjacent to Ferrocenyl Group.* The silicon–silicon bond adjacent to a ferrocenyl group undergoes cleavage with unusual ease in protic organic solvents containing traces of an acid (*116, 117*). Thus, both 1,1′-bis(pentamethyldisilanyl)ferrocene and 1,2-(1,1′-ferrocenylene)tetramethyldisilane are cleaved to give two compounds, ferrocene and 1,3-(1,1′-ferrocenylene)tetramethyldisiloxane, when refluxed for 2 hours in extremely dilute methanolic or ethanolic solution of hydrogen chloride. The relative yields of these two products depend upon the reaction conditions. A lower concentration of the acid and/or lower reaction temperature favors the formation of the ferrocenylenedisiloxane, i.e., the selective cleavage of the silicon–silicon bond. With 10^{-3} *M* HCl in ethanol at room temperature, the ferrocenylenedisiloxane is obtained after 2 days in essentially theoretical yield from both of the ferrocenes. The selective scission of the silicon–silicon bond is also observed when the ferrocenes are allowed to stand for 2 days in glacial acetic acid or in ethanol containing a catalytic amount of silver perchlorate (*116*).



The hydrogen chloride cleavage of pentamethyldisilanylferrocene and 1,1′-bis(heptamethyltrisilanyl)ferrocene proceeds in a similar manner to that above, as illustrated in the following equations:

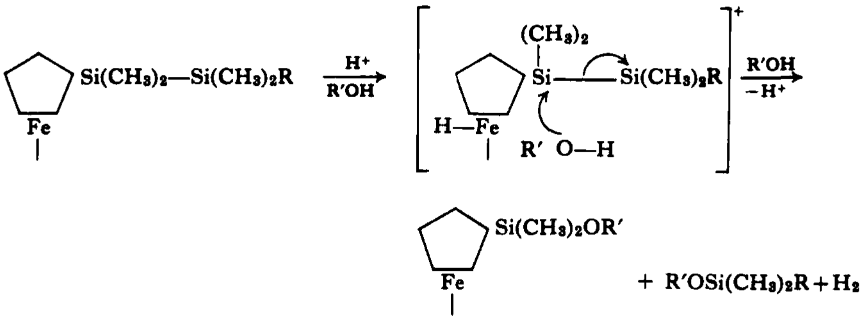




The reaction depicted by the last equation demonstrates that the cleavage of the silicon–silicon bond occurs exclusively at the alpha position to a ferrocenyl group.

These ferrocenes containing the silicon–silicon bond are very stable under basic conditions, e.g., at reflux with 0.14 *M* sodium methoxide in methanol, with the exception of the 1,2-(1,1′-ferrocenylene)disilane with bridged structure, which in part undergoes cleavage. Cyclopentadienylpentamethyldisilane itself is stable to the acid-catalyzed cleavage under the same conditions as used for the ferrocenes mentioned above.

The mechanism for the unusually rapid acid cleavage of the Si—Si bond in disilanylferrocenes is not yet clearly understood. A mechanism was originally proposed involving an α-ferrocenylsiliconium ion intermediate (or transition state), possibly stabilized by overlap of filled 3*d* orbitals of iron with the electron-deficient *p* orbital of silicon (*117*). However, the observations described above and the current concepts of electrophilic substitution



R = CH_3, $(CH_3)_3Si$; R′ = CH_3, C_2H_5

on ferrocenes (*142*) make an alternate mechanism, involving protonation on the metal atom followed by nucleophilic attack of alcohol solvent on the α-silicon, appear probable.

B. *Alkenyl and Alkynyl Polysilanes*

1. *Synthesis*

The preparation of alkenyl and alkynyl derivatives of polysilanes is mostly by means of the reaction of an appropriate unsaturated Grignard reagent with a chloropolysilane. Some examples are illustrated below.

$$CH_2{=}CH(CH_2)_nMgX + ClSi_2(CH_3)_5 \rightarrow CH_2{=}CH(CH_2)_nSi_2(CH_3)_5$$

$n = 0$, in THF, 61% (*154*)
$n = 1$, in ether 65% (*25, 213*)

$$2\,CH_2{=}C(CH_3)MgBr + Cl[Si(CH_3)_2]_nCl \xrightarrow{THF} CH_2{=}C(CH_3)[Si(CH_3)_2]_nC(CH_3){=}CH_2$$

$n = 2$, 81% (*119*)
$n = 3$, 86% (*119*)

$$2\,C_5H_5MgBr + Cl[Si(CH_3)_2]_nCl \xrightarrow{\text{Benzene}} C_5H_5[Si(CH_3)_2]_nC_5H_5$$

$n = 2$, 36% (*117*)
$n = 3$, 55% (*116*)

$$CH{\equiv}CMgBr + ClSi_2(CH_3)_5 \rightarrow CH{\equiv}CSi_2(CH_3)_5$$

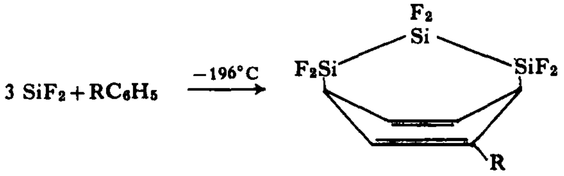
74% (*213*)

Certain ω-alkenyl derivatives are obtained from reaction of a silicon–silicon containing Grignard reagent with allyl bromide, as exemplified by the equation

$$(CH_3)_5Si_2CH_2MgCl + BrCH_2CH{=}CH_2 \rightarrow (CH_3)_5Si_2CH_2CH_2CH{=}CH_2$$

70% (*25*)

An interesting class of compounds of the formula $ArH(SiF_2)_n$, where $n = 2$ to 8, has recently been prepared by the reaction of silicon difluoride with aromatic compounds at low temperatures (*186*). The compounds

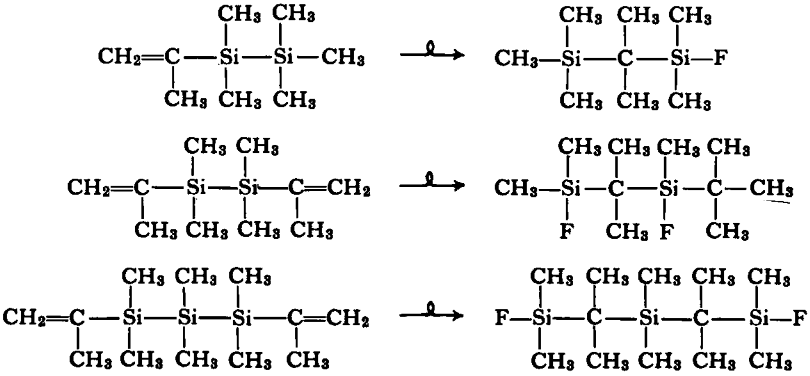


R = H or CH₃

$C_6H_6(SiF_2)_3$ and $CH_3C_6H_5(SiF_2)_3$ are 1,4-cyclohexadiene derivatives with —SiF_2—SiF_2—SiF_2— bridges across the 3,6-positions.

2. *Chemical Properties*

a. *Intramolecular Rearrangement of Isopropenyl Derivatives.* Isopropenyl derivatives of disilane and trisilane readily undergo intramolecular rearrangement with cold concentrated sulfuric acid to give, after treatment with ammonium hydrogen fluoride, fluorosilanes with the $SiC(CH_3)_2Si$ grouping in the framework of the molecule, in good yield (*119*).



$$CH_2{=}C(CH_3){-}Si(CH_3)_2{-}Si(CH_3)_2{-}CH_3 \xrightarrow{\ell} CH_3{-}Si(CH_3)_2{-}C(CH_3)_2{-}Si(CH_3)_2{-}F$$

$$CH_2{=}C(CH_3){-}Si(CH_3)_2{-}Si(CH_3)_2{-}C(CH_3){=}CH_2 \xrightarrow{\ell} CH_3{-}Si(CH_3)(F){-}C(CH_3)_2{-}Si(CH_3)(F){-}C(CH_3)_2{-}CH_3$$

$$CH_2{=}C(CH_3){-}Si(CH_3)_2{-}Si(CH_3)_2{-}Si(CH_3)_2{-}C(CH_3){=}CH_2 \xrightarrow{\ell} F{-}Si(CH_3)_2{-}C(CH_3)_2{-}Si(CH_3)_2{-}C(CH_3)_2{-}Si(CH_3)_2{-}F$$

The formation of these products may be rationalized in terms of a mechanism involving protonation by sulfuric acid at the terminal carbon of an isopropenyl group to produce an α-carbonium ion intermediate, followed by rearrangement of vicinal silyl group from silicon to this electron-deficient carbon.

b. *Cleavage of Silicon–Silicon Bond Adjacent to a Vinyl Group.* When vinylpentamethyldisilane (XXVIII) is stirred with a catalytic amount of palladium(II) chloride in ethanol at a temperature near 0° C, reaction is complete within a few minutes to give several compounds, of which (XXIX)-(XXXII) are major products (*128*).

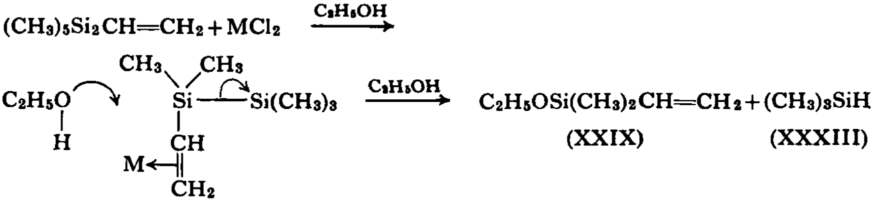
$$\underset{\text{(XXVIII)}}{CH_2{=}CHSi_2(CH_3)_5} \xrightarrow[C_2H_5OH]{PdCl_2} \underset{\text{(XXIX)}}{(CH_2{=}CH)(CH_3)_2SiOC_2H_5} +$$

$$\underset{\text{(XXX)}}{(C_2H_5)(CH_3)_2SiOC_2H_5} + \underset{\text{(XXI)}}{(CH_3)_3SiOC_2H_5} + \underset{\text{(XXII)}}{C_2H_5Si_2(CH_3)_5}$$

Similar results are obtained with platinum(II) chloride as catalyst, although in this case yields of (XXX) and (XXXII) are relatively low.

Hexamethyldisilane is quite inert and allylpentamethyldisilane is sluggish under the same conditions; in the latter case, it seems likely that the olefin first isomerizes to the propenyldisilane which is then cleaved. In the absence of protic solvent, such cleavage of the vinyldisilane does not take place, and only isomerization of the allyldisilane is observed.

A possible mechanism for the cleavage may involve the formation of an olefin–metal complex intermediate in which the silicon atom alpha to the vinyl group would be vulnerable to the attack of ethanol.



$$(CH_3)_5Si_2CH{=}CH_2 + MCl_2 \xrightarrow{C_2H_5OH}$$

$$\xrightarrow{C_2H_5OH} C_2H_5OSi(CH_3)_2CH{=}CH_2 + (CH_3)_3SiH$$

(XXIX) (XXXIII)

M = Pd or Pt

Trimethylsilane (XXXIII) thus produced immediately undergoes ethanolysis catalyzed by palladium or platinum with liberation of hydrogen, which is effectively transfered to the olefins present. Three other products (XXX), (XXXI), and (XXXII) are formed in this way.

With chloroplatinic acid as catalyst and under similar conditions, not only cleavage of the silicon–silicon bond, but also addition of trimethylsilane, formed from cleavage, to the starting olefin occurs to some extent.

c. *Copolymerization of Vinylpolysilanes with Styrene and Acrylonitrile.* A study of free radical copolymerization of vinylpentamethyldisilane and 2-vinylheptamethyltrisilane with styrene and with acrylonitrile at 60° C indicates that the Q values in the Price–Alfrey's Q–e scheme for these two vinylpolysilanes are low (0.02 for either of them) and in the same range as for many vinyl-substituted monosilanes (*154*). This fact suggests that the 3d orbital participation may not be important in the stabilization of an odd electron adjacent to a silicon atom in a free radical intermediate in copolymerization, although there is spectral evidence indicating conjugation between a vinyl group and a polysilanyl one. The more negative e values of both monomers (-0.6 for the disilane, and -0.7 for the trisilane) than the value for vinyltrimethylsilane (-0.1 or so) could be ascribed to a slightly greater electron-releasing character of the disilanyl group and of the 2-trisilanyl group.

d. *Reactivities of Alkenylsilanes toward Thiocyanogen and Bromotrichloromethane.* The γ-butenyl derivative of disilane, $CH_2{=}CH(CH_2)_2Si_2(CH_3)_5$, is more reactive than that of monosilane, $CH_2{=}CH(CH_2)_2Si(CH_3)_3$ to the electrophilic addition of thiocyanogen. This fact can be understood in terms of the stronger inductive (+I) effect of the $(CH_3)_5Si_2$ group (*25*). The peroxide-initiated addition of bromotrichloromethane to vinylpentamethyldisilane at 80° C proceeds 1.35 times faster than that to vinyltrimethylsilane. In view of the electrophilic nature of the trichloromethyl radical $Cl_3C\cdot$, this result may also be accounted for on the same basis (*147*).

e. *Reaction of Silicon-Substituted Acetylenes with Ethyl Grignard.* A kinetic study of the reaction of substituted acetylenes, $RC{\equiv}CH$, with ethylmagnesium bromide in boiling ether (*213*) indicates that the reaction is second order, first in each reactant, and the decreasing order of reactivity with the variation in R is $C_6H_5 > n\text{-}C_4H_9 > (C_6H_5)(CH_3)_2Si > (CH_3)_3Si > (CH_3)_3SiSi(CH_3)_2 > (CH_3)_3SiSi(CH_3)_2Si(CH_3)_2 > (CH_3)_3SiCH_2Si(CH_3)_2 > (CH_3)_3CSi(CH_3)_2 > [(CH_3)_3Si]_2Si(CH_3)$. The results may well be explained in terms of the inductive effect of the substituents unless serious steric effects are present, as is possibly true of the last two cases.

V

ULTRAVIOLET AND NMR SPECTRA

A. Ultraviolet Spectra

One of the most striking physical properties of organopolysilanes is their ultraviolet spectra. Recent studies by several research groups (*5, 50, 52–54, 57, 60, 70, 79–81, 153, 154, 157*) have revealed that phenyl- and vinyl-substituted polysilanes, and also even aliphatic derivatives of linear polysilanes higher than disilane exhibit intense absorptions in the ultraviolet region at 210–260 mμ. The spectral data are listed in Table II–IV. Unlike the polysilanes, most monosilanes containing phenyl or vinyl groups have no absorption in this region; for example, tetraphenylsilane exhibits only the spectrum of benzene itself, although slightly perturbed.

As can be seen from Table II, hexamethyldisilane has no absorption in the ultraviolet region, whereas phenylpentamethyldisilane exhibits the most striking red shift in the absorption maxima; namely, substitution of one pentamethyldisilanyl group, $(CH_3)_5Si_2$, into the benzene ring gives rise to a

TABLE II

ULTRAVIOLET SPECTRAL PROPERTIES OF POLYSILANES CONTAINING π-ELECTRON SYSTEMS

Compound	Band position λ_{max} (mμ)	Molar absorptivity ϵ	References
Phenyl-substituted polysilanes			
$(Me_3SiSiMe_3)$	197.1–199.5	8,500–7,230	*53*
$PhMe_2SiSiMe_3$	230.0	4,900	*80, 81*
	230.5	11,200	*53*
	231.0	10,900	*153*
$Ph_2MeSiSiMe_3$	230.5	16,500	*53*
$PhMe_2SiSiMe_2Ph$	236.0	18,200	*52, 53*
	237.5	16,400	*80, 81*
	238.0	18,500	*153*
$Ph_3SiSiMe_3$	234.0	19,300	*53*
	236.0	18,400	*80, 81*
$Ph_2MeSiSiMe_2Ph$	237.0	21,300	*53*
$Ph_3SiSiMe_2Ph$	239.0	23,800	*53*
$Ph_2MeSiSiMePh_2$	239.0	25,500	*153*
	240.0	25,900	*53*
$Ph_3SiSiMePh_2$	242.0	28,200	*53*
$Ph_3SiSiPh_3$	246.5	32,600	*53*
$PhMe_2SiSiMe_2SiMe_3$	221.3	13,000	*153*
	240.0	15,400	*153*
$PhMeSi(SiMe_3)_2$	243.0	13,000	*153*
	243.0	11,500	*54*
$Ph(SiMe_2)_3Ph$	243.0	18,900	*52*
	243.0	19,500	*54*
$Ph(SiMe_2)_4Ph$	250.5	21,500	*52*
$Ph(SiMe_2)_5Ph$	257.5	24,900	*52*
$Ph(SiMe_2)_6Ph$	265.0	30,500	*52*
$Ph(SiPh_2)_3Ph$	255	32,200	*54*
$Ph(SiPh_2)_4Ph$	255 (shoulder)	32,800	*50*
	288	22,800	*50*
$Ph(SiPh_2)_5Ph$	250 (shoulder)	36,300	*50*
	296.5	27,300	*50*
$Ph(SiPh_2)_6Ph$	255 (shoulder)	38,300	*50*
	312	30,800	*50*
$Ph(SiPh_2)_7Ph$	255 (shoulder)	48,300	*50*
	324	38,000	*50*
$(p\text{-}MeC_6H_4)Me_2SiSiMe_2Ph$	238.5	21,100	*157*
$[(p\text{-}MeC_6H_4)Me_2Si\text{-}]_2$	239.0	24,900	*157*
$[(p\text{-}MeOC_6H_4)Me_2Si\text{-}]_2$	242.0	32,600	*157*
$(p\text{-}MeOC_6H_4)Me_2SiSiMe_2Ph$	241.0	25,800	*157*

TABLE II—*continued*

Compound	Band position λ_{max} (mμ)	Molar absorptivity ϵ	References
$(p\text{-}MeOC_6H_4)Me_2SiSiMe_2\text{-}(C_6H_4Me\text{-}p)$	241.5	28,200	*157*
$[(p\text{-}ClC_6H_4)Me_2Si\text{-}]_2$	242.5	28,000	*157*
	241.5	28,300	*70*
$(p\text{-}MeC_6H_4)Me_2SiSiMe_2(C_6H_4Cl\text{-}p)$	240.5	24,600	*157*
$[(p\text{-}BrC_6H_4)Me_2Si\text{-}]_2$	244	32,300	*70*
$[(p\text{-}Me_3SiC_6H_4)Me_2Si\text{-}]_2$	245	30,300	*70*
$[(p\text{-}Me_2NC_6H_4)Me_2Si\text{-}]_2$	274	50,600	*70*
$Cl_5C_6(SiMe_2)_2C_6Cl_5$	216	90,700	*70*
$Cl_5C_6(SiMe_2)_3C_6Cl_5$	213	105,000	*70*
$Cl_5C_6(SiMe_2)_4C_6Cl_5$	217	106,000	*70*
$Cl_5C_6(SiMe_2)_5C_6Cl_5$	216.5	108,000	*70*
$Cl_5C_6(SiMe_2)_6C_6Cl_5$	216	110,000	*70*
$F_5C_6(SiMe_2)_3C_6F_5$	208	21,300	*70*
	221	15,700	*70*
	239	14,700	*70*
Vinyl-substituted polysilanes			
$(CH_2{=}CH)Me_2SiSiMe_3$	223.2	5,200	*153*
$[(CH_2{=}CH)Me_2Si\text{-}]_2$	227.0	9,790	*153*
	225.0	7,900	*53*
$(CH_2{=}CH)Me_2SiSiMe_2SiMe_3$	218.0 (shoulder)	—	*154*
	237.0	6,760	*154*
$(CH_2{=}CH)MeSi(SiMe_3)_2$	221.0 (shoulder)	—	*154*
	238.0	6,090	*154*
$[(CH_2{=}CH)Me_2SiSiMe_2\text{-}]_2$	243.5	14,000	*53*
Branched-chain polysilanes			
$(Ph_3Si)_3SiH$	240	41,900	*54*
$(PhMe_2Si)_3SiH$	237	30,200	*54*
$(Me_3Si)_3SiPh$	241	13,200	*54*
Phenyl-substituted cyclopolysilanes			
$(SiPh_2)_4$	234	64,500	*50*
	270	35,000	*50*
$(SiPh_2)_5$	251 (shoulder)	60,000	*50*
$(SiPh_2)_6$	248 (shoulder)	60,000	*50*
$(Ph_2Si)_4SiMe_2$	249 (shoulder)	41,000	*50*
$(Ph_2Si)_5SiMe_2$	250 (shoulder)	56,800	*50*
$(Ph_2Si)_5Si(CH_2)_5$	250 (shoulder)	50,300	*50*

TABLE III

ULTRAVIOLET SPECTRAL PROPERTIES OF ALIPHATIC POLYSILANES CONTAINING NEGATIVE SUBSTITUENTS

Compound	Band position λ_{max} (mμ)	Molar absorptivity ϵ	References
H(SiMe$_2$)$_n$H series			
$n=2$	198.0	2,033	*57*
$n=3$	218.0	6,841	*57*
	218	7,400	*5*
$n=4$	235.5	12,250	*57*
	236	12,600	*5*
$n=5$	214.0	9,440	*57*
	249.0	13,590	*57*
	248	22,000	*5*
$n=6$	225.0	11,150	*57*
	257.5	19,456	*57*
H(SiMe$_2$)$_n$Cl series			
$n=2$	194.0	2,770	*57*
$n=3$	217.5	7,150	*57*
$n=4$	235.0	13,340	*57*
$n=5$	215.0	8,770	*57*
	249.5	16,380	*57*
$n=6$	225.0	11,900	*57*
	258.0	21,807	*57*
Cl(SiMe$_2$)$_n$Cl series			
$n=2$	204.0	3,228	*57*
$n=3$	219.0	8,610	*57*
$n=4$	235.0	17,426	*57*
$n=5$	214.0	9,906	*57*
	250.0	19,532	*57*
$n=6$	225.0	11,091	*53, 57*
	259.0	23,250	*53, 57*
MeO(SiMe$_2$)$_n$OMe series			
$n=2$	Below 200	—	*5*
$n=3$	222	6,300	*5*
$n=4$	238	12,000	*5*
$n=5$	250	18,000	*5*

red shift to the extent of 28 mμ in the 200-mμ band (*153*). Further substitution of a methyl group by phenyl in phenylpentamethyldisilane either at the geminal or at the vicinal position results, respectively, in little or only a small shift in the position of absorption maximum, although it increases the molar absorptivity. Successive substitution of methyl by phenyl gives the same

TABLE IV

ULTRAVIOLET SPECTRAL PROPERTIES OF PERMETHYLATED POLYSILANES

Compound	Band position λ_{max} (mμ)	Molar absorptivity ϵ	References
$Me(SiMe_2)_nMe$ series			
$n=2$	197.1–199.5	8,500–7,230	*53*
$n=3$	215.0	9,020	*53*
$n=4$	235.0	14,700	*53*
$n=5$	250.0	18,400	*53*
$n=6$	220.0 (shoulder)	14,000	*53*
	260.0	21,100	*53*
$n=7$	233.0	14,000	*53*
	266.5	23,000	*53*
$n=8$	215.0 (shoulder)	29,000	*53*
	240.5	18,000	*53*
	272.5	38,000	*53*
$n=10$	215.0 (shoulder)	28,200	*53*
	230.0 (shoulder)	21,000	*53*
	255.0 (shoulder)	24,600	*53*
	279.0	42,700	*53*
$n>12$	288	—	*60*
$(Me_2Si)_n$ series			
$n=5$	210 (shoulder)	—	*21*
	261	1,100	*21*
	272	970	*21*
$n=6$	232	5,800	*50*
	255 (shoulder)	2,000	*50*
$n=7$	217 (shoulder)	—	*21*
	242	2,100	*21*
Branched-chain polysilane			
$(Me_3Si)_4Si$	None above 210	—	*54*
$(Me_3Si)_3SiMe$	None above 200	—	*4*

results. Essentially the same trends are observed with vinylpentamethyldisilane and 1,2-divinyltetramethyldisilane. Furthermore, in the $C_6H_5[Si(CH_3)_2]_nC_6H_5$ series (*52*, *70*), both the position of absorption maximum and the molar absorptivity increase regularly with increasing chain length, a property which is observed with other linearly conjugated systems.

The ultraviolet spectral properties of polysilanes with negative substituents and of permethylated polysilanes, listed in Table III and IV, respectively, are of particular interest because these compounds with linear silicon–silicon structure possess characteristic absorptions in the range of 215–290 mμ, although they contain no substituents with π-electron systems. Permethylated cyclosilanes also exhibit ultraviolet absorptions, but aliphatic derivatives of branched-chain polysilanes do not display absorption above 200 mμ (*4*, *54*). Moreover, interestingly enough, in the homologous series of linear polysilanes of the general formula $X[Si(CH_3)_2]_nX$, where $X = Cl$, H, OCH_3 or CH_3, the position of absorption maximum is relatively independent of the end group (*5*, *53*). Accordingly, the band position is of considerable value in determining the chain length of polysilanes of such types.

The foregoing facts suggest that the unique spectral properties of polysilanes are due to the silicon–silicon bond acting as a chromophore, probably through the use of vacant *d* orbitals of the silicon atom. In addition, it seems likely that there exists an enhanced conjugation through overlap of *d* and π orbitals between substituents with π-electron systems, such as phenyl and vinyl, and polysilane chains (*53*, *81*, *153*).

B. *NMR Spectra*

The proton NMR spectral data of organopolysilanes have often been published incidental to preparative studies (*51*, *54*, *62*, *74*, *108*, *119*, *177*, *187*, *190*). Only recently has a systematic investigation to determine the chemical shifts and coupling constants in linear and cyclic permethylated polysilanes, and to study the effects of substituents on the NMR properties of methyl derivatives of disilane and trisilane been reported (see Table V–VII) (*206*).

For linear permethylpolysilanes, the chemical shift of the methyl protons generally appears at lower field as the distance of the methyl group from the end of the chain increases. Octamethyltrisilane represents an exceptional case, in which the chemical shift for methyl protons on the central silicon

TABLE V

PROTON NMR CHEMICAL SHIFTS FOR PERMETHYL POLYSILANES, 10 v/v % IN CCl_4 SOLUTION (ppm, δ)

Compound	Terminal	2	3	4	5
$Me(SiMe_2)_nMe$ series					
$n=2$	0.040	—	—	—	—
$n=3$	0.079	0.067	—	—	—
$n=4$	0.089	0.109	—	—	—
$n=5$	0.090	0.122	0.153	—	—
$n=6$	0.101	0.142	0.192	—	—
$n=7$	0.105	0.152	0.205	—	—
$n=8$	0.097	0.135	0.189	0.205	—
$n=9$	0.095	0.132	0.183	0.201	0.205
$n=10$	0.098	0.135	0.186	0.204	0.209
$(Me_2Si)_n$ series					
$n=5$	—	0.135	—	—	—
$n=6$	—	0.132	—	—	—
$n=7$	—	0.125	—	—	—

TABLE VI

PROTON NMR CHEMICAL SHIFTS FOR SUBSTITUTED DISILANES AND TRISILANES (ppm, δ)

	Chemical shifts				
Compound[a]	$-Si(CH_3)_3$	$-Si(CH_3)_2-$	$-Si(CH_3)_2X$	$Si-H$	C_6H_5
$Me_3SiSiMe_3$	0.055	—	—	—	—
$HMe_2SiSiMe_3$	0.096	—	0.108[d]	3.75[e]	—
$ClMe_2SiSiMe_3$	0.148	—	0.435	—	—
$PhMe_2SiSiMe_3$	0.060	—	0.339	—	7.25
$O(SiMe_2SiMe_3)_2$	0.057	—	0.163	—	—
$Me_3SiSiMe_2SiMe_3$	0.097	0.087	—	—	—
$HMe_2SiSiMe_2SiMe_3$	0.103	0.125	0.145[d]	3.86[e]	—
$ClMe_2SiSiMe_2SiMe_3$[b]	0.141	0.176	0.497	—	—
$PhMe_2SiSiMe_2SiMe_3$[c]	−0.007	0.080	0.382	—	7.30
$O(SiMe_2SiMe_2SiMe_3)_2$	0.067	0.082	0.178	—	—

[a] Samples are neat unless otherwise stated.

[b] Concentration is 20% in CCl_4.

[c] Concentration is 50% in CCl_4.

[d] Center of a doublet.

[e] Center of a septet.

TABLE VII

NMR COUPLING CONSTANTS (cps)

Compound	$\mathit{Si}(\mathrm{C}\mathit{H}_3)_3$	$\mathit{Si}(\mathrm{C}\mathit{H}_3)_2$	$\mathit{Si}(\mathrm{C}\mathit{H}_3)_2\mathrm{X}$	$\mathit{Si}\text{—}\mathrm{Si}(\mathrm{C}\mathit{H}_3)_3$	$\mathit{Si}\text{—}\mathrm{Si}(\mathrm{C}\mathit{H}_3)_2$	$\mathit{Si}\text{—}\mathrm{Si}(\mathrm{C}\mathit{H}_3)_2\mathrm{X}$	$\mathrm{Si}(\mathit{CH}_3)_3$	$\mathrm{Si}(\mathit{CH}_3)_2$	$\mathrm{Si}(\mathit{CH}_3)_2\mathrm{X}$
$\mathrm{Me_4Si}$	6.75	—	—	—	—	—	118.0	—	—
$\mathrm{Me_3SiSiMe_3}$	6.5	—	—	2.7	—	—	119.0	—	—
$\mathrm{Me(SiMe_2)_3Me}$	6.4	6.4	—	2.6	—	—	119.0	119.0	—
$\mathrm{Me(SiMe_2)_4Me}$	6.3	6.2	—	2.7	2.0	—	120.0	121.0	—
$\mathrm{Me(SiMe_2)_5Me}$	6.4	6.0[a]	—	2.7	3.0	—	—	—	—
$\mathrm{Me(SiMe_2)_6Me}$	6.6	6.3[a]	—	3.1	3.0, 3.1	—	120.0	121.0, 122.0	—
$\mathrm{(SiMe_2)_5}$	—	6.3	—	—	3.2	—	—	121.0	—
$\mathrm{(SiMe_2)_6}$	—	6.4	—	—	3.4	—	—	120.0	—
$\mathrm{(SiMe_2)_7}$	—	6.3	—	—	3.2	—	—	—	—
$\mathrm{Me_3SiSiMe_2H}$[b]	6.6	—	6.9	2.8	—	2.8	120.0	—	121.0
$\mathrm{Me_3SiSiMe_2Cl}$	6.9	—	6.6	3.8	—	1.8	121.0	—	122.0
$\mathrm{Me_3SiSiMe_2Ph}$	6.6	—	6.7	3.0	—	2.8	119.0	—	118.0
$\mathrm{(Me_3SiSiMe_2)_2O}$	6.7	—	6.4	3.1	—	2.3	118.5	—	118.0
$\mathrm{Me(SiMe_2)_3H}$[c]	6.8	—	6.6	—	—	2.3	119.5	120.0	—
$\mathrm{Me(SiMe_2)_3Cl}$	6.8	6.6	6.6	2.7	3.0±0.2	1.9	122.0	122.3	124.0
$\mathrm{Me(SiMe_2)Ph}$	6.7	6.5	6.9	2.6	2.7±0.2	2.5	120.5	120.0	120.0
$\mathrm{[Me(SiMe_2)_3]_2O}$	6.6	6.5	6.5	2.8	—	2.5±0.2	119.0	119.0	119.0

[a] Data for internal (3) silicon atom.

[b] $J(\mathit{CH}_3)_2\mathrm{Si}\mathit{H}$, 4.75 cps.

[c] $J(\mathit{CH}_3)_2\mathrm{Si}\mathit{H}$, 4.5 cps.

atom is at slightly higher field than for the terminal methyl groups. This could be understood by considering the unique steric environment of the internal methyl protons in the trisilane compound. In permethylpolysilanes with more than three silicon atoms in the chain, there are always conformations in which the internal methyl groups are closely approached by methyl groups two silicon atoms distant on the chain. However, in the trisilane compound the internal methyl groups are free of this kind of steric interaction.

The permethylated cyclopolysilanes all show a single resonance at nearly the chemical shift, about 0.13 ppm downfield from TMS.

Electronegative substituents at the end of the chain in the permethylated di- and trisilanes deshield the protons of the methyl groups on the silicon atoms to which they are attached (Table VI). This effect is greatest (about 20 cps) for chlorine, and decreases in the order $Cl > C_6H_5 > —O— > H$ in both series.

^{13}C and ^{29}Si coupling constants, i.e., $J(Si—CH_3)$, $J(Si—Si—CH_3)$ and $J(^{13}C—H)$, in some of the polysilanes are listed in Table VII. $J(Si—CH_3)$ decreases slightly with increasing catenation in the same way as found for analogous polymethyltin compounds, but differences are quite small for the polysilanes.

VI

LIST OF ALIPHATIC ORGANOPOLYSILANES

A list of the known organopolysilanes containing at least one aliphatic radical attached to silicon, together with properties and the references to the original preparations, is given in Table VIII.

TABLE VIII

ORGANOPOLYSILANES

Formula		B.p., °C/mm (m.p., °C)	n_D^{20}	d_4^{20}	References
Molecular	Structural				
$Si_2C_1H_3Cl_5$	$Cl_2MeSiSiCl_3$	134°–135°	—	—	*6, 133*
$Si_2C_1H_8$	$MeSi_2H_5$	—	—	—	*193*
$Si_2C_2H_5Cl_5$	$EtCl_2SiSiCl_3$	182°–184°	—	—	*208*
$Si_2C_2H_6Cl_4$	$Me_2ClSiSiCl_3$	157°	—	—	*133, 134*
$Si_2C_2H_6Cl_4$	$(Cl_2MeSi\text{-})_2$	158°	1.467 (25°)	1.235 (25°/4°)	*22, 27,*
		152°–153°			*134, 156*
$Si_2C_2H_6F_4$	$(F_2MeSi\text{-})_2$	57°–58°	1.3370	1.1098	*106*
$Si_2C_2H_{10}$	$EtSi_2H_5$	—	—	—	*11*
$Si_2C_2H_{10}$	$(H_2MeSi\text{-})_2$	49°	1.4331	0.7008	*29, 107*
		$(< -144°)$			*135*
$Si_2C_3H_9Cl_3$	$Cl_3SiSiMe_3$	149°–150°	—	—	*116*
$Si_2C_3H_9Cl_3$	$Cl_2MeSiSiMe_2Cl$	144°–146°	—	—	*23, 27, 113*
		146°–152°	—	1.158	*114, 134*
		154.4°–156.8°	—	—	*155, 156*
$Si_2C_3H_9F_3$	$F_2MeSiSiMe_2F$	76°	1.3574	0.9978	*106*
$Si_2C_3H_{12}$	$H_2MeSiSiMe_2H$	68°–69°	1.4296	0.7101	*107, 190*
$Si_2C_4H_{10}Cl_4$	$Et_2Si_2Cl_4$	206°–209°	—	—	*208*
$Si_2C_4H_{11}Cl_3$	$(ClCH_2)(Cl)MeSiSiMe_2Cl$	92°–93°/28	1.4834	1.1592	*110*
$Si_2C_4H_{12}Br_2$	$(BrMe_2Si\text{-})_2$	79°–82°/30 (~40°)	—	—	*109, 207*
$Si_2C_4H_{12}ClF$	$ClMe_2SiSiMe_2F$	120°	1.4201	0.9623	*126*
$Si_2C_4H_{12}Cl_2$	$Cl_2MeSiSiMe_3$	144°	—	1.0014	*116, 134*
$Si_2C_4H_{12}Cl_2$	$(ClMe_2Si\text{-})_2$	146°–148°	1.4545	1.0103	*57, 66, 99*
					125, 134,
					155, 183

TABLE VIII—(*continued*)

Formula		B.p., °C/mm (m.p., °C)	n_D^{20}	d_4^{20}	References
Molecular	Structural				
$Si_2C_4H_{12}F_2$	$(FMe_2Si\text{-})_2$	92°–93°	1.3837	0.9120 (20°)	*99, 126*
$Si_2C_4H_{12}O_4S$	$(\text{–}Me_2SiMe_2SiSO_4\text{–})_n$	(172°–177°) (160°/3 sublimes)	—	—	*115*
$Si_2C_4H_{13}Cl$	$HMe_2SiSiMe_2Cl$	119°/760	1.4421	—	*56, 57*
$Si_2C_4H_{14}$	$(HMe_2Si\text{–})_2$	88° (−92°)	—	—	*57, 107*
		86°–87°	1.4290	0.7202	*135, 190*
		85.5°–86°	1.4260 (25°)	0.7076 (25°/4°)	*207*
$Si_2C_5H_{14}ClF$	$(ClCH_2)Me_2SiSiMe_2F$	155°–160° 54°/19	1.4416	0.9807	*100*
$Si_2C_5H_{14}Cl_2$	$(ClCH_2)Me_2SiSiMe_2Cl$	91.5°/38 (9°)	1.4735	1.0206	*100, 120*
$Si_2C_5H_{15}Br$	$Me_3SiSiMe_2Br$	148°–149° (~35°) 84°/90 (32°)	—	—	*106, 178*
$Si_2C_5H_{15}Cl$	$Me_3SiSiMe_2Cl$	134°–135.6°	1.4430	0.868	*30, 99, 133*
		136°–137°	1.4336 (30°)	0.8537 (30°/4°)	*134, 155, 178, 209*
$Si_2C_5H_{15}F$	$Me_3SiSiMe_2F$	102°	1.4031	0.8083	*99, 126, 188*
$Si_2C_5H_{15}I$	$Me_3SiSiMe_2I$	78°/71 (53°)	—	—	*178*
$Si_2C_5H_{15}N_3$	$Me_3SiSiMe_2N_3$	158°–160°	—	—	*185*
$Si_2C_5H_{16}$	$Me_3SiSiMe_2H$	100°	1.4239	0.7007	*107, 171*
		97°	1.4300	0.7331	*178, 190*
		98.5°–98.7°	1.4317 (25°)	0.7093 (25°/4°)	
$Si_2C_5H_{16}O$	$Me_3SiSiMe_2(OH)$	33°/2 148°/760	1.4430	0.8311	*178*
$Si_2C_6H_{12}N_2$	$[(NC)Me_2Si\text{–}]_2$	—	—	—	*187*

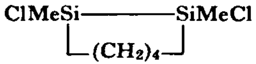
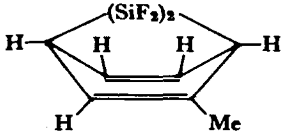
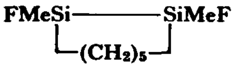
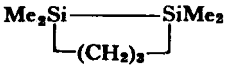
$Si_2C_6H_{14}Cl_2$	 $ClMeSi\underbrace{\qquad\qquad}_{(CH_2)_4}SiMeCl$	102°/27 107°–108°/35	1.4973 1.4972	1.0915 1.0904	*112*
$Si_2C_6H_{14}F_2$		147°–148°	1.4282	1.0013	*112*
$Si_2C_6H_{15}Cl_3$	$Et_3Si_2Cl_3$ (impure)	219°–223°	—	—	*208*
$Si_2C_6H_{15}N$	$Me_3SiSiMe_2(CN)$	87°/34 (25.0°–25.5°)	1.43735 (30°)	0.8136 (30°/4°)	*30, 187*
$Si_2C_6H_{15}NO$	$Me_3SiSiMe_2(NCO)$	159.4°–160°	1.4337 (30°)	0.8537 (30°/4°)	*188*
$Si_2C_6H_{16}Cl_2$	$(Cl_2CH)Me_2SiSiMe_3$	72°/10 (23°–24°)	1.4740 (30°)	1.0004 (30°/4°)	*103, 158* *166*
$Si_2C_6H_{16}Cl_2$	$[(ClCH_2)Me_2Si–]_2$	85°/9 (34°)	—	—	*103*
$Si_2C_6H_{16}I_2$	$[(ICH_2)Me_2Si–]_2$	104°–105°/3	1.5840	1.7264	*103*
$Si_2C_6H_{17}Cl$	$(ClCH_2)Me_2SiSiMe_3$	52°/10 (22°–23.5°)	—	—	*103, 111* *102, 166*
$Si_2C_6H_{17}ClHg$	$(ClHgCH_2)Me_2SiSiMe_3$	(60°–70°)	—	—	*103*
$Si_2C_6H_{17}I$	$(ICH_2)Me_2SiSiMe_3$	96°–97°/23	1.5110	1.2675	*103*
$Si_2C_6H_{18}$	$(Me_3Si–)_2$	112.6°–112.8°/750 112.8°–113° (14.2°–14.4°)	1.4229	0.7257	*9, 16, 19,* *34a, 34b,* *102, 133,* *135, 178,* *180, 181,* *194, 207,* *209*
$Si_2C_6H_{18}O$	$(HOCH_2)Me_2SiSiMe_3$	90°/40 (~20°)	1.4563	0.8414	*101*
$Si_2C_6H_{18}O_2$	$[(MeO)Me_2Si–]_2$	84°/90	1.4207 (26°)	—	*5*
$Si_2C_6H_{18}O_3S$	$Me_3SiSiMe_2SO_3Me$	125°–127°/20	1.4485	1.037	*13*
$Si_2C_6H_{18}O_4$	$[(MeO)_2MeSi–]_2$	86.2°–87°/30	1.4166 (25°)	0.9875 (25°/4°)	*4, 143*
		70°/26	1.4218	0.9404	*184*
$Si_2C_6H_{18}O_5$	$(MeO)_2MeSiSi(OMe)_3$	78°/26	1.4106	0.9957	*184*
$Si_2C_6H_{18}O_6S_2$	$[(MeSO_3)Me_2Si–]_2$	170°–172°/3 (120°–122°)	—	—	*13*

TABLE VIII—(*continued*)

Formula		B.p., °C/mm (m.p., °C)	n_D^{20}	d_4^{20}	References
Molecular	Structural				
$Si_2C_7H_8F_4$		—	—	—	*186*
$Si_2C_7H_{16}$	$(HC\equiv C)Me_2SiSiMe_3$	127° 63°/92	1.4403	0.7689	*213*
$Si_2C_7H_{16}F_2$	 $\underbrace{FMeSi\text{———}SiMeF}_{(CH_2)_5}$	83°–86°/30	1.4518	1.0331	*124*
$Si_2C_7H_{17}N$	$(NCCH_2)Me_2SiSiMe_3$	105°/25 (~30°)	—	—	*111*
$Si_2C_7H_{18}$	$(CH_2{=}CH)Me_2SiSiMe_3$	131°–132°	1.4497	0.7673	*25, 36, 128 153, 154*
$Si_2C_7H_{18}$	 $\underbrace{Me_2Si\text{———}SiMe_2}_{(CH_2)_3}$	154°–155°	1.4708	0.8258	*124*
$Si_2C_7H_{18}O_2$	$(HO_2CCH_2)Me_2SiSiMe_3$	(57°)	—	—	*25*
$Si_2C_7H_{19}Cl$	$(ClCH_2)Me_2SiSiMe_2Et$	79°/26	1.4662	0.8933	*120*
$Si_2C_7H_{19}ClHg$	$(ClHgCH_2)Me_2SiSiMe_2Et$	(55°–56°)	—	—	*104*
$Si_2C_7H_{20}$	$Me_3SiSiMe_2Et$	137°–138°	1.4361	0.7512	*124, 128*
$Si_2C_7H_{20}Hg$	$(MeHgCH_2)Me_2SiSiMe_3$	56°/2	1.5136	1.5786	*104*
$Si_2C_7H_{20}O$	$Me_3SiSiMe_2OEt$	143.5°–144.5°	1.4229	0.7993	*103, 114, 184*
$Si_2C_7H_{20}O$	$(MeOCH_2)Me_2SiSiMe_3$	57°/37	1.4342	0.7982	*111*
$Si_2C_7H_{20}O$	$(HOCH_2CH_2)Me_2SiSiMe_3$	98°/23	1.4607	0.8466	*101*
$Si_2C_7H_{20}O$	$[Me(HO)CH]Me_2SiSiMe_3$	80°/23	1.4583	0.8413	*101*
$Si_2C_8H_{14}$	$[(HC\equiv C)Me_2Si\text{–}]_2$	79°/81	1.4606	0.8081	*213*

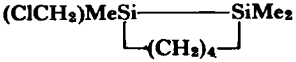
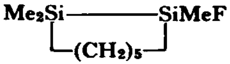
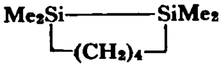
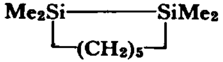
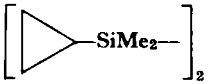
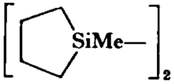
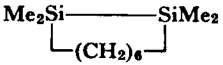
$Si_2C_8H_{18}$	$[(CH_2{=}CH)Me_2Si{-}]_2$	69.5°/24	1.4626	0.7803	*53, 118, 153, 154*
$Si_2C_8H_{18}BrCl_3$	$(Cl_3CCH_2BrCH)Me_2SiSiMe_3$	120°–122°/2	1.5139	1.3026	*118, 147*
$Si_2C_8H_{19}Cl$	 $(ClCH_2)\underbrace{MeSi\text{———}SiMe_2}_{(CH_2)_4}$	117°–119°/29	1.4983	0.9700	*110*
$Si_2C_8H_{19}ClO$		113°–114°/38	1.4716	—	*112*
$Si_2C_8H_{19}F$	 $\underbrace{Me_2Si\text{———}SiMeF}_{(CH_2)_5}$	—	1.4627	0.9331	*124*
$Si_2C_8H_{20}$	$(CH_2{=}CHCH_2)Me_2SiSiMe_3$	155°/760	1.4505 1.4484	0.7782 0.7692	*25, 36, 128*
$Si_2C_8H_{20}$	$[CH_2{=}(Me)C]Me_2SiSiMe_3$	152°	1.4517	0.7720	*119*
$Si_2C_8H_{20}$		159°–160°	1.4520	0.7941	*146*
$Si_2C_8H_{20}$		71°–72°/28	—	—	*112*
$Si_2C_8H_{20}$	 $\underbrace{Me_2Si\text{———}SiMe_2}_{(CH_2)_4}$	174° (−14°−−12°)	1.4722	0.8360	*124*
$Si_2C_8H_{20}F_2$	$(n\text{-}C_5H_{11})(F)MeSiSiMe_2F$	—	1.4113	0.9128	*124*
$Si_2C_8H_{20}O_2$	$(AcOCH_2)Me_2SiSiMe_3$	72°/14	1.4424	0.8774	*111*
$Si_2C_8H_{22}$	$Me_3SiSiMe_2(C_3H_7\text{-}n)$	147°–148°	1.4378	0.7572	*183*
$Si_2C_8H_{22}$	$(EtMe_2Si{-})_2$	168°–171°	1.4440	0.7720 (20°)	*129*
$Si_2C_8H_{22}Hg$	$(MeHgCH_2)Me_2SiSiMe_2Et$	57°/3	1.5129	1.5193	*104*
$Si_2C_8H_{22}O_2$	$[(EtO)Me_2Si{-}]_2$	169°–170°	1.4240	0.8507	*103, 114*
		166°	1.4223	0.8516	*126, 184*
$Si_2C_8H_{22}O_2$	$[(MeOCH_2)Me_2Si{-}]_2$	81°/26	1.4432	0.8518	*122*
$Si_2C_8H_{22}S$	$(EtSCH_2)Me_2SiSiMe_3$	94°/18	1.4778	0.8523	*111*

TABLE VIII—(*continued*)

Formula		B.p., °C/mm (m.p., °C)	n_D^{20}	d_4^{20}	References
Molecular	Structural				
$Si_2C_9H_{21}NO$	$(NCCH_2CH_2OCH_2)Me_2SiSiMe_3$	106°/18	1.4511	0.8795	*127*
$Si_2C_9H_{22}$	$(CH_2{=}CHCH_2CH_2)Me_2SiSiMe_3$	171°	1.4517	0.7839	*25, 36, 128*
$Si_2C_9H_{22}$	 $\underbrace{Me_2Si\text{———}SiMe_2}_{(CH_2)_5}$	76°–77°/16	1.4811	0.8473	*124*
$Si_2C_9H_{22}O_2$	$(EtO_2CCH_2)Me_2SiSiMe_3$	108°/36	1.4483	0.8662	*101*
$Si_2C_9H_{23}F$	$(n\text{-}C_5H_{11})Me_2SiSiMe_2F$	68°/15	1.4278	0.8341	*124*
$Si_2C_9H_{24}$	$EtMe_2SiSiMeEt_2$	192°–194°	1.4540	0.7890 (20°)	*42, 113, 129*
$Si_2C_9H_{24}O_3$	$(EtO)Me_2SiSiMe(OEt)_2$	72°–73°/13	1.4220	0.8873	*114, 126, 184*
$Si_2C_{10}H_{17}Cl$	$Me_3SiSiMe(Ph)(Cl)$	117°–118°/20	—	0.9754	*116*
$Si_2H_{10}H_{17}Cl$	$PhMe_2SiSiMe_2Cl$	119°/20	1.5225	0.9845	*107*
$Si_2C_{10}H_{18}$	$PhMe_2SiSiMe_2H$	111.5°–112°/27	1.5150	—	*51*
$Si_2C_{10}H_{20}$	$(C_5H_5)Me_2SiSiMe_3$	86°/22	1.4913	0.8505	*117*
$Si_2C_{10}H_{22}$	$[(CH_2{=}CHCH_2)Me_2Si\text{–}]_2$	86°/24	1.4712	0.8132	*146*
$Si_2C_{10}H_{22}$	$\{[H_2C{=}C(Me)]Me_2Si\text{–}\}_2$	97°–98°/32	1.4750	0.8081	*119*
$Si_2C_{10}H_{22}$		92°–95°/24	1.4730	0.8543	*146*
$Si_2C_{10}H_{22}$		98°/10 126°–127°/37	1.5049	0.8956	*110*
$Si_2C_{10}H_{24}$	 $\underbrace{Me_2Si\text{———}SiMe_2}_{(CH_2)_6}$	95°/14 (7°–9°)	1.4882	0.8579	*124*
$Si_2C_{10}H_{24}O_2$		117°–118°/38	1.4534	0.9078	*112*

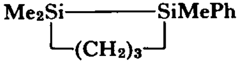
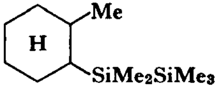
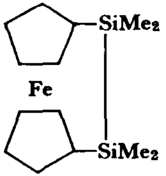
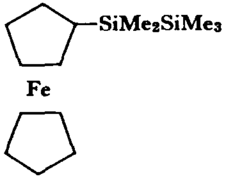
$Si_2C_{10}H_{25}Br$	$Et_3SiSiEt_2Br$	88°/2	1.4860	—	*140, 197*
$Si_2C_{10}H_{26}$	$(n\text{-}C_5H_{11})Me_2SiSiMe_3$	71°/10	1.4442	0.7705	*124*
$Si_2C_{10}H_{26}$	$[Et_2MeSi\text{–}]_2$	207°–212°	1.4603	0.8051	*113, 129, 183*
$Si_2C_{10}H_{26}$	$Et_3SiSiEt_2H$	78°–83°/1.5	1.4608	—	*198*
$Si_2C_{10}H_{26}O_4$	$[(EtO)_2MeSi\text{–}]_2$	99°/19	1.4200	0.9282	*109, 126*
		101.5°–102°/22	1.4174	0.9222	*184*
$Si_2C_{10}H_{27}N$	$(Et_2NCH_2)Me_2SiSiMe_3$	82°/15	1.4549	0.7986	*111*
$Si_2C_{11}H_{19}Br$	$(p\text{-}BrC_6H_4)Me_2SiSiMe_3$	131°–133°/9	1.5345	1.1439	*25*
$Si_2C_{11}H_{19}Cl$	$(p\text{-}MeC_6H_4)Me_2SiSiMe_2Cl$	134°/7	1.5210	0.9832	*158*
$Si_2C_{11}H_{19}Cl$	$(m\text{-}ClC_6H_4)Me_2SiSiMe_3$	136°/22	1.5209	0.9689	*152*
$Si_2C_{11}H_{19}Cl$	$(p\text{-}ClC_6H_4)Me_2SiSiMe_3$	108°–110°/6	1.5223	0.9753	*25, 149*
$Si_2C_{11}H_{20}$	$Me_3SiSiMe_2Ph$	113°–114.5°/25	1.5056	0.8738 (20°)	*25, 53, 67*
		100°–102°/19	1.5078	0.8760	*149, 153*
$Si_2C_{11}H_{20}O$	$(p\text{-}HOC_6H_4)Me_2SiSiMe_3$	124°/13 (38°)	—	—	*145*
$Si_2C_{11}H_{28}O_5$	$(EtO)_2MeSiSi(OEt)_3$	147°/24	1.4164	0.9447	*184*
$Si_2C_{12}H_{20}$	 $\underbrace{Me_2Si\text{———}SiMePh}_{(CH_2)_3}$	105°/2.5	1.5334	0.9324 (20°)	*201*
$Si_2C_{12}H_{20}O_2$	$(p\text{-}HO_2CC_6H_4)Me_2SiSiMe_3$	(148°)	—	—	*25*
$Si_2C_{12}H_{22}$	$(PhCH_2)Me_2SiSiMe_3$	105°–106°/11	1.5092	0.8762	*25*
$Si_2C_{12}H_{22}$	$(m\text{-}MeC_6H_4)Me_2SiSiMe_3$	106°/14	1.5080	0.8699	*149*
$Si_2C_{12}H_{22}$	$(p\text{-}MeC_6H_4)Me_2SiSiMe_3$	119°/21	1.5060	0.8651	*149*
$Si_2C_{12}H_{22}O$	$PhMe_2SiSiMe_2(OEt)$	121°/20	1.5030	0.9199	*107*
$Si_2C_{12}H_{22}O$	$(p\text{-}MeOC_6H_4)Me_2SiSiMe_3$	117°–118°/9	1.5159	0.9156	*149*
$Si_2C_{12}H_{22}S$	$(PhSCH_2)Me_2SiSiMe_3$	109°/2	1.5419	0.9485	*111*
$Si_2C_{12}H_{23}N$	$(PhNHCH_2)Me_2SiSiMe_3$	104°/1.5	1.5247	0.9070	*111*
$Si_2C_{12}H_{28}$	 (probably *trans*)	83°–84°/5	1.4812 (25°)	0.8449 (25°/4°)	*190*

TABLE VIII—(*continued*)

Formula		B.p., °C/mm (m.p., °C)	n_D^{20}	d_4^{20}	References
Molecular	Structural				
$Si_2C_{12}H_{30}$	$[Et_3Si-]_2$	251.7°/760	1.4790	0.8351	*33, 39–41, 55, 87, 144, 161, 194, 199*
$Si_2C_{12}H_{30}$	$(n\text{-}C_8H_{17})Me_2SiSiMe_2H$	80.5°–81.5°/3.5	1.4505 (25°)	0.7819 (25°/4°)	*190*
$Si_2C_{12}H_{30}Hg$	$Et_3SiSiEt_2HgEt$	100°–104°/0.1	1.5353	—	*198*
$Si_2C_{13}H_{25}N$	$(p\text{-}Me_2NC_6H_4)Me_2SiSiMe_3$	137°–138°/5 (44°–46°)	—	—	*25*
$Si_2C_{13}H_{32}$	$(n\text{-}C_8H_{17})Me_2SiSiMe_3$	93.5°–94°/5	1.4486 (25°)	0.7791 (25°/4°)	*190*
$Si_2C_{14}H_{16}Cl_2$	$[(Cl)(Ph)(Me)Si-]_2$	135°–136°/3 (65.0°–68.5°)	—	—	*112*
$Si_2C_{14}H_{18}$	$[(H)(Ph)(Me)Si-]_2$	81°–83°/0.003	1.5769	0.980 (20°/20°)	*175*
$Si_2C_{14}H_{20}Fe$		(132°–133°)	—	—	*116*
$Si_2C_{14}H_{22}$	$[(C_5H_5)Me_2Si-]_2$	102°/24	1.5422	0.9604	*116*
$Si_2C_{15}H_{20}$	$PhMe_2SiSiMe(Ph)(H)$	86°–87°/0.05	1.5690	—	*51*
$Si_2C_{15}H_{24}Fe$		(58.0°–59.6°)	—	—	*117*

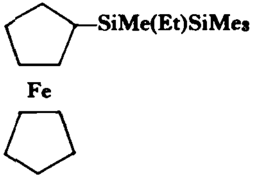
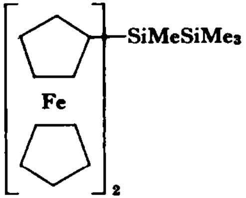
$Si_2C_{16}H_{12}Cl_{10}$	[(C$_6$Cl$_5$)Me$_2$Si–]$_2$	—	—	—	*70*
$Si_2C_{16}H_{20}Br_2$	[(*p*-BrC$_6$H$_4$)Me$_2$Si–]$_2$	(81.5°–82.5°)	—	—	*51, 70*
$Si_2C_{16}H_{20}Cl_2$	[(*p*-ClC$_6$H$_4$)Me$_2$Si–]$_2$	132°/0.1 (61°–62°) (58.0°–59.0°)	— —	— —	*70, 157, 158*
$Si_2C_{16}H_{20}Cl_2$	[(*m*-ClC$_6$H$_4$)Me$_2$Si–]$_2$	(62°–64.5°)	—	—	*147*
$Si_2C_{16}H_{20}F_2$	[(*m*-FC$_6$H$_4$)Me$_2$Si–]$_2$	122°–123°/0.7 (40°–41°)	—	—	*51, 70*
$Si_2C_{16}H_{21}Cl$	(*p*-ClC$_6$H$_4$)Me$_2$SiSiMe$_2$Ph	148°/3 (45.8°–46.5°)	—	—	*158*
$Si_2C_{16}H_{22}$	Ph$_2$MeSiSiMe$_3$	81.5°–82°/0.01 126°/1	1.5606 1.5593	0.9678 (20°/20°) 0.9557	*53, 67, 116*
$Si_2C_{16}H_{22}$	[PhMe$_2$Si–]$_2$	128°–130°/1.8 (34°–35°)	—	—	*2, 32, 53,* *68, 153, 170*
$Si_2C_{16}H_{22}$	[(H)(Ph)(Et)Si–]$_2$	110°–111°/0.1	1.5656	0.969 (20°/20°)	*96, 159, 175*
$Si_2C_{16}H_{26}Fe$		127°/2	—	—	*116*
$Si_2C_{16}H_{30}$	Et$_3$SiSiEt$_2$Ph	144°/3.5	1.5225	0.9122	*25*
$Si_2C_{16}H_{40}GeHg$	Et$_3$SiSiEt$_2$HgGeEt$_3$	159°–163°/1	—	—	*198*
$Si_2C_{17}H_{23}Cl$	(*p*-MeC$_6$H$_4$)Me$_2$SiSiMe$_2$(C$_6$H$_4$Cl-*p*)	193°/1 (47.0°–48.0°)	—	—	*157, 158*
$Si_2C_{17}H_{23}ClO$	(*p*-MeOC$_6$H$_4$)Me$_2$SiSiMe$_2$(C$_6$H$_4$Cl-*p*)	164°/4	1.5752	1.0733	*158*
$Si_2C_{17}H_{24}$	(*p*-MeC$_6$H$_4$)Me$_2$SiSiMe$_2$Ph	171°/12 (20°–21°)	1.5612	0.9517	*158*
$Si_2C_{17}H_{24}O$	(*p*-MeOC$_6$H$_4$)Me$_2$SiSiMe$_2$Ph	150°/2	1.5702	0.9967	*157, 158*
$Si_2C_{18}H_{24}$		161°/4 148°/3	1.5820	1.0030	*112*
$Si_2C_{18}H_{24}$	$\underbrace{\text{PhMeSi}\text{———}\text{SiMePh}}_{(\text{CH}_2)_4}$	158°–162°/3	1.5821 1.5863	1.0115 1.0150	*112*
$Si_2C_{18}H_{26}$	[(*p*-MeC$_6$H$_4$)Me$_2$Si–]$_2$	128°/1 (72°–73°)	—	—	*70, 157, 158*
$Si_2C_{18}H_{26}O$	(*p*-MeC$_6$H$_4$)Me$_2$SiSiMe$_2$(C$_6$H$_4$OMe-*p*)	195°/4 (31°–31.5°)	—	—	*157, 158*

TABLE VIII—(*continued*)

Formula		B.p., °C/mm (m.p., °C)	n_D^{20}	d_4^{20}	References
Molecular	Structural				
$Si_2C_{18}H_{26}O_2$	$[(p\text{-}MeOC_6H_4)Me_2Si\text{-}]_2$	166°/0.4 (45°–46°)	—	—	*51, 70, 157,*
		(38.0°–39.5°)	—	—	*158*
$Si_2C_{18}H_{26}O_2$	$[(EtO)(Ph)(Me)Si\text{-}]_2$	136°–138°/2	1.5344	1.0068	*112*
$Si_2C_{18}H_{42}$	$[(n\text{-}C_3H_7)_3Si\text{-}]_2$	114°/3	1.4740	0.8693 (26°/4°)	*161, 194*
		128.5°–129°/1.5	1.4721	0.8291 (20°)	
$Si_2C_{19}H_{26}$	 PhMeSi—SiMePh (CH₂)₅	180°–184°/4	1.5884	1.0164	*124*
$Si_2C_{20}H_{21}Cl$	$PhMe_2SiSiPh_2Cl$	—	—	—	*75*
$Si_2C_{20}H_{22}$	$Ph_3SiSiMe_2H$	(92.5°–93.0°)			*63*
$Si_2C_{20}H_{22}$	$PhMe_2SiSiPh_2H$	123°–126°/0.002	1.6077	1.0270 (20°/20°)	*75*
$Si_2C_{20}H_{22}$	$[(PhC{\equiv}C)Me_2Si\text{-}]_2$	(76°–78°)	—	—	*51*
$Si_2C_{20}H_{30}$	$[(Ph)Et_2Si\text{-}]_2$	190°–192°/3.5	1.5563	0.9629	*25*
$Si_2C_{20}H_{32}N_2$	$[(p\text{-}Me_2NC_6H_4)Me_2Si\text{-}]_2$	(150.5°–151.5°)	—	—	*51, 70*
$Si_2C_{21}H_{24}$	$Me_3SiSiPh_3$	218°–220°/11	—	—	*15, 46, 53, 67,*
		(108°–109°)			*77, 77a, 116,*
		(105.5°–106.5°)			*163, 175*
$Si_2C_{21}H_{24}$	$Ph_2MeSiSiMe_2Ph$	156°–157°/0.17	1.6027	—	*51, 53*
$Si_2C_{22}H_{34}$	$[(n\text{-}C_3H_7)(Et)(Ph)Si\text{-}]_2$	265°–270°/100	—	—	*97*
$Si_2C_{23}H_{46}Sn$	$[p\text{-}(n\text{-}C_4H_9)_3SnC_6H_4]Me_2SiSiMe_3$	170°/2	1.5189	1.0681	*152*
$Si_2C_{24}H_{30}$	$Et_3SiSiPh_3$	(98°–99°)	—	—	*10, 77a*
		(92.5°–93.5°)			
$Si_2C_{24}H_{30}Fe_2$		(121°–122°)	—	—	*116*

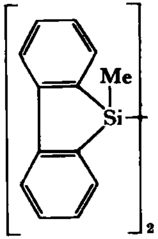
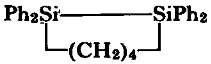
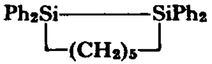
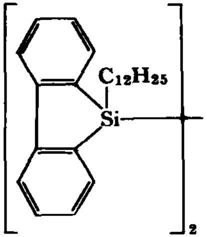
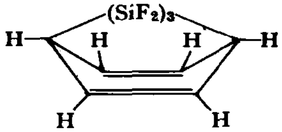
$Si_2C_{24}H_{38}$	$[(n\text{-}C_3H_7)(Et)(PhCH_2)Si\text{-}]_2$	244°–248°/20	—	—	*97*
$Si_2C_{24}H_{38}O_6S_2$	$[(n\text{-}C_3H_7)(Et)(HOSO_2C_6H_4CH_2)Si\text{-}]_2$ and salts	—	—	—	*97*
$Si_2C_{24}H_{46}O_2$	$[(C_6H_{11})_2(HO)Si\text{-}]_2$	—	—	—	*139*
$Si_2C_{24}H_{54}$	$[(n\text{-}C_4H_9)_3Si\text{-}]_2$	187.5°–188.5°/1.5	1.4694	0.8306 (20°)	*194*
$Si_2C_{25}H_{24}$	$Ph_2MeSiSiPh_2H$	(71°–73°)	—	—	*210*
$Si_2C_{25}H_{32}$	(*tert*-$BuCH_2$)(Ph)MeSiSiMePh_2	$[\alpha]_D$ −5.03° (C_6H_6; c, 6.3)		—	*172*
$Si_2C_{26}H_{22}$		(191.0°–191.5°) (185°–186°)	—	—	*58, 127*
$Si_2C_{26}H_{26}$	$Ph_3SiSiPhMe_2$	(85°–86°)	—	—	*53, 68, 106*
$Si_2C_{26}H_{26}$	$[Ph_2MeSi\text{-}]_2$	(142°–144°)	—	—	*53, 64, 67, 68, 153, 175*
$Si_2C_{28}H_{28}$	 $Ph_2Si\text{—}SiPh_2$, $(CH_2)_4$	(110°–111°)	—	—	*51*
$Si_2C_{29}H_{30}$	 $Ph_2Si\text{—}SiPh_2$, $(CH_2)_5$	(114.5°–115.5°)	—	—	*51*
$Si_2C_{30}H_{66}$	$[(iso\text{-}C_5H_{11})_3Si\text{-}]_2$	185.9°–186°/2	1.4667	0.8260 (20°)	*194*
$Si_2C_{31}H_{28}$	$Ph_3SiSiPh_2Me$	(147°–148°)	—	—	*67, 71*
$Si_2C_{32}H_{30}$	$Ph_3SiSiPh_2Et$	(148°–149°)	—	—	*211*
$Si_2C_{32}H_{38}$	$[(n\text{-}C_4H_9)Ph_2Si\text{-}]_2$	(101°–102°)	—	—	*72*

TABLE VIII—(*continued*)

Formula		B.p., °C/mm (m.p., °C)	n_D^{20}	d_4^{20}	References
Molecular	Structural				
$Si_2C_{34}H_{34}$	$Ph_3SiSiPh_2(C_4H_9\text{-}n)$	(224°–226°)	—	—	*51*
$Si_2C_{36}H_{66}$	$[(cyclo\text{-}C_6H_{11})_3Si\text{–}]_2$	(349°–351.5°)	—	—	*94*
$Si_2C_{36}H_{78}$	$[(n\text{-}C_6H_{13})_3Si\text{–}]_2$	235°–236°/0.5	1.4691	0.8366 (20°)	*194*
$Si_2C_{42}H_{42}$	$[(PhCH_2)_3Si\text{–}]_2$	(194°)	—	—	*162*
$Si_2C_{48}H_{66}$		470°–480° (dec.) (59°–61°)	—	—	*58*
$Si_2C_{50}H_{42}$	$[(Ph_2CH)Ph_2Si\text{–}]_2$	(251°–252.5°)	—	—	*51*
$Si_2C_{66}H_{114}$	$Ph_3SiSi(C_{16}H_{33}\text{-}n)_3$	320°–325°/0.001	1.5142	0.9081	*69*
$Si_3C_5H_{15}Cl_3$	$(ClMe_2Si)_2SiMeCl$	113°–115°/47	—	—	*156*
$Si_3C_6H_6F_6$		(72.5°)	—	—	*186*
$Si_3C_6H_{17}Cl_3$	$(ClCH_2)MeSi(SiMe_2Cl)_2$	126°/18	—	—	*106*
$Si_3C_6H_{18}Cl_2$	$(ClMe_2Si)_2SiMe_2$	82°–83°/11 89°–92°/15	1.4852	0.9865	*56, 57, 66, 102, 155*

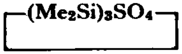
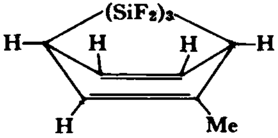
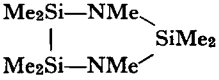
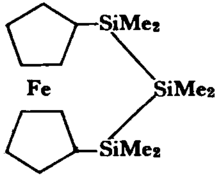
$Si_3C_6H_{18}Cl_2$	$(Me_3Si)_2SiCl_2$	76°–77°/10	1.4800 (20.3°)	0.9708 (20.3°)	*59*
$Si_3C_6H_{18}O_4S$	 $(Me_2Si)_3SO_4$	(82°–83°) (100°–110°/7 sublimes)	—	—	*115*
$Si_3C_6H_{19}Cl$	$Cl(Me_2Si)_3H$	77°/14, 183°	1.4735	—	*56, 57*
$Si_3C_6H_{20}$	$H(Me_2Si)_3H$	54°/22 (−68°)	1.4658	0.7716	*57, 107, 135, 207*
$Si_3C_6H_{20}$	$(Me_3Si)_2SiH_2$	65°/45	1.4590 (20.3°)	0.7620 (20.3°)	*59*
$Si_3C_7H_8F_6$		(37°)	—	—	*186*
$Si_3C_7H_{21}Br$	$Me(Me_2Si)_3Br$	98°/38	1.4781	1.0289	*178*
$Si_3C_7H_{21}Cl$	$Me(Me_2Si)_3Cl$	84°/21	1.4734	0.8802	*107, 155*
$Si_3C_7H_{21}Cl$	$(Me_3Si)_2SiMeCl$	80.5°/20	1.4727	0.8766	*107*
$Si_3C_7H_{22}$	$Me(Me_2Si)_3H$	61°/22	1.4637	0.7729	*107*
$Si_3C_7H_{22}$	$(Me_3Si)_2SiMeH$	59°/21	1.4616	0.7710	*107*
$Si_3C_8H_{21}N$	$Me(Me_2Si)_3CN$	36°–40°/0.4	—	—	*187*
$Si_3C_8H_{22}Cl_2$	$Cl_2CH(Me_2Si)_3Me$	78°/4	1.4993	0.9858	*158*
$Si_3C_8H_{23}Cl$	$(ClCH_2)MeSi(SiMe_3)_2$	108°–109°/23	1.4851	0.8891	*106*
$Si_3C_8H_{24}$	$Me(Me_2Si)_3Me$	112°–112.5°/106 175°–176° (−48°) 62°/13	1.4610	0.7763	*102, 176, 178, 187, 189, 209*
$Si_3C_8H_{24}N_2$	 Me₂Si—NMe SiMe₂ Me₂Si—NMe	70°/13 (−18°)	—	—	*202*
$Si_3C_8H_{24}O_2$	$MeO(Me_2Si)_3OMe$	77°/10	1.4569 (26°)	—	*5*
$Si_3C_9H_{22}$	$HC{\equiv}C(Me_2Si)_3Me$	77.0°/22	1.4744	0.8036	*213*
$Si_3C_9H_{22}$	$(HC{\equiv}C)MeSi(SiMe_3)_2$	74.5°/19	1.4738	0.8007	*213*
$Si_3C_9H_{24}$	$H_2C{=}CH(Me_2Si)_3Me$	79°/16	1.4741	0.7972	*154*

TABLE VIII—(*continued*)

Formula		B.p., °C/mm (m.p., °C)	n_D^{20}	d_4^{20}	References
Molecular	Structural				
$Si_3C_9H_{24}$	$(H_2C{=}CH)MeSi(SiMe_3)_2$	75°/17	1.4761	0.7945	*154*
$Si_3C_9H_{26}$	$(Me_3Si)_2SiMeEt$	67°/5	1.4679 (20.3°)	0.7984 (20.3°)	*60*
$Si_3C_{10}H_{28}$	$Me_3Si(CH_2)_2SiMe_2SiMe_3$	103.5°/42	1.4478	0.7815	*128*
$Si_3C_{10}H_{28}$	$Et(Me_2Si)_3Et$	97°/15	1.4771	0.8052	*115*
$Si_3C_{10}H_{28}Hg$	$Me_3SiCH_2HgCH_2SiMe_2SiMe_3$	90°/3	1.5010	1.3766	*104*
$Si_3C_{11}H_{30}$	$Me_3Si(CH_2)_3SiMe_2SiMe_3$	75°/38	—	—	*128*
$Si_3C_{11}H_{30}Hg$	$Me_3SiCH_2HgCH_2(Me_2Si)_2Et$	101°/3	1.5040	1.3621	*104*
$Si_3C_{12}H_{24}$	$(Me_3Si)_2SiPh(H)$	75°–80°/0.55	1.5273	—	*54*
$Si_3C_{12}H_{26}$	$C_5H_5(Me_2Si)_3Me$	80°/2.5	1.5126	0.8681	*116*
$Si_3C_{12}H_{28}$	$CH_2{=}(Me)C(Me_2Si)_3C(Me){=}CH_2$	110°/15	1.4983	0.8340	*119*
$Si_3C_{13}H_{26}$	$Ph(Me_2Si)_3Me$	142°/23	1.5204	0.8769	*107, 153*
$Si_3C_{13}H_{26}$	$(Me_3Si)_2SiMePh$	133°/19	1.5236	0.8683	*54, 107, 153*
$Si_3C_{14}H_{28}$	$PhMe_2SiCH_2SiMe_2SiMe_3$	100°–101°/4.5	1.5053	0.8827	*156*
$Si_3C_{14}H_{28}O$	$(p\text{-}Me_3SiOC_6H_4)Me_2SiSiMe_3$	142°/15	1.4983	0.9115	*145*
$Si_3C_{16}H_{26}Fe$		142°–144°/1	—	—	*116*
$Si_3C_{16}H_{28}$	$C_5H_5(Me_2Si)_3C_5H_5$	110°/1.7	1.5508	0.9760	*116*
$Si_3C_{18}H_{18}Cl_{10}$	$Cl_5C_6(Me_2Si)_3C_6Cl_5$	—	—	—	*70*
$Si_3C_{18}H_{18}F_{10}$	$F_5C_6(Me_2Si)_3C_6F_5$	—	—	—	*70*
$Si_3C_{18}H_{28}$	$Ph(Me_2Si)_3Ph$	120°–122°/0.15	1.5663	—	*51, 52, 54*
$Si_3C_{18}H_{28}$	$(Me_3Si)_2SiPh_2$	105.5°–106°/0.2	1.5736	—	*72*

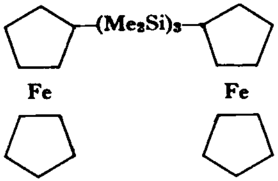
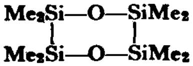
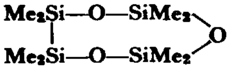
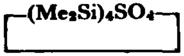
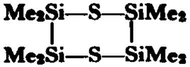
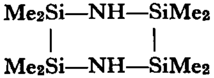
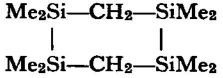
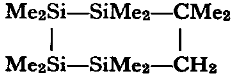
$Si_3C_{22}H_{28}$	$PhC{\equiv}C(Me_2Si)_3C{\equiv}CPh$	165°–167°/0.15	1.5895	—	*51*
$Si_3C_{23}H_{30}$	$Me_3SiSiMe_2SiPh_3$	198°–201°/3 (68°–70°)	—	—	*115*
$Si_3C_{26}H_{36}Fe_2$		(136°–137°)	—	—	*116*
$Si_3C_{28}H_{32}$	$(Ph_2MeSi)_2SiMe_2$	(62.5°–64°)	—	—	*51*
$Si_3C_{38}H_{36}$	$(Ph_3Si)_2SiMe_2$	(230°–232.5°)	—	—	*76, 115*
		(223°–227°)	—	—	
$Si_4C_7H_{24}$	$(HMe_2Si)_3SiMe$	68°/5.2	—	—	*63*
$Si_4C_8H_{24}Cl_2$	$Cl(Me_2Si)_4Cl$	98°/5	1.5066	0.9736	*56, 57, 66,*
		76°–78°/1.0	—	—	*107*
$Si_4C_8H_{24}O_2$	 $\begin{array}{l}\mathrm{Me_2Si{-}O{-}SiMe_2}\\ \quad\vert\qquad\quad\vert\\ \mathrm{Me_2Si{-}O{-}SiMe_2}\end{array}$	(45.0°–45.5°)	—	—	*109*
$Si_4C_8H_{24}O_3$	 $\begin{array}{l}\mathrm{Me_2Si{-}O{-}SiMe_2}\\ \quad\vert\\ \mathrm{Me_2Si{-}O{-}SiMe_2}\end{array}\!>\mathrm{O}$	67°/10	1.4254	0.9284	*109*
$Si_4C_8H_{24}O_4S$	 $(Me_2Si)_4SO_4$	125°–130°/0.8	—	—	*115*
$Si_4C_8H_{24}S_2$	 $\begin{array}{l}\mathrm{Me_2Si{-}S{-}SiMe_2}\\ \quad\vert\qquad\quad\vert\\ \mathrm{Me_2Si{-}S{-}SiMe_2}\end{array}$	(111°–112°) (100°/3 sublimes)	—	—	*204*
$Si_4C_8H_{25}Cl$	$Cl(Me_2Si)_4H$	59°/0.8–1.0	1.4986	—	*56, 57*
		226°–232°	—	—	
$Si_4C_8H_{26}$	$H(Me_2Si)_4H$	74°/9, 68°–70°/1	1.4922	0.8056	*57, 107, 207*
$Si_4C_8H_{26}N_2$	 $\begin{array}{l}\mathrm{Me_2Si{-}NH{-}SiMe_2}\\ \quad\vert\qquad\qquad\vert\\ \mathrm{Me_2Si{-}NH{-}SiMe_2}\end{array}$	61°/2 (1°)	1.4760	0.8458 (20°)	*203*

TABLE VIII—(*continued*)

Formula		B.p., °C/mm (m.p., °C)	n_D^{20}	d_4^{20}	References
Molecular	Structural				
$Si_4C_9H_{27}Cl$	$(Me_3Si)_3SiCl$	70°–72°/0.5 (51°–52°)	—	—	*59*
$Si_4C_9H_{28}$	$(Me_3Si)_3SiH$	80°–83°/8	—	—	*63*
$Si_4C_9H_{28}O$	$(Me_3Si)_3SiOH$	81°/1.5	1.4990 (20.3°)	0.8668 (20.3°)	*59*
$Si_4C_{10}H_{27}N$	$Me(Me_2Si)_4CN$	65°–75°/0.4	—	—	*187*
$Si_4C_{10}H_{28}$	 $\begin{array}{c}Me_2Si{-}CH_2{-}SiMe_2\\ \vert \qquad\qquad \vert\\ Me_2Si{-}CH_2{-}SiMe_2\end{array}$	108°–109°/15 (51°–53°)	—	—	*26, 106*
$Si_4C_{10}H_{30}$	$Me(Me_2Si)_4Me$	109°/15	1.4878	0.8073	*57, 66, 102, 176, 179, 187, 189, 209*
		242°	1.4876	0.7889	
		(−12°) (−4°)			
$Si_4C_{10}H_{30}$	$(Me_3Si)_3SiMe$	94°–96°/7	—	—	*59, 63*
$Si_4C_{10}H_{30}NNa$	$(Me_3SiSiMe_2)_2NNa$	(58°–62°)	—	—	*203*
$Si_4C_{10}H_{30}O$	$(Me_3SiSiMe_2)_2O$	214.4°	1.4334 (30°)	0.8028 (30°/4°)	*30, 109, 178*
		101°/20	1.4395	—	
$Si_4C_{10}H_{30}O_2$	$(Me_3SiOSiMe_2{-})_2$	196°–197°, 90°/20	1.4080 (30°)	0.8222 (30°/4°)	*109*
$Si_4C_{10}H_{30}O_2$	$MeO(Me_2Si)_4OMe$	116°/10	1.4809 (26°)	—	*5*
$Si_4C_{10}H_{30}O_4S$	$(Me_3SiSiMe_2)_2SO_4$	117°–118°/3	—	—	*115*
$Si_4C_{10}H_{30}O_6$	$[(MeO)_2MeSi]_3SiMe$	110°–111°/1.8	—	—	*4*
$Si_4C_{10}H_{31}N$	$(Me_3SiSiMe_2)_2NH$	132.5°–134°/40.5	1.4556 (30°)	0.8053 (30°/4°)	*188, 203*
		102°–103°/13	1.4609	0.8154 (20°)	
$Si_4C_{11}H_{32}$	$(Me_3SiSiMe_2)_2CH_2$	103°/12	1.4706	0.8082	*156*
$Si_4C_{11}H_{33}N$	$Me_3SiSiMe_2N(SiMe_3)_2$	90°–93°/14 (< −70°)	1.442	0.822 (20°)	*203*
$Si_4C_{12}H_{30}$	$Me_3SiSiMe_2C{\equiv}CSiMe_2SiMe_3$	118°–119°/24	1.4678	0.8057	*213*
$Si_4C_{12}H_{30}$	$CH_2{=}CH(Me_2Si)_4CH{=}CH_2$	97°/1.4	1.5097	—	*51, 53*
$Si_4C_{12}H_{32}$	 $\begin{array}{c}Me_2Si{-}SiMe_2{-}CMe_2\\ \vert \qquad\qquad \vert\\ Me_2Si{-}SiMe_2{-}CH_2\end{array}$	(44°–45°)	—	—	*137*

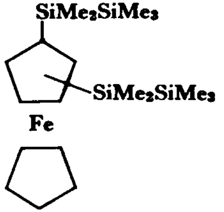
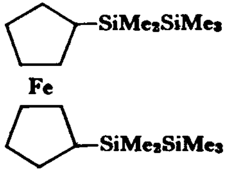
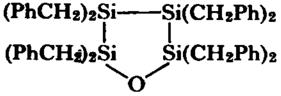
$Si_4C_{12}H_{34}$	$(Me_3SiSiMe_2CH_2-)_2$	121°–123°/20	1.4664	0.8054	*150*
$Si_4C_{14}H_{29}Cl$	$Ph(Me_2Si)_4Cl$	158°/5	—	—	*115*
$Si_4C_{15}H_{32}$	$(Me_3Si)_3SiPh$	140°/0.05 (waxy solid)	—	—	*54*
$Si_4C_{16}H_{34}$	p-$(Me_3SiSiMe_2)_2C_6H_4$	130°/4 (80°)	—	—	*25*
$Si_4C_{16}H_{42}$	$Et_6Me_4Si_4$	—	—	—	*43*
$Si_4C_{20}H_{24}Cl_{10}$	$Cl_5C_6(Me_2Si)_4C_6Cl_5$	—	—	—	*70*
$Si_4C_{20}H_{34}$	$Ph(Me_2Si)_4Ph$	(59.5°–60.0°) (59°–61°)	—	—	*52, 66, 107*
$Si_4C_{20}H_{38}Fe$		142°–150°/1	1.5452	—	*124a*
$Si_4C_{20}H_{38}Fe$		(58.4°)	—	—	*117*
$Si_4C_{20}H_{50}$	$Et(Et_2Si)_4Et$	164°–170°/1	1.5160	—	*140, 197*
$Si_4C_{20}H_{50}Hg$	$(Et_3SiSiEt_2)_2Hg$	180°–190°/1	—	—	*198*
$Si_4C_{22}H_{38}$	$[(p\text{-}Me_3SiC_6H_4)Me_2Si-]_2$	(111°–112°)	—	—	*51, 70*
$Si_4C_{24}H_{33}Cl$	$(PhMe_2Si)_3SiCl$	—	—	—	*54*
$Si_4C_{24}H_{34}$	$PhC\equiv C(Me_2Si)_4C\equiv CPh$	154°–161°/0.025	1.5943	—	*51*
$Si_4C_{24}H_{34}$	$(PhMe_2Si)_3SiH$	(91°–93°)	—	—	*54*
$Si_4C_{24}H_{58}$	$(Et_3SiSiEt_2C_2H_4-)_2$	183°–190°/2	1.5040	—	*196*

TABLE VIII—(*continued*)

Formula		B.p., °C/mm (m.p., °C)	n_D^{20}	d_4^{20}	References
Molecular	Structural				
$Si_4C_{30}H_{38}$	$(Me_3SiSiPh_2-)_2$	(265°–267°)	—	—	*51, 72*
$Si_4C_{40}H_{42}$	$(Ph_3SiSiMe_2-)_2$	(215°–217°)	—	—	*51, 115*
		(209°–210°)			
$Si_4C_{41}H_{44}$	$(Ph_3SiSiMe_2)_2CH_2$	(112.3°–112.5°)	—	—	*115*
$Si_4C_{50}H_{46}$	$Me(Ph_2Si)_4Me$	(220°–222°)	—	—	*88, 89*
$Si_4C_{52}H_{50}$	$Et(Ph_2Si)_4Et$	(253°–254°)	—	—	*98*
$Si_4C_{56}H_{56}O$		(40°–60°)	—	—	*174*
$Si_4C_{64}H_{50}$	$[(PhC{\equiv}C)Ph_2SiPh_2Si-]_2$	(187°–189°)	—	—	*51*
$Si_5C_8H_{24}Cl_4$	$(ClMe_2Si)_4Si$	—	—	—	*156*
$Si_5C_8H_{28}$	$(HMe_2Si)_4Si$	77°/1.4 (40°–42°)	—	—	*63*
$Si_5C_{10}H_{30}$	$(Me_2Si)_5$	(188°–190°)	—	—	*21, 115*
$Si_5C_{10}H_{30}Cl_2$	$Cl(Me_2Si)_5Cl$	87°–89°/0.1	1.5220	—	*56, 57, 115*
		122°–123°/4	1.5209	0.9688	
$Si_5C_{10}H_{31}Cl$	$Cl(Me_2Si)_5H$	79°/0.1	1.5145	—	*56, 57*
		75°/0.06			
$Si_5C_{10}H_{32}$	$H(Me_2Si)_5H$	—	—	—	*57, 207*
$Si_5C_{12}H_{33}N$	$Me(Me_2Si)_5CN$	81°–85°/0.4	—	—	*187*
$Si_5C_{12}H_{36}$	$Me(Me_2Si)_5Me$	135°–136°/13	1.5060	0.8329	*102, 187*
		(−34°)	1.5009 (30°)	0.8235 (30°/4°)	
$Si_5C_{12}H_{36}$	$(Me_3Si)_4Si$	(261°–263°)	—	—	*63, 74*
		(75°/0.01 sublimes)			

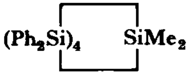
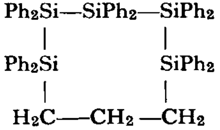
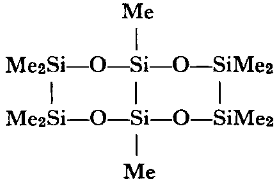
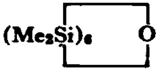
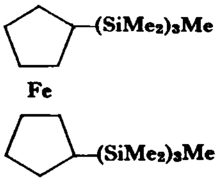
$Si_5C_{12}H_{36}O_2$	$MeO(Me_2Si)_5OMe$	125°/3	1.4974 (25°)	—	*5*
$Si_5C_{22}H_{30}Cl_{10}$	$Cl_5C_6(Me_2Si)_5C_6Cl_5$	—	—	—	*70*
$Si_5C_{22}H_{40}$	$Ph(Me_2Si)_5Ph$	208°–211°/2 (66°)	—	—	*52, 115*
$Si_5C_{32}H_{44}$	$(Me_3SiSiPh_2)_2SiMe_2$	(97°–97.5°)	—	—	*51*
$Si_5C_{42}H_{48}$	$Me_3Si(Ph_2Si)_3SiMe_3$	(315°–320°)	—	—	*72*
$Si_5C_{42}H_{48}$	$Ph_3Si(Me_2Si)_3SiPh_3$	(190°–191°) (185°–186.5°)	—	—	*51, 115*
$Si_5C_{50}H_{46}$		(315°–317°)	—	—	*50, 51*
$Si_5C_{62}H_{56}$	$Me(Ph_2Si)_5Me$	(189°–190°)	—	—	*72*
$Si_5C_{63}H_{56}$		(290°–291°)	—	—	*65*
$Si_5C_{64}H_{60}O_2$	$HOCH_2CH_2(Ph_2Si)_5CH_2CH_2OH$	(167°–169°)	—	—	*51*
$Si_5C_{68}H_{68}$	$n\text{-}C_4H_9(Ph_2Si)_5C_4H_9\text{-}n$	(162°–164°)	—	—	*72*
$Si_6C_{10}H_{30}O_4$		(55.5°–56.5°) (55°–60°/4–2 sublimes)	—	—	*109*
$Si_6C_{12}H_{36}$	$(Me_2Si)_6$	(250°–252°) (sublimes)	—	—	*17, 18, 50, 76, 86, 168, 177*
$Si_6C_{12}H_{36}Cl_2$	$Cl(Me_2Si)_6Cl$	143°–144°/0.02 160°–162°/0.8 (45°–46.5°)	—	—	*56, 57, 66*

TABLE VIII—(*continued*)

Formula		B.p., °C/mm (m.p., °C)	n_D^{20}	d_4^{20}	References
Molecular	Structural				
$Si_6C_{12}H_{36}I_2$	$I(Me_2Si)_6I$	(185°/2 sublimes)	—	—	*177*
$Si_6C_{12}H_{36}O$		(144°–147°)	—	—	*51*
$Si_6C_{12}H_{36}O_2$	$(-SiMe_2SiMe_2SiMe_2O-)_2$	101°/3	1.4849	0.9000	*106*
$Si_6C_{12}H_{37}Cl$	$Cl(Me_2Si)_6H$	105°/0.1, 100°/0.06	1.5302	—	*56, 57*
$Si_6C_{12}H_{38}$	$H(Me_2Si)_6H$	103°/0.12	1.5251	—	*51, 57*
$Si_6C_{14}H_{39}N$	$Me(Me_2Si)_6CN$	—	—	—	*187*
$Si_6C_{14}H_{42}$	$Me(Me_2Si)_6Me$	165°/10 (28°–29°)	1.5139 (30°)	0.8401 (30°/4°)	*66, 102*
$Si_6C_{14}H_{42}O_2$	$Me(Me_2SiSiMe_2O)_2SiMe_2SiMe_3$	110°–111°/3	1.4472	0.8458	*30, 109*
		—	1.4395 (30°)	0.8238 (30°/4°)	
$Si_6C_{14}H_{42}O_3$	$Me_3SiO(SiMe_2SiMe_2O)_2SiMe_3$	160°–161°/34	1.4235 (30°)	0.8524 (30°/4°)	*109*
$Si_6C_{16}H_{46}$	$(Me_3SiSiMe_2)_3CH$	146°/0.8 (64.5°–65°)	—	—	*156*
$Si_6C_{18}H_{51}B$	$(Me_3SiSiMe_2CH_2)_3B$	156°/3.6	1.4854	0.8341	*101*
$Si_6C_{24}H_{36}Cl_{10}$	$Cl_5C_6(Me_2Si)_6C_6Cl_5$	—	—	—	*70*
$Si_6C_{24}H_{46}$	$Ph(Me_2Si)_6Ph$	(86°–87°)	—	—	*52, 66*
$Si_6C_{24}H_{50}Fe$		(46°–46.5°)	—	—	*116*
$Si_6C_{28}H_{46}$	$PhC{\equiv}C(Me_2Si)_6C{\equiv}CPh$	180°–181°/0.015	1.5910	—	*51*
$Si_6C_{28}H_{56}N_2$	$p\text{-}Me_2NC_6H_4(Me_2Si)_6C_6H_4NMe_2\text{-}p$	(148.5°–149.5°)	—	—	*51*
$Si_6C_{36}H_{86}$	$(Et_3SiSiEt_2C_4H_8Et_2Si-)_2$	239°–246°/2	1.5120	—	*196*

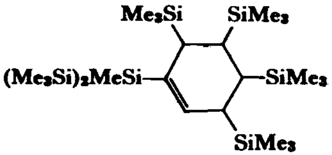
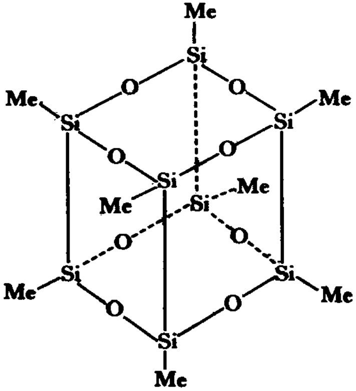
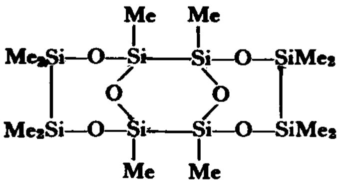
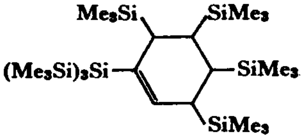
$Si_6C_{44}H_{54}$	$Ph_3Si(Me_2Si)_4SiPh_3$	(180°–182°) (189°–190°)	—	—	*51, 115*
$Si_6C_{54}H_{58}$	$Me_3Si(Ph_2Si)_4SiMe_3$	(293°–296°)	—	—	*72*
$Si_6C_{62}H_{56}$		(472°–476°)	—	—	*51, 72*
$Si_6C_{65}H_{60}$		—	—	—	*50*
$Si_6C_{74}H_{66}$	$Me(Ph_2Si)_6Me$	(182°–183°) (209°–211°)	—	—	*61, 210*
$Si_7C_{14}H_{42}$	$(Me_2Si)_7$	(228°–232°)	—	—	*21*
$Si_7C_{16}H_{48}$	$Me(Me_2Si)_7Me$	194°/16 (19°–20°)	1.5264 (30°)	0.8492 (30°/4°)	*102*
$Si_7C_{25}H_{62}$		(120°–121°)	—	—	*62*
$Si_7C_{46}H_{60}$	$Ph_3Si(Me_2Si)_5SiPh_3$	(151°–152°)	—	—	*115*
$Si_7C_{66}H_{68}$	$Me_3Si(Ph_2Si)_5SiMe_3$	(197°–198°)	—	—	*72*
$Si_8C_8H_{24}O_8$		(315°–318° decomp.) (120°–160°/11 sublimes)	—	—	*109*

TABLE VIII—(*continued*)

Formula		B.p., °C/mm (m.p., °C)	n_D^{20}	d_4^{20}	References
Molecular	Structural				
$Si_8C_{12}H_{36}O_6$		(126°–127°) (85°/2 sublimes)	—	—	*109*
$Si_8C_{18}H_{48}N_2$	$NC(Me_2Si)_8CN$	—	—	—	*187*
$Si_8C_{18}H_{51}N$	$Me(Me_2Si)_8CN$	—	—	—	*187*
$Si_8C_{18}H_{54}$	$Me(Me_2Si)_8Me$	198°/4 (63°)	—	—	*108*
$Si_8C_{18}H_{54}$	$[(Me_3Si)_3Si\text{–}]_2$	(372°–374°) (decomp.)	—	—	*59*
$Si_8C_{18}H_{54}O_3$	$Me(Me_2SiSiMe_2O)_3SiMe_2SiMe_3$	156°/3	1.4514	0.8624	*109*
$Si_8C_{18}H_{54}O_4$	$Me_3SiO(Me_2SiSiMe_2O)_3SiMe_3$	158°–159°/3	1.4331 (30°)	0.8662 (30°/4°)	*109*
$Si_8C_{27}H_{68}$		(222°–227°)	—	—	*62*
$Si_8C_{48}H_{66}$	$Ph_3Si(Me_2Si)_6SiPh_3$	(154°–156°)	—	—	*51*
$Si_9C_{20}H_{60}$	$Me(Me_2Si)_9Me$	231°/4 (90.5°)	—	—	*108*
$Si_9C_{100}H_{92}$	$PhMe_2Si(Ph_2Si)_7SiMe_2Ph$	(230°–232°)	—	—	*75*
$Si_{10}C_{22}H_{66}$	$Me(Me_2Si)_{10}Me$	245°/4 (115°)	—	—	*108*
$Si_{10}C_{22}H_{66}O_4$	$Me(SiMe_2SiMe_2O)_4SiMe_2SiMe_3$	190°–191°/3	1.4533	0.8743	*109*
$Si_{10}C_{22}H_{66}O_5$	$Me_3SiO(SiMe_2SiMe_2O)_4SiMe_3$ (slightly impure)	192°–196°/2	1.4400 (30°)	0.8790 (30°/4°)	*109*
$Si_{10}C_{72}H_{86}$	$Ph_3SiSiPh_2(Me_2Si)_6SiPh_2SiPh_3$	(215°–218°)	—	—	*51*
$Si_{11}C_{24}H_{72}$	$Me(Me_2Si)_{11}Me$	257°/3 (130°)	—	—	*108*
$Si_{12}C_{26}H_{78}$	$Me(Me_2Si)_{12}Me$	280°/4 (153°)	—	—	*108*

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Catalysis by Cobalt Carbonyls

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I

INTRODUCTION

Transition metal carbonyls and their derivatives are remarkably effective and varied in their ability to catalyze reactions between unsaturated molecules (e.g., CO and olefinic compounds) or between certain saturated and unsaturated molecules (e.g., olefins and H_2 or H_2O). The carbonyl derivatives of cobalt are particularly active catalysts for such reactions and have been put to use in the industrial synthesis of higher aliphatic alcohols. In fact, much of the growth in knowledge concerning catalysis by metal carbonyls has been stimulated by the industrial importance of the Fischer–Tropsch synthesis, and by the economically less important, but chemically more tractable, hydroformylation reaction.

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In the present review we shall describe recent developments in the catalysis of reactions by dicobalt octacarbonyl. Although many of the reactions to be described do not necessarily involve dicobalt octacarbonyl directly in the catalytic cycle, but some derivative, there are several reasons for choosing this compound as a starting point. The most important reason being that dicobalt octacarbonyl is a reasonably stable, commercially available, fairly well characterized compound which easily gives active catalytic intermediates. Although by no means unique in their catalytic properties, the cobalt carbonyls do provide a particularly active and versatile example of metal carbonyl catalysis. Their catalytic reactions are also by far the most investigated and best understood.

Two excellent reviews summarize the literature up to 1961. The first reviews the chemistry and catalytic properties of cobalt and iron carbonyls (*158*) while the second stresses the synthetic aspects (*15*).

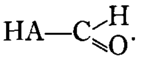
Since 1961, the industrial importance of the hydroformylation reaction has been threatened by newer processes (*19*) such as the Ziegler polymerization of ethylene, the Wacker process, and the direct oxidation of petroleum (*153*). The industrial aspects of the Oxo reaction were reviewed in 1965 when the world production capacity for Oxo products was estimated at 0.5 million tons per year (*39*).

In spite of some declining industrial interest, the last 5 years have seen an unusual academic interest in the catalytic properties of the metal carbonyls. This has been part of a wider surge of interest in the organometallic chemistry of the transition metals and its application to homogeneous catalysis. Reactions such as Ziegler polymerization, the Oxo reaction, and the Wacker process are but a few of the many reactions of unsaturated molecules catalyzed in the coordination sphere of transition metal complexes (*20*). These coordination catalyses have much in common, and the study of one is often pertinent to the study of the others.

Most of the growth in our understanding of reactions catalyzed by dicobalt octacarbonyl has resulted from a study of the individual reactions of catalytic intermediates such as cobalt hydrocarbonyl. At much lower temperatures and pressures than are used in the corresponding catalytic processes, cobalt hydrocarbonyl has been found to give rise to similar reactions, but stoichiometrically. The study of these noncatalytic reactions has enhanced our understanding of the corresponding catalytic reactions to the point where we can focus on the reasons for the smaller differences rather than the larger similarities. Because of their importance, a discussion of the stoichiometric reactions precedes consideration of the corresponding catalytic reactions where appropriate.

Since most of the advances since 1961 have been made in our understanding of mechanism, reactions will be considered according to reaction type rather than according to product. Such a classification cannot be too rigid, however, since many reactions frequently occur together. Thus the hydroformylation reaction itself is sometimes complicated by side reactions such as the hydrogenation and isomerization of the olefin. Although such side reactions will receive consideration in the section on hydroformylation, for the most part we shall attempt to systematize reported results according to the reaction of major importance to the particular study.

The classifications of reactions are as follows:

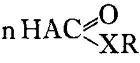
(i) Hydroformylation: addition of H_2 and CO to a substrate A to produce a product of composition  $\mathrm{HA{-}C}\begin{matrix}\diagup\mathrm{H}\\ \diagdown\!\!\diagdown\mathrm{O}\end{matrix}$.

(ii) Hydrogenation: addition of H_2 to a substrate A to produce a product of composition AH_2.

(iii) Hydrogenolysis: addition of H_2 to a substrate A—B to produce products of composition AH and BH.

(iv) Hydrosilation: addition of R_3SiH to a substrate A to produce R_3SiAH.

(v) Isomerization: rearrangement of the atoms of substrate A.

(vi) Carboxylation: addition of CO and RXH to a substrate A to produce a product of composition  $\mathrm{HAC}\begin{matrix}\diagup\!\!\diagup\mathrm{O}\\ \diagdown\mathrm{XR}\end{matrix}$, where RXH = H_2O, ROH, RNH_2, etc.

(vii) Carbonylation: addition of CO to a substrate A to produce a product of composition ACO.

(viii) Polymerization: reaction of n molecules of A to produce a polymer A_n.

The detailed chemistry of the alkyl- and acylcobalt carbonyls which are reaction intermediates in many of these catalyses has recently been excellently reviewed by Heck (*59*). For this reason we have confined ourselves to the catalytic implications so as to supplement that review.[2]

Much of the literature concerning catalysis by metal carbonyls is in the form of patents. Many of the claims of catalyst improvement are of doubtful

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[2] We are grateful to Dr. R. F. Heck for a copy of this review in advance of publication.

scientific value and will receive only brief mention. Synthetic uses were extensively covered in the last review in tabular form and these are brought up to date in this review. Extensive quotations have been avoided, however. in favor of a limited number of selected examples.

II

HYDROFORMYLATION

A. The Stoichiometric Hydroformylation of Olefins

1. *Mechanism*

The noncatalytic reaction of cobalt hydrocarbonyl with olefins to produce aldehydes

$$2\ HCo(CO)_4 + CO + \text{Olefin} \rightarrow Co_2(CO)_8 + \text{Aldehyde} \qquad (1)$$

has been known for some time (*159*). This stoichiometric reaction has received particular study (*62*, *73*, *147*) since the last review as cobalt hydrocarbonyl is now generally accepted as the key intermediate in the catalytic reaction. The relevance to the mechanism of the catalytic reaction will be considered later. Equation (1) had been shown to proceed in two stages (*60*).

$$RCH{=}CH_2 + HCo(CO)_4 + CO \rightarrow RCH_2CH_2COCo(CO)_4 \qquad (2)$$

$$RCH_2CH_2COCo(CO)_4 + HCo(CO)_4 \rightarrow RCH_2CH_2CHO + Co_2(CO)_8 \qquad (3)$$

Aldehyde was also produced under nitrogen (*73*), but the ratio of branched to straight-chain aldehyde was much greater than in the presence of 1 atm of carbon monoxide. Under nitrogen the carbon monoxide must have come from the cobalt hydrocarbonyl so that in this case an acylcobalt tricarbonyl would be formed in Eq. (2).

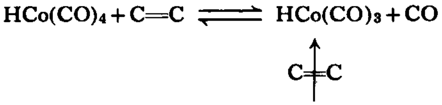
When a large excess of olefin was used, the cobalt hydrocarbonyl was completely used up in Eq. (2), and Eq. (3) did not occur. In this case the products have been recovered as the triphenylphosphine derivatives, or as the esters by reaction of the acylcobalt carbonyls with iodine and an alcohol.

For 1-pentene, Karapinka and Orchin (*73*) found that Eq. (2) was strongly inhibited by carbon monoxide at 0° C. This was confirmed by Heck and Breslow (*62*) who noted that the inhibition also retarded the formation of alkyl- and acylcobalt carbonyls as well as aldehydes. Thus, about 30% less alkyl- and acylcobalt carbonyls were formed in 15 minutes under 1 atm of carbon monoxide than under 1 atm of nitrogen. These results should not, of course, be taken as implying that nitrogen promotes the reaction. Takegami *et al.* (*147*) have noted that under nitrogen a side reaction consumes cobalt hydrocarbonyl so that even if carbon monoxide is added subsequently, little carbon monoxide uptake occurs. This was not found to be the case when the treatment with nitrogen was preceded by a short period under carbon monoxide. These observations are probably related to the fact that, under nitrogen, olefins can react with cobalt hydrocarbonyl to produce ketones and cobalt carbonyls (*14*), e.g.,

$$RCOCo(CO)_4 + R'Co(CO)_3 \rightarrow RCOR' + Co_2(CO)_7 \qquad (4)$$

This reaction will be discussed in greater detail later.

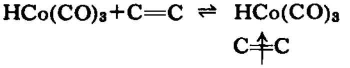
Karapinka and Orchin suggested that the inhibition of Eq. (2) results from the suppression of the formation of an olefin intermediate formed by an S_N2 reaction



$$HCo(CO)_4 + C{=}C \rightleftharpoons \underset{\substack{\uparrow \\ C=C}}{HCo(CO)_3} + CO \qquad (5)$$

Heck and Breslow preferred to postulate this occurring in two stages involving an initial S_N1 reaction

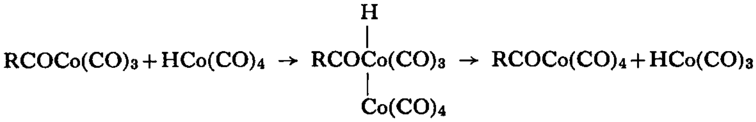
$$HCo(CO)_4 \rightleftharpoons HCo(CO)_3 + CO \qquad (6)$$



$$HCo(CO)_3 + C{=}C \rightleftharpoons \underset{C \overset{\uparrow}{=} C}{HCo(CO)_3} \qquad (7)$$

It is not easy to distinguish between these alternatives since they give rise to such a similar kinetic pattern. It is possible that each may occur under appropriate conditions; analogies for both possibilities exist in metal carbonyl chemistry (*96*). Subsequent steps such as the insertion of olefin to give the alkylcobalt carbonyl are also susceptible to S_N1 or S_N2 interpretations. Carbon monoxide insertion does occur in the absence of an atmosphere of carbon monoxide but the reaction could be assisted here by the presence of olefin (*73*).

The results of Takegami *et al.* (*147*) on the formation of acylcobalt carbonyls from olefins include curves of carbon monoxide uptake against time which are autocatalytic. This implies that the intermediate suppressed by carbon monoxide is also formed as the product of a subsequent reaction. This intermediate is likely to be $HCo(CO)_3$, which might be formed by a reaction such as



$$RCOCo(CO)_3 + HCo(CO)_4 \rightarrow \underset{\substack{| \\ Co(CO)_4}}{\overset{\substack{H \\ |}}{RCOCo(CO)_3}} \rightarrow RCOCo(CO)_4 + HCo(CO)_3 \qquad (8)$$

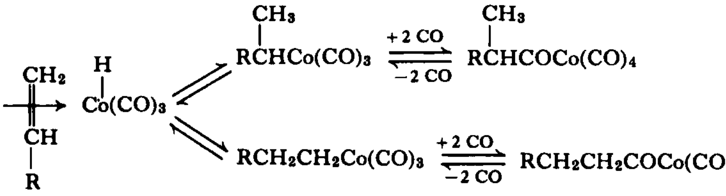
Reactions such as this are analogous to the oxidative cleavage reactions of other d^8 complexes such as Ir^I and Pt^{II} (*59*).

The conditions under which cobalt hydrocarbonyl was reacted with olefin were also found to affect the distribution of products and the extent of isomerization of excess olefin (*62*, *73*, *147*). At low temperatures (0° C) under carbon monoxide (1 atm) very little isomerization of excess 1-pentene occurred and the main product was the terminal aldehyde. Under nitrogen or under carbon monoxide at 25° C, extensive olefin isomerization occurred and the branched aldehyde was mainly produced. The olefin isomerization is most satisfactorily accounted for by an equilibrium between alkylcobalt and olefin–hydride cobalt complexes [Eqs. (9) and (10)]. The carbon monoxide inhibition is most easily explained if the isomerization proceeds via the tricarbonyls rather than tetracarbonyls. This also explains why ethylcobalt tetracarbonyl is not in equilibrium with hydrocarbonyl and ethylene under conditions where the isomerization is rapid (*62*, *73*).

2. *Distribution of Products*

The products of the reaction are determined by two factors: (1) the initial direction of the addition of hydrocarbonyl; (2) isomerization of the resulting alkyl- or acylcobalt carbonyls.

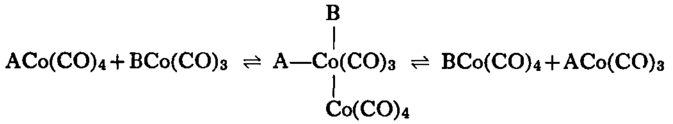
Heck and Breslow (*62*) have postulated equilibria between acylcobalt carbonyls and olefin–hydride complexes.



(9)

(10)

This seems to be the most likely mechanism, both for the isomerization of the acylcobalt carbonyls and excess olefin. The fact that the isomerizing species contains two molecules of carbon monoxide less than the acylcobalt tetracarbonyl would suggest a very slow rate of isomerization. However, it is conceivable that the reaction may be catalyzed by the tricarbonyls, e.g.,



$$ACo(CO)_4 + BCo(CO)_3 \rightleftharpoons A\text{—}\underset{\substack{|\\ Co(CO)_4}}{\overset{\substack{B\\ |}}{Co(CO)_3}} \rightleftharpoons BCo(CO)_4 + ACo(CO)_3 \qquad (11)$$

where A and B are alkyl or acyl. This type of reaction has already been considered; cf. Eq. (8). Both olefin isomerization and the isomerization of acylcobalt carbonyls are inhibited by carbon monoxide (*62*, *73*, *149*), suggesting a common intermediate as required by Heck and Breslow's mechanism. If little or no isomerization occurs, the products will be determined by the initial addition of hydrocarbonyl, but if isomerization is extensive, the products will depend on the relative stability of the acylcobalt carbonyls formed.

Of the two acylcobalt tetracarbonyls, the linear isomer is likely to be the more stable thermally at any given pressure of carbon monoxide since the dissociation of the acylcobalt tetracarbonyl to the acylcobalt tricarbonyl is promoted by steric effects (*52*, *118*). Increasing temperature should therefore favor the linear product if the carbon monoxide pressure is sufficient to form mainly acylcobalt tetracarbonyls. The stability of the tricarbonyls, however, is more likely to be determined by the electronic effects which determine the initial addition of cobalt hydrocarbonyl.

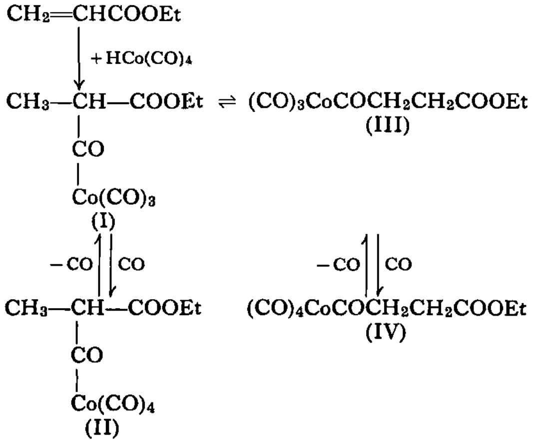
The distribution of products is therefore only likely to reflect the direction of the initial addition of hydrocarbonyl if acylcobalt tricarbonyls are formed or if the temperature is sufficiently low and the carbon monoxide pressure is sufficiently high to allow no isomerization.

For a more detailed consideration of the isomerization of alkyl- and acylcobalt carbonyls, Section V,B should be consulted. It is sufficient to say here that this isomerization is normally slow at room temperature, especially for the linear acylcobalt tetracarbonyls. The reaction also appears to be quite sensitive to solvent for reasons which have not yet been adequately explained. Alkylcobalt carbonyls are rapidly converted to the acylcobalt carbonyls and do not appear to give rise to any significantly faster isomerization.

Prior to Takegami's studies, the effect of isomerization of acylcobalt carbonyls on the products of the reaction between cobalt hydrocarbonyl and olefins had received little attention. Terminal olefins had been found to give a mixture of linear and branched products at low temperatures under carbon monoxide, and this was taken as reflecting the mode of addition of cobalt hydrocarbonyl (*62*, *73*, *147*). In view of the slow rate of isomerization of acylcobalt carbonyls this seems justified. However, it is worth noting that branched products predominated in the reaction of 1-pentene with hydrocarbonyl under nitrogen even when the olefin had isomerized only to the extent of 50% (*73*). Both isobutylene and alkyl acrylates had been found to produce branched products. It was suggested that isobutylene, with an electron-rich double bond, reacted by an acid-type addition while methyl acrylate, having a low electron density, reacted by a hydride-type addition (*62*).

Takegami *et al.* (*147*) reexamined the reaction of olefins with cobalt hydrocarbonyl to determine the effect of reaction variables and the possibility of isomerization on the structure of the acylcobalt carbonyls formed. Products were recovered as their ethyl esters as described previously. Additionally, the uptake of carbon monoxide was measured. This is important since the presence of an acylcobalt tricarbonyl can be inferred when the amount of ester produced exceeds the amount of carbon monoxide absorbed.

The most detailed results were obtained with ethyl acrylate, which gave varying amounts of the linear product (diethyl succinate) and the branched product (diethyl methylmalonate) depending on the temperature and the gas used (carbon monoxide or nitrogen). The following scheme accounts for their observations:



(12)

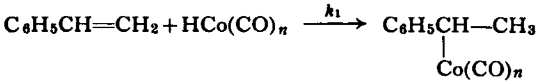
(13)

At 0° C under carbon monoxide the ester produced was the methylmalonate and its yield exceeded the carbon monoxide uptake, indicating the formation of complex (I). The existence of the tricarbonyl here as the predominant species is probably assisted by coordination of an ester oxygen to cobalt (*63*). At lower temperatures, carbon monoxide uptake increased until at −15° C it was similar to the amount of ester produced which was still methylmalonate, indicating that (II) then predominated. At 25° C the succinate was the main product and the amount of carbon monoxide absorbed again corresponded to the yield of ester, indicating the existence of (IV) in solution which must have been formed via an isomerization of (I) to (III). If this is true, one would expect that following carbon monoxide uptake at 0° C, a rise in temperature would rapidly convert (I) to (IV) under carbon monoxide, but the reverse reaction on lowering the temperature would be inhibited by carbon monoxide. This is exactly what was found. Further, this interpretation requires that the branched acylcobalt tetracarbonyl (II) should dissociate to the acylcobalt tricarbonyl more readily (at a lower temperature) than the linear isomer (IV). This is in accord with the steric acceleration of dissociation found by Heck (*52*).

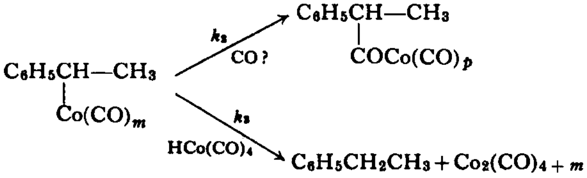
Comparisons of the products found for the stoichiometric reaction (low pressure of CO, low temperature) vs the catalytic reaction (high pressure of CO, high temperature) have stressed the importance of the thermal stability of the acylcobalt tetracarbonyls (*62*). It is now clear that the carbon monoxide pressure is also important and that for compounds which add cobalt hydrocarbonyl to give branched products (isobutylene and the acrylates) an increase in temperature will only favor the linear product if the carbon monoxide pressure is sufficiently high to produce the acylcobalt tetracarbonyl at that temperature. Terminal linear olefins have been said to give rise to similar products in the stoichiometric and catalytic reactions (*62*). Again one would expect this to depend on carbon monoxide pressure, the linear products being favored by a higher carbon monoxide pressure.

For styrene and *n*-butyl vinyl ether, isomerization of the acylcobalt carbonyls (branched → linear) on raising the temperature from −20° to +25° C was slower than for ethyl acrylate. Takegami *et al.* (*147*) concluded that these differences in isomerization rates were responsible for the fact that the products of the catalytic reaction were branched for the first two olefins but linear for ethyl acrylate, i.e., only in the latter case did the acylcobalt carbonyl have time to isomerize before reduction to aldehyde occurred. An equally probable hypothesis is that under Oxo conditions the combination of temperature and carbon monoxide pressure result in the branched acylcobalt tricarbonyl for the first two olefins but a linear acylcobalt tetracarbonyl for ethyl acrylate. In order to distinguish between these two possibilities it should only be necessary to examine the products formed at a higher carbon monoxide pressure. If kinetic factors are controlling the products, all three olefins would then give branched products whereas if the products are thermodynamically controlled a higher pressure should tend to give linear products in all three cases.

The results of Takegami *et al.* for styrene are interesting in that they show the formation of a constant amount of ethylbenzene, independent of temperature or carbon monoxide pressure. The ethylbenzene must have resulted from a reduction of the initially formed alkylcobalt carbonyl as follows:



$$C_6H_5CH{=}CH_2 + HCo(CO)_n \xrightarrow{k_1} C_6H_5\underset{\displaystyle Co(CO)_n}{CH}{-}CH_3 \quad (14)$$



(15)

(16)

Since Eq. (15) must compete with Eq. (16) one would expect carbon monoxide pressure to affect this competition unless Eq. (15) is an S_N1 reaction independent of carbon monoxide pressure. This appears to be so in this particular case; presumably therefore, $m = 4$ and $p = 3$. A more detailed study of the variables would seem to be necessary, however, to substantiate this tentative conclusion.

B. *The Catalytic Hydroformylation of Olefins*

1. *Mechanism and Participation of Coordinatively Unsaturated Intermediates*

Up to the time of the last review (*15*), the mechanism of the catalytic reaction had been investigated to the point where there was general agreement on the following steps:

$$Co_2(CO)_8 + H_2 \rightarrow 2\,HCo(CO)_4 \quad (17)$$

$$HCo(CO)_n + RCH{=}CH_2 \rightarrow RCH_2CH_2Co(CO)_n \quad (18)$$

$$RCH_2CH_2Co(CO)_4 + CO \rightarrow RCH_2CH_4COCo(CO)_4 \quad (19)$$

or

$$RCH_2CH_2Co(CO)_4 \rightleftharpoons RCH_2CH_2COCo(CO)_3 \quad (20)$$

$$RCH_2CH_2COCo(CO)_n + HCo(CO)_4 \rightarrow RCH_2CH_2CHO + Co_2(CO)_{4+n} \quad (21)$$

or

$$RCH_2CH_2COCo(CO)_n + H_2 \rightarrow RCH_2CH_2CHO + HCo(CO)_n \quad (22)$$

In dispute at that time was the value of *n* and the alternatives Eq. (19) or Eq. (20) and Eq. (21) or Eq. (22).

Heck and Breslow (*60*) demonstrated the feasibility of Eq. (22) by the successful reduction of $CH_3COCo(CO)_4$ with hydrogen at 3000 psi and

25° C. The reaction was inhibited by a high CO pressure which they interpreted as due to Eq. (22) having $n = 3$ such that inhibition resulted from

$$RCH_2CH_2COCo(CO)_3 + CO \rightleftharpoons RCH_2CH_2COCo(CO)_4 \tag{23}$$

Many of the individual steps of the Oxo reaction are inhibited or have rates varying inversely with carbon monoxide pressure. This could be due to an equilibrium of the tetracarbonyls with carbon monoxide to produce less active pentacarbonyls or, more likely, an equilibrium of the more reactive tricarbonyls with carbon monoxide to form the tetracarbonyls. It seems more likely that hydrogen would react with a tricarbonyl rather than a tetracarbonyl in Eq. (22). Such reactions of molecular hydrogen are expected to be facilitated by electronically (*48*) or coordinatively unsaturated molecules (*156*).

The reaction of dicobalt octacarbonyl with molecular hydrogen Eq. (17), can occur at room temperature and is similarly inhibited by carbon monoxide, again suggesting an unsaturated intermediate (*158*). Pino *et al.* (*116*) suggested that dicobalt octacarbonyl is in equilibrium with a more reactive lower carbonyl. Natta *et al.* have also shown that $Co_4(CO)_{12}$ and $Co_2(CO)_8$, in the absence of hydrogen, coexist at carbon monoxide pressures corresponding to the highest rates of hydroformylation (*104*, *158*).

In support of the existence of an acylcobalt tricarbonyl, Heck and Breslow cited the appearance of an infrared band at 5.8 μ similar to that occurring in acylcobalt tetracarbonyls when alkylcobalt tetracarbonyls are examined in solution. They postulated the equilibrium, Eq. (20). There is now some doubt of the value of this evidence since the 5.8 μ band is due in part at least to the acylcobalt tetracarbonyl formed by some kind of disproportionation, or decomposition during the preparation (*53*). However, evidence for Eq. (23) has since been found in a study of the reaction of acylcobalt tetracarbonyls with triphenylphosphine, where a first-order dissociation was indicated (*52*).

Evidence on the probable mechanism of the carbonyl insertion in Eq. (19) or Eq. (20) has come from a study of manganese carbonyls. It had previously been established by ^{14}C labeling that in the equilibrium

$$CH_3Mn(CO)_5 + CO \rightleftharpoons CH_3COMn(CO)_5 \tag{24}$$

the carbon monoxide molecule which inserts is one which is already attached to manganese. This has been discussed elsewhere (*15*).

More recently, the kinetics of the reaction of methylmanganese pentacarbonyl with carbon monoxide and various other nucleophiles have been studied. The reaction with carbon monoxide had a first-order dependence on both reactants (*16*) which does not unfortunately distinguish between Eq. (19) and Eqs. (20) and (23). A third alternative is that Eqs. (20) and (23) are "solvent-assisted."

$$\mathrm{RCo(CO)_4 + S \rightleftharpoons RCOCo(CO)_3S} \tag{25}$$

$$\mathrm{RCOCo(CO)_3S + CO \rightleftharpoons RCOCo(CO)_4 + S} \tag{26}$$

$$\mathrm{S = Solvent}$$

Calderazzo *et al.* (*16*) rejected this possibility for the reaction of methylmanganese pentacarbonyl and carbon monoxide, but this conclusion has been challenged by Mawby *et al.* (*96*). In studying the reaction of methylmanganese pentacarbonyl with a variety of ligands, Mawby *et al.* have found both a first-order dependence and a lack of dependence on the concentration of the ligand, depending on the solvent. They have interpreted their results in terms of a single mechanism similar to Eqs. (25) and (26).

Although Eq. (24) has been termed an "insertion" it could equally well result from the cleavage of a manganese–methyl bond and a subsequent migration of methyl (*97*). Evidence on this point has come from a reaction similar to the reverse of Eq. (24) in which the position of the methyl was labeled by the presence of another group. Thus *trans*-$CH_3COMn(CO)_4P(C_6H_5)_3$ gave *cis*-$CH_3Mn(CO)_4P(C_6H_5)_3$, consistent with methyl migration rather than insertion of carbon monoxide into a manganese–methyl bond. However, *cis*-$CH_3COMn(CO)_4[P(OCH_2)_3CR]$ has recently been found to decarbonylate to a cis product (*45*).

Equation (21) had also been demonstrated at room temperature (*62*, *73*) (see Section II, A,1) but was rejected by Heck and Breslow for Oxo conditions where the concentration of $HCo(CO)_4$ is very low [due to Eq. (18)]. This point was questioned by Bird (*15*). In view of the greater reactivity of $HCo(CO)_4$ over H_2 as a reducing agent, it is possible that Eq. (21) could compete with Eq. (22) in spite of the low concentration of $HCo(CO)_4$. The same criticism can be made of Heck and Breslow's reduction of acetylcobalt tetracarbonyl with hydrogen, since hydrocarbonyl must be formed in the reaction and could therefore take over as the reducing agent. The dicobalt octacarbonyl produced could then regenerate hydrocarbonyl by reacting with hydrogen even at room temperature (*158*). However, Heck and Breslow repeated their experiment in the presence of dicyclohexylethylamine, which forms an inert salt with the hydrocarbonyl. Reduction occurred at essentially the same rate (*61*).

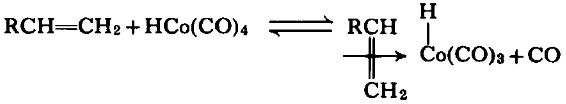
In view of the fact that no free hydrocarbonyl is normally detected in the presence of olefin under Oxo conditions (*92*, *107*), Eq. (22) seems more likely than Eq. (21).

The stoichiometric hydroformylation of olefins with cobalt hydrocarbonyl is also inhibited by an atmosphere of carbon monoxide (*62*, *73*) (Section II, A) and this has been shown to involve a CO inhibition of alkylcobalt carbonyl formation (Eq. (18)).

Inhibition of Eq. (18) was interpreted as being due to an equilibrium of cobalt hydrotetracarbonyl with a more reactive tricarbonyl

$$\mathrm{HCo(CO)_4 \rightleftharpoons HCo(CO)_3 + CO} \qquad (27)$$

thus making $n = 3$ in Eq. (18). The alternative S_N2 mechanism



$$\mathrm{RCH{=}CH_2 + HCo(CO)_4 \rightleftharpoons \begin{array}{c} \mathrm{RCH} \\ \| \\ \mathrm{CH_2} \end{array} \rightarrow \overset{\displaystyle H}{\overset{|}{\mathrm{Co}}}(CO)_3 + CO} \qquad (28)$$

was preferred by Bird (*15*) and is discussed in the section on the stoichiometric reaction.

Equation (27) has been criticized (*14*) on the grounds that a mass-spectrometric analysis of cobalt hydrocarbonyl showed no hydrogen-containing fragments related to the tricarbonyl (*141*). In the absence of any additional information, however, it is difficult to assess the value of negative mass-spectrometric results.

It should also be mentioned that at high carbon monoxide pressures (270–430 atm) a higher carbonyl $Co_2(CO)_9$ was formed from $Co_2(CO)_8$ (*98*), but it seems unlikely that this would play any role under Oxo conditions.

In summary, there is now strong evidence for the participation of lower, coordinatively unsaturated, carbonyls in the Oxo reaction, which is probably best represented at this time by Eqs. (17), (27), (18), (20), and (22) where $n = 3$, and additional equilibria between tri- and tetracarbonyls. However, it is entirely possible that yet unpublished evidence may provide a more satisfactory picture (*115*).

2. *The Formation of Isomeric Products*

The factors affecting the distribution of products formed in the hydroformylation reaction have already received attention in Section II, A,2. The isomerizations of both olefin and acylcobalt carbonyl can be of importance and the extent of these isomerizations will be dependent on carbon monoxide pressure as well as the temperature. Failure to make sufficient allowance for this appears to be the cause of much of the controversy (*72*, *115*).

The extent to which isomerization affects the distribution of products was examined by Pino *et al.* (*120*), who made use of the optical activity of (+)(S)-3-methyl-1-pentene.[3]

Formation of the 2-olefin was then conveniently measured by the percent racemization. Under conventional Oxo conditions the products were 4-methylhexanal (V), 3-ethylpentanal (VI), and 2,3-dimethylvaleraldehyde (VII) in the ratio 93:4:3 and there was only 1.8% racemization of (V). At higher temperature the racemization of (V) increased to 32.2% at 145° and 93.9% at 180° C. The yield of (V) also dropped off to 61.3% at 180° C. The carbon monoxide pressures in these cases were in the range 71–95 atm. Decreasing the carbon monoxide pressure from 95 to 16 atm at 90° C increased the racemization from 1.8% to 8.7%. These results clearly show that under normal Oxo conditions (V) was mainly formed by a mechanism which did not change the stereochemistry at C_3. The degree of racemization can be explained by the reversible formation of a 2-olefin intermediate. Pino *et al.* concluded that under conventional Oxo conditions, little isomerization occurred.

This conclusion was challenged by Johnson (*72*), who followed the formation of isomeric aldehydes and isomeric olefins during the hydroformylation of 4-methyl-1-pentene. He found that 2-olefin was formed very rapidly under Oxo conditions and suggested that this did not affect the preferential formation of terminal aldehyde significantly, due to the fact that 2-olefin was so much less reactive to hydroformylation. These results have now been checked by Piacenti *et al.* (*115*), who found that 2-olefin was only rapidly formed if the rate of the reaction was sufficiently high that the solution was no longer saturated with carbon monoxide. By using a lower catalyst concentration in benzene solvent they were able to avoid this deficiency and found very little olefin isomerization.

A further difference with Johnson's work, which, however, received no comment, was the fact that under these conditions, 3-methylhexanal appeared as a product to the extent of 2.9% of the total aldehydes when only 1% of the olefin present had isomerized. Johnson found no 3-methylhexanal

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[3] See ref. *114* for explanation of nomenclature. (The "S" and "R" nomenclature is also covered in E. L. Eliel's "Stereochemistry of Carbon Compounds," 1st ed., p. 92, McGraw Hill, New York, 1962).

until olefin isomerization had practically gone to completion. This together with the late appearance of 2-ethyl-3-methylbutanal among the reaction products had led Johnson to the conclusion that aldehydes are only formed from the corresponding olefin. He also found that the olefins were formed in a stepwise manner.

This is to be expected if there is an equilibrium between olefin–cobalt hydrocarbonyl complexes and the rate of exchange of olefin in such complexes is faster than the rate of hydride transfer. Thus, 1-olefin would tend to displace 2-olefin since it forms a stronger complex. Similarly, it should displace *trans*-2-olefin more easily than *cis*-2-olefin, accounting for the unusual predominance of *trans*-2-olefin early in the reaction. Thus 3-methylhexanal, which can only be formed if the double bond has migrated all the way along the carbon chain, should be the last aldehyde to form, as found by Johnson. The fact that it appeared early in the reaction studied by Pino suggests that a multistep isomerization cocurred while the olefin was attached to cobalt. This could result if hydride transfer were faster than olefin exchange and agrees with Manuel's earlier conclusions for iron-carbonyl-catalyzed isomerizations (*89*). This also leads to the interesting speculation that the racemization of 4-methylhexanal, found earlier (*120*), might have been due to a double bond migration from one end of the molecule to the other as well as to and from the 2-olefin.

The effect of carbon monoxide pressure on the hydroformylation of 1-pentene was also examined by Piacenti *et al.* (*115*). They found that for low pressures (below 5 atm) the percent straight-chain aldehyde in the aldehyde product was approximately the same for both 1-pentene and 2-pentene. The value rose rapidly to ~70% and then leveled off for 2-pentene at 75.8%, but continued to climb for 1-pentene to over 80%, where it began to level off (Fig. 1).

Piacenti *et al.* suggested that the different results at low and high carbon monoxide pressure were due to different catalytic intermediates (A and B) under the two sets of conditions. Thus at low pressures A caused a rapid olefin isomerization and the formation of similar product distributions of aldehydes from 1- and 2-pentene. At high pressures little olefin isomerization occurred and 1-olefin yielded significantly more straight-chain aldehyde than 2-olefin. This would seem consistent with Heck and Breslow's mechanism (*62*) if A were an acylcobalt tricarbonyl in equilibrium with isomeric olefin–cobalt hydrocarbonyl complexes and B were an acylcobalt tetracarbonyl.

Piacenti's results for 1- and 2-pentene at high pressure would then fit in quite well with the fact that Takegami *et al.* (*147–149*) found that linear acylcobalt tetracarbonyls were much more difficult to isomerize than their branched-chain isomers. However, Piacenti *et al.* reject the possibility of an isomerization of alkylcobalt carbonyls in view of their work on the hydroformylation of orthoformic esters (Section II, D,2).

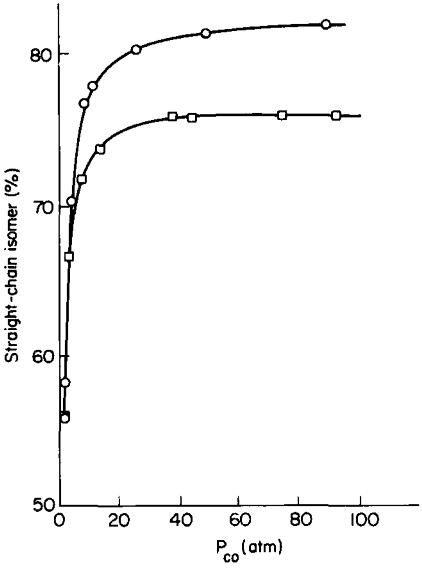


FIG. 1. The effect of CO partial pressure on the isomeric composition of aldehydes formed by hydroformylation of ○ 1-pentene; □ 2-pentene.

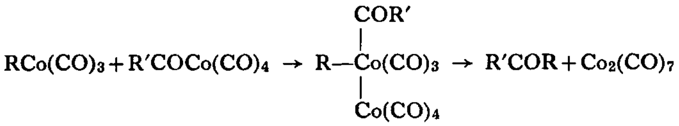
The present authors feel this point needs further investigation in view of the results of Takegami *et al.* They found that the isomerization of the acylcobalt tetracarbonyl was very solvent-dependent, and it could well be that conditions in the hydroformylation of olefins and orthoformates were sufficiently different to cause faster isomerization in the former case. Thus, for example, the presence of olefins in the former case may contribute to a faster isomerization, or perhaps orthoformates, like tetrahydrofuran, inhibit the isomerization. A further factor to be considered is the presence of cobalt hydrocarbonyl, which must be present in larger amount in the case of olefin hydroformylation. Takegami *et al.* (*143*) have shown that cobalt hydrocarbonyl strongly promotes the isomerization of phenylacetylcobalt carbonyl to *o*-toluylcobalt carbonyl. Its effect on the isomerization of aliphatic acylcobalt carbonyls obviously needs to be checked.

3. *The Formation of Ketones*

Ketones have been observed as a major product of the Oxo synthesis when ethylene is used (*158*).

Some light has been thrown on this unusual reaction by a study of the reaction of cobalt hydrocarbonyl with olefins under nitrogen (*14*). It has also be discussed recently by Heck (*59*).

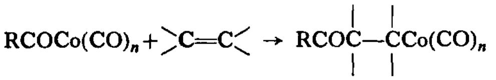
Heck discussed two possible mechanisms. The first involved a reaction between acyl and alkylcobalt carbonyls. This should produce saturated ketones, e.g.,



$$\mathrm{RCo(CO)_3 + R'COCo(CO)_4 \rightarrow R{-}\underset{\displaystyle Co(CO)_4}{\overset{\displaystyle COR'}{Co}}(CO)_3 \rightarrow R'COR + Co_2(CO)_7} \qquad (29)$$

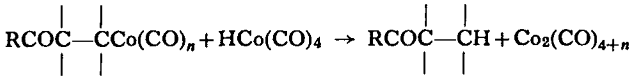
This reaction could explain the decomposition of alkylcobalt tetracarbonyls under nitrogen and also the reactions observed by Bertrand *et al.* (*14*) in which 1-butene gave various nonanones, and some diolefins gave cyclic ketones.

The second mechanism involved the insertion of an olefin into an acylcobalt carbonyl, e.g.,



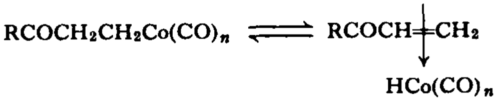
$$\mathrm{RCOCo(CO)_{\mathit{n}} + {>}C{=}C{<} \rightarrow RCO\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}Co(CO)_{\mathit{n}}} \qquad (30)$$

In the presence of cobalt hydrocarbonyl or hydrogen this could produce a saturated ketone, e.g.,



$$\mathrm{RCO\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}Co(CO)_{\mathit{n}} + HCo(CO)_4 \rightarrow RCO\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}H + Co_2(CO)_{4+\mathit{n}}} \qquad (31)$$

However, in the absence of a reducing agent, some unsaturated ketone would be expected by a disproportionation or the following reaction:



$$\mathrm{RCOCH_2CH_2Co(CO)_{\mathit{n}} \rightleftharpoons \underset{\displaystyle \downarrow \atop \displaystyle HCo(CO)_{\mathit{n}}}{RCOCH{=}CH_2}} \qquad (32)$$

Unsaturated ketones have been observed among the decomposition products of 5-hexenoylcobalt tetracarbonyl at room temperature (*56*).

Heck explained the formation of ketones under Oxo conditions by the second mechanism, but the first mechanism seems equally likely. The second mechanism alone seems capable of explaining unsaturated products and is important in providing an example of an olefin insertion into a carbon–transition metal bond.

An unusual synthesis of acyldienes from conjugated dienes, carbon monoxide, and alkyl or acyl halides using cobalt carbonylate anion as a catalyst should be mentioned here (*57*). The reaction apparently involves the addition of an acylcobalt carbonyl to a conjugated diene to produce a 1-acylmethyl-π-allylcobalt tricarbonyl, followed by elimination of cobalt hydrocarbonyl in the presence of base. The reaction can thus be made catalytic. Since the reaction was discussed in detail in the recent review by Heck (*59*), it will not be pursued further here.

4. *Catalyst Modification*

One of the potential advantages of transition metal complexes as homogeneous catalysts is the possibility of variation of the ligands and the correlation of catalytic activity with some function of this variable. Few catalytic systems have been examined in the necessary detail, however, and the hydroformylation reaction is no exception. Much of the work in this area has therefore taken a more empirical approach to catalyst modification. The result has been the production of an extensive patent literature of little scientific value other than to suggest areas in need of further study.

A useful study has just been completed by Roos and Orchin (*125*), who have examined the effect of ligands such as benzonitrile on the stoichiometric hydroformylation of olefins. A variety of such reagents (acetonitrile, anisole) were found to act in a similar manner to carbon monoxide by suppressing the formation of branched products and the isomerization of excess olefin. The yield of aldehyde was also increased by increasing ligand concentration up to 2 moles per mole of cobalt hydrocarbonyl. Benzonitrile was not found to affect the rate of the reaction of cobalt hydrocarbonyl with acylcobalt tetracarbonyl, so the ligand must have affected an earlier step in the reaction sequence. It seems most likely that cobalt hydrocarbonyl reacts with olefin in the presence of benzonitrile to form an acylcobalt tricarbonyl–benzonitrile complex which is reduced more rapidly than the acylcobalt tetracarbonyl.

$$RCH{=}CH_2 + L + HCo(CO)_4 \rightarrow RCH_2CH_2COCo(CO)_3L \qquad (33)$$

$$RCH_2CH_2COCo(CO)_3L + HCo(CO)_4 \rightarrow RCH_2CH_2CHO + Co_2(CO)_7L \qquad (34)$$

This interpretation is consistent with the increased yield of aldehyde which requires that Eq. (34) should be able to compete effectively with Eq. (33) for cobalt hydrocarbonyl. It is also consistent with the decreased branching found since such isomerizations are reduced by coordinatively saturated complexes.

Pyridine and triphenylphosphine were found to stop the reaction by combining with cobalt hydrocarbonyl, the former to produce $PyH^+[Co(CO)_4]^-$ and the latter to form $HCo(CO)_3P(C_6H_5)_3$.

A summary of the effects claimed by catalyst modification follows.

a. *Reduction of Inhibition.* When cobalt salts are used as Oxo catalysts, somewhat higher temperatures (about 35° C) are required than when using cobalt carbonyls (*158*). Additives have therefore been claimed as promoting the formation of the carbonyl, thus facilitating the reaction. These include amines (*50*), ammonia (*82*, *86*), pyridines (*71*, *137*), and thiols (*101*). An excess of such reagents over the amount of cobalt present is likely to deactivate the catalyst (*82*, *158*). The rate of formation of the hydrocarbonyl under Oxo conditions has been studied by Iwanaga (*68*), who found a direct dependence on hydrogen pressure and an inverse dependence on carbon monoxide pressure as in the Oxo reaction.

The use of dicobalt octacarbonyl itself has also been recommended for eliminating the inhibition caused by diolefins (*84*).

b. *Use of Phosphines and Phosphites.* Trivalent phosphorus strongly stabilizes intermediates in the Oxo reaction, so that it is not surprising to find a number of references to the use of such compounds as catalyst modifiers (*46*, *47*). Phosphines and phosphites have been claimed to promote both the preferential formation of aldehydes (*25*, *26*) and alcohols (*29*).

c. *Dimerization.* A number of additives have been claimed as increasing the yield of dimeric alcohols (*28*, *123*). These include compounds of Pb (*22*, *85*) and Mg (*154*, *155*). An aldol condensation is most probably the cause of the dimerization, which explains why many of the additives are basic. Compounds of the type $M^{n+}[Co(CO)_4]_n$ are expected to form and thus deactivate the catalyst to some extent, (*83*, *85*) but it seems unnecessary to invoke such compounds as specific dimerization catalysts (*155*).

d. *Other Catalyst Modifiers.* A number of other compounds have been claimed as improving cobalt catalysts (*3*, *4*, *27*, *99*, *138*).

e. *Non-cobalt-containing Catalysts.* It should be mentioned that cobalt carbonyls are not unique in catalyzing the Oxo and related reactions. Iron carbonyl has some similarities in its catalyses (*158*), and the search for other catalysts has produced a number of patents claiming other carbonyl-forming metals (*136*), including Rh (*71a*, *100*, *150*), Ru (*31*, *140*), and Mn (*30*, *80*). Higher rates or yields are often claimed (*80*, *140*), one paper giving the order of catalytic activity Rh > Co > Ir (*67*). Besides higher rates of hydroformylation ($\times 10^2$ to 10^3) rhodium is also reported to give a higher ratio of normal to branched aldehydes than cobalt (*157*). Rhodium and iridium carbonyls are also more active in hydrogenating certain olefins, however (*67*).

5. *Solvent Effects*

The reaction of dicobalt octacarbonyl with basic solvents (B) is well known (*158*).

$$3\ Co_2(CO)_8 + 2\,x\mathrm{B} \rightarrow 2\,[Co(B)_x]^{2+}[Co(CO)_4]_2^- + 8\ CO \tag{35}$$

It has now been found that the list of "basic" solvents that give such reactions includes benzophenone, phenyl acetate, cyclooctanone, and many other oxygen-containing solvents. Even benzene has been found to give such a complex (*64*).

Solvent effects on the rate of hydroformylation have been found to be small, however. A small increase in the rate of hydroformylation of cyclohexene has been found in the series methanol > benzene > heptane; but the overall increase is only by a factor of 1:5 (*158*). Alcohols have been reported to increase the yield of hydrogenated products (*66*, *88*).

By-product formation has been avoided by stabilizing the aldehydes produced as acetals with ethylene glycol (*79*). Ethyl orthoformate had earlier been used for a similar purpose (*118*).

6. *Acetal Formation and Decomposition*

Since alcohols and aldehydes are both formed in the Oxo reaction, acetals are formed (*158*). A recent paper by Macho (*87*) studied their further reactions under Oxo conditions, hydrolysis, hydrogenolysis, and thermal decomposition. Decomposition to saturated and unsaturated ethers increased with temperature from 12% at 120° to 41% at 170° C. Thus isobutyl ether, isobutenyl isobutyl ether, isobutanol, and isobutyraldehyde were identified by gas-phase chromatography among the reaction products of the decomposition of isobutyraldehyde diisobutyl acetal.

C. *Hydroformylation of Substituted Olefins*

The stoichiometric hydroformylation of substituted olefins has already received sufficient discussion (Section II, A). Table I gives a list of references

TABLE I

THE HYDROFORMYLATION OF OLEFINS

Olefin	Products	Yield (%)	References
Acrylonitrile	β-Cyanopropionaldehyde	—	*74, 75*
Acrylonitrile	Glutamic acid[a]	—	*76, 161*
Methyl acrylate	Methyl γ-oxobutyrate	—	*69–71*
Hexafluoropropylene	Hexafluoropropane	50	
	Hexafluoropropionaldehydes	5–8	
	Hexafluorobutanols	40	*133*
N-Acylamino olefins	*N*-Acylamino aldehydes		*1*
N-Phthaloyl(allyl)amine	*N*-Phthaloyl-γ-aminobutyraldehyde	87.5	
	N-Phthaloyl-β-amino isobutyraldehyde		*1*
N,N-Diacetylallylamine	*N,N*-Diacetyl-γ-aminobutyraldehyde	87	*1*
N-Acetylallylamine	*N*-Acetylaminobutyraldehyde	—	*1*
Steroids	6-Hydroxymethyl steroids	—	*12*
Sterols	6-Hydroxymethyl sterols	—	*12*
Pregnenolone acetate	6-Hydroxymethylpregnan-3-ol-20-one 3-acetate	—	*12*
α,β-Unsaturated carboxylic acid esters	γ-(and δ-)Lactones	—	*32, 35, 135*
β,γ-Unsaturated carboxylic acid esters	δ-Lactones	—	*32, 35, 135*
Ethyl acrylate	γ-Butyrolactone	88	*135*
Methyl crotonate	δ-Valerolactone	72	
	β-Methyl-γ-butyrolactone	20	*135*
Vinyl acetate	α-Acetoxypropionaldehyde	72	*2*
Eugenol	5,6,7,8-Tetrahydro-3-methoxy-2-naphthol	30–40	
	3-Methoxy-4-hydroxy-1-*n*-propylbenzene	40	
	4-(3-Methoxy-4-hydroxyphenyl)-1-butanol	5	*42*
3,4-Dihydro-2H-pyran-2-methylol	2,6-Dimethyloltetrahydropyran	64	*36*
p-Chlorophenyl allyl ether	*p*-Chlorophenyloxybutyric acid[b]	82	*83*
2,4-Dichlorophenylallyl ether	2,4-Dichlorophenyloxybutyric acid[b]	—	*93*
p-Fluorophenylallyl ether	*p*-Fluorophenyloxybutyric acid[b]	51	*93*
Nonconjugated diolefins	Dialdehydes		*100*
α-Methylstyrene	β-Methyl-β-phenylpropionaldehyde	35	
	Isopropylbenzene	66	*132*
Glycals	Anhydrodeoxyaldoses	—	*126, 130*
Ethyl acrylate	Ethyl-γ,γ-diethoxybutyrate[c]	—	*117*

[a] Obtained after secondary chemical treatment.

[b] After oxidation.

[c] Ethyl orthoformate/ethanol solvent.

to the catalytic hydroformylation of a variety of olefins. Brief comments on some of these examples follow.

Eugenol (3-methoxy-4-hydroxyallylbenzene) was found to give a 30–40% yield of 5,6,7,8-tetrahydro-3-methoxy-2-naphthol (*42*). In agreement with the tendency of conjugated double bonds to be hydrogenated under hydroformylation conditions (Section III, A), a 40% yield of 3-methoxy-4-hydroxy-1-*n*-propylbenzene was also obtained. The cyclization, however, must have been preceded by a carbon monoxide insertion to provide the necessary number of carbon atoms. However, none of the expected carbonyl compounds was found in short-time, low-temperature reactions so the authors postulated a direct ring closure by the acylcobalt carbonyl [$CH_3O(HO)C_6H_3(CH_2)_3COCo(CO)_4$] to form 5,6-dihydro-3-methoxy-2-naphthol, which was isolated in the early stages of the experiment.

Acrylonitrile has now been successfully hydroformylated (*76*). The β-cyanopropionaldehyde which was formed, polymerized unless the cobalt carbonyls were decomposed before work-up. Yields were highest in Lewis base solvents, which were said to suppress reduction of acrylonitrile and give higher rates of hydroformylation than hydrocarbon solvents.

A considerable amount of work has been done on the hydroformylation of alkyl acrylates. The formation of γ-oxobutyrates has previously been reported (*15*). Iwanaga (*70*) studied the effect of solvent variation and found that the rate of hydroformylation was in the order alcohols > acetone > toluene. Pyridine and some of its homologs also increased the rate of reaction. At higher temperatures and pressures, lactones were formed (*32*, *35*, *135*), presumably by reduction of the Oxo ester to the hydroxy ester followed by ring closure with elimination of alcohol.

The reactions of ethyl acrylate and ethyl crotonate were studied (*117*) in the presence of ethyl orthoformate using 1:1 CO/H_2 and 250 and 200 atm pressure. For ethyl acrylate, the distribution of products corresponded to β-hydroformylation 78.2%, (γ,γ-diethoxybutyrate and β-formylpropionic acid), and α-hydroformylation 21.7%, (α-methyl-β-ethoxyacrylate and α-methyl-β,β-diethoxypropionate). For ethyl crotonate, γ-hydroformylation occurred to the extent of 67–73% (δ,δ-diethoxyvalerate and γ-formylbutyrate) and α-hydroformylation to the extent of only 13.6% (α-ethyl-β-ethoxyacrylate and β-ethyl-β-diethoxypropionate).

Hexafluoropropylene has been hydroformylated in yields approaching 50% (*133*). There was a strong tendency for hydrogenation to occur, however (50% yield of hexafluoropropane). One would expect alkyl metal carbonyls to be greatly stabilized by electronegative substituents, making carbonylation more difficult and hence favoring hydrogenation. It has been reported that trifluoroacetylmanganese pentacarbonyl converts to the trifluoromethyl compound on heating, but the reverse process of carbonylation could not be achieved (*15*, *17*). Section III, A should be consulted for further discussion.

Unsaturated polymers derived from dienes have also been hydroformylated (*102*, *113*, *122*).

D. Hydroformylation of Other Compounds

Table II lists nonolefinic compounds which have been hydroformylated.

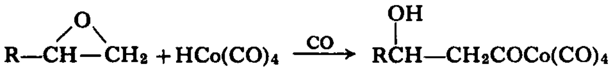
TABLE II

HYDROFORMYLATION OF OTHER COMPOUNDS

Compound	Products	Yields (%)	References
Ethylene oxide	Acetaldehyde	28	
	Acrolein	1	*160*
Ethylene oxide	β-Hydroxypropionaldehyde	15	*144*
Propylene oxide	β-Hydroxy-*n*-butyraldehyde	42	
	Acetone	4.6	*160*
Propylene oxide	Methyl β-hydroxybutyrate	40.3	*24*
Cyclohexene oxide	Hexahydrosalicylaldehyde		
	Dimer	43	
	Cyclohexanol	10	*124*
Cyclohexene oxide	2-ethoxycyclohexanol	60	
	Cyclohexenecarboxaldehyde	20	*124*
Propionaldehyde	Propyl formate	35	
Hexahydrobenzaldehyde	Cyclohexyl formate	35	*94*
Orthoformic esters	—	—	*119*
Ethyl orthoformate	1,1-Diethoxypropane		*114*
n-Propyl orthoformate	1,1-Dipropoxybutane	90	*114*

1. *Epoxides*

a. *The Reaction of Cobalt Hydrocarbonyl with Epoxides.* Cobalt hydrocarbonyl has been found to react rapidly with epoxides at 0° C under carbon monoxide, and up to 1 mole of gas per mole of hydrocarbonyl was absorbed. Heck (*54*) has shown that β-hydroxyacylcobalt tetracarbonyls were formed by isolating the products as their triphenylphosphine derivatives. These complexes were further characterized by cleavage with alcohol and iodine to produce the corresponding esters. Propylene oxide gave exclusively the 3-hydroxybutyryl derivatives (*54*, *145*, *146*), while isobutylene oxide gave 93% of the methyl 3-hydroxy-3-methylbutyrate and 7% of the methyl 3-hydroxy-2,2-dimethylpropionate. The reaction therefore tends to produce the less highly branched products.



$$R{-}\overset{O}{CH{-}CH_2} + HCo(CO)_4 \xrightarrow{CO} R\overset{OH}{\overset{|}{C}}H{-}CH_2COCo(CO)_4 \qquad (36)$$

Since cobalt forms a bond to carbon rather than oxygen, it would appear that cobalt hydrocarbonyl is acting as an acid as it does when reacting with double bonds having a low electron density (ethyl acrylate). This leaves open the question as to whether ring opening is initiated by $H^+, Co(CO)_4^-$ or whether the hydrocarbonyl adds by a concerted cis addition. The major product from the ring opening of isobutylene oxide was the one expected from anionic attack (*54*). However, cobalt hydrocarbonyl is not sufficiently nucleophilic to react with methyl iodide under the conditions of its reaction with epoxides. Heck therefore suggested that the mechanism involved an acid opening of the epoxide which was more sensitive to steric effects than to electronic factors.

However, addition of hydrocarbonyl to isobutylene gave exclusive addition of cobalt to the tertiary carbon atom. To explain this apparent discrepancy, Heck pointed out that addition to olefins was believed to involve $HCo(CO)_3$ which would be less subject to steric requirements than $HCo(CO)_4$, which was probably involved in the addition to epoxides. Consistent with this hypothesis, no inhibitory affect of CO on the latter reaction had been reported. More recently, however, Takegami *et al.* (*145*) have reported some results which suggest that CO inhibition can occur in the reaction of cobalt hydrocarbonyl with propylene oxide. Thus, at 0° C, after 30 minutes and with a mole ratio propylene oxide:cobalt hydrocarbonyl of 2.7, the amounts of acylcobalt carbonyl formed were, under nitrogen, 0.14; under CO ~0.05. Unfortunately, as with olefins, a side reaction occurs under nitrogen resulting in low yields for longer time periods. They also found that a variety of polar solvents strongly promoted the reaction (*144*), ethanol increasing the rate 120-fold. This resembles the effect of polar solvents on the isomerization of acylcobalt tetracarbonyls and may be explained in the same way; namely a solvent-assisted dissociation, this time of $HCo(CO)_4$ to produce $HCo(CO)_3$, which reacts more rapidly with epoxides.

The possibility that $HCo(CO)_4$ is reacting by a concerted cis addition is ruled out at least in the case of cyclohexene oxide by the isolation of *trans*-methyl 2-hydroxycyclohexanecarboxylate as the only product (*54*). This has recently been confirmed by Roos *et al.* (*124*), who obtained a dimer of *trans*-hexahydrosalicylaldehyde.

As with the hydroformylation of olefins, aldehydes are expected by a reduction of acylcobalt carbonyls by cobalt hydrocarbonyl. They are formed in small amounts for a number of epoxides (*145*).

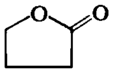
Styrene oxide reacted in an unusual manner in that the only products isolated were α- and β-phenylethylalcohol (*145*). This is similar to the hydrogenation found with styrene. Some carbonylation occurs, however, when ethanol is used as solvent (*144*).

Further support for Heck's suggestion that $HCo(CO)_4$ reacts as an acid with epoxides was found by Takegami *et al.* (*145*), who pointed out that the relative reactivities of propylene oxide/epichlorohydrin is ~30/1 for cobalt hydrocarbonyl. The same order of reactivity is shown to acids (propylene oxide/epichlorohydrin = 70 for perchloric acid) while the reactivity propylene oxide/epichlorohydrin for bases is in the reverse order (0.25 for ammonia).

In view of the many differences noted above between the hydroformylation of olefins and epoxides, it is not surprising to find that changes in structure result in a different order of reactivity in each case. Thus for epoxides the reactivity to cobalt hydrocarbonyl is cyclohexene oxide > propylene oxide, whereas with olefins the order is terminal olefins > internal olefins > cyclic olefins (*145*).

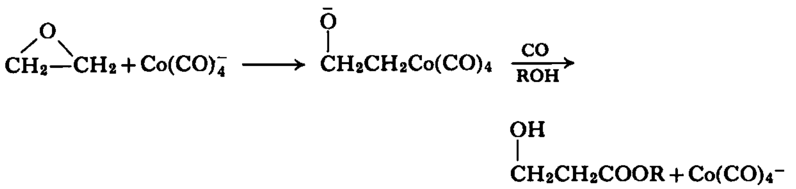
Trimethylene oxide also reacts rapidly with cobalt hydrocarbonyl and carbon monoxide at 0° C to produce 4-hydroxybutyrylcobalt tetracarbonyl, identified by means of its triphenylphosphine derivative, and the reaction of the tetracarbonyl with dicyclohexylethylamine to produce γ-butyrolactone (*54*).

$$HOCH_2CH_2CH_2COCo(CO)_4 + (C_6H_{11})_2NC_2H_5 \longrightarrow$$



$$+ \ (C_6H_{11})_2(C_2H_5)NH^+Co(CO)_4^- \qquad (37)$$

The preceding stoichiometric reactions are clearly closely related to the catalytic hydroformylation of epoxides. Somewhat less clear is their relation to the carboxylations of epoxides with water or alcohols to produce hydroxy acids or hydroxy esters where cobalt carbonyl anion or dicobalt octacarbonyl are used as catalysts. Heck (*54*) has pointed out that cobalt hydrocarbonyl must be present in low concentration in the former case and that it is probably present in the latter case also from a reaction between dicobalt octacarbonyl and water or an alcohol. However, he suggested that cobalt carbonyl anion may also attack epoxides at the temperature of these reactions, e.g.,



(38)

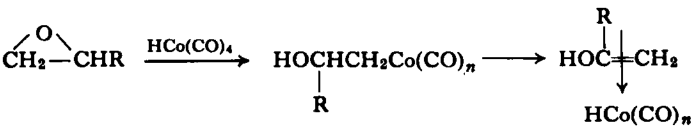
Thus either or both may be catalysts.

As in the hydroformylation of olefins, isomerization (of excess epoxide) occurs, producing ketones (*23*). Since the catalysis by dicobalt octacarbonyl is promoted by methanol, which is known to cause disproportionation,

$$3\ Co_2(CO)_8 + 12\ CH_3OH \rightarrow 2\{Co(CH_3OH)_6^{2+}[Co(CO)_4^-]_2\} + 8\ CO \qquad (39)$$

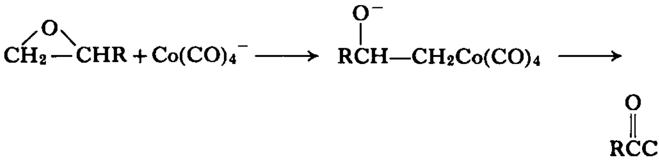
it was suggested that isomerization took place during a reversible exchange between methanol and propylene oxide in the cation. In support of this, benzene was found to give poorer acetone yields and pyridine stopped the reaction. Pyridine is expected to coordinate too strongly to the cobalt to allow displacement by propylene oxide. Further, the cobalt tetracarbonyl anion is present also in pyridine $\{Co(C_5H_5N)_6^{2+}[Co(CO)_4]_2^-\}$ so that the anion is not the catalyst.

This isomerization to ketones also occurs under the milder conditions under which cobalt hydrocarbonyl is reacted with epoxides, however, and it seems likely that cobalt hydrocarbonyl was also present under the conditions of Eisenmann's experiment. Heck has therefore suggested that the mechanism could involve the formation of a hydroxyalkylcobalt carbonyl followed by elimination to produce the enol form of the ketone in the same way that alkylcobalt carbonyls can give olefins.



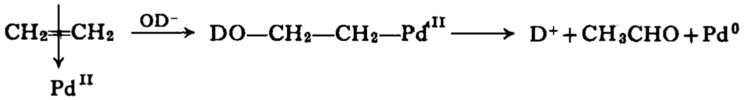
(40)

Alternatively, he suggested attack by cobalt carbonyl anion, followed by a hydride shift and elimination of cobalt carbonyl anion.



(41)

The latter mechanism is of interest since the elimination is formerly a two-electron transfer and directly analogous to the mechanism of the formation of acetaldehyde in the oxidation of ethylene by palladous chloride (*139*).



$$\underset{\underset{Pd^{II}}{\downarrow}}{CH_2{=}CH_2} \xrightarrow{OD^-} DO{-}CH_2{-}CH_2{-}Pd^{II} \longrightarrow D^+ + CH_3CHO + Pd^0$$

(42)

b. *Catalytic Hydroformylation of Epoxides.* Epoxides have been hydroformylated in both hydrocarbon and alcohol solvents. In the former case, β-hydroxyaldehydes were formed, while in the latter case esters of the corresponding acids were produced. Thus, as in the stoichiometric reaction, the less-branched alternative was the main product.

In hydrocarbons a variety of by-products was formed. Propylene oxide gave some β-hydroxyisobutyraldehyde as well as the normal product, also acetone, isobutyraldehyde, methacrolein, *n*-butyraldehyde, isobutanol, crotonaldehyde, and *n*-butanol. Presumably these by-products were formed by dehydration and hydrogenation of the hydroxyaldehydes, except for acetone which was formed by isomerization. The side reactions can be kept to a minimum by operating below 95° C (*160*). Fewer by-products appear to be formed using alcohols as solvents. Using methanol, Eisenmann (*24*) noted that carbon monoxide had an inhibitory effect at high pressures.

2. *Orthoformic Esters*

Under Oxo conditions, alkyl orthoformates react to produce the acetals or aldehyde corresponding to the alcohol represented by the orthoformate (*114*).

$$2\ HC(OEt)_3 + CO + H_2 \xrightarrow{Co_2(CO)_8} EtCH(OEt)_2 + 2\ HCOOEt + EtOH \qquad (43)$$

When esters of straight-chain alcohols were employed, only straight-chain products were obtained for temperatures up to 150° C and pressures of carbon monoxide as low as 10 atm (*119*). (+) S-2-Methylbutyl orthoformate gave (+)-1,1-bis(S)-2-methylbutoxy-3-methylpentane in 95% yield.

These facts together with the absence of any detectable amount of olefin show that olefins are not intermediates in the reaction.

Isopropyl orthoformate gave branched products, e.g., isobutyraldehyde, but also small amounts of normal products, e.g., *n*-butyraldehyde. The amount of normal product was 4–6% at 80° C and increased with rise in temperature. Piacenti *et al.* suggested the following mechanism:

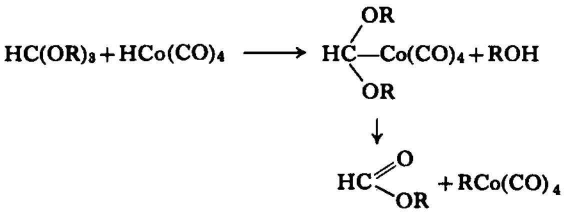
$$HC(OR)_3 + HCo(CO)_4 \rightarrow HCOOR + ROH + RCo(CO)_4 \tag{44}$$

$$RCo(CO)_4 + CO \rightleftharpoons RCOCo(CO)_4 \tag{45}$$

$$RCOCo(CO)_4 + H_2 \rightarrow RCHO + HCo(CO)_4 \tag{46}$$

$$RCHO + HC(OR)_3 \rightarrow RCH(OR)_2 + HCOOR \tag{47}$$

Equation (44) is reminiscent of the reaction of cobalt hydrocarbonyl with epoxides which therefore suggests the preceding step



$$HC(OR)_3 + HCo(CO)_4 \longrightarrow HC(OR)_2\text{—}Co(CO)_4 + ROH \rightarrow HC(=O)OR + RCo(CO)_4 \tag{48}$$

Originally, Piacenti *et al.* explained the formation of isomeric products in terms of an equilibrium of alkylcobalt carbonyls with olefin–hydrocarbonyl complexes as in the Oxo reaction. More recently, however, they have noted that the conditions under which *n*-propyl orthoformate gave no isomeric products (below 150° C, carbon monoxide pressure 10 atm) are conditions under which isomerization occurs readily in the hydroformylation of olefins (*115*). Since alkylcobalt carbonyls were formed in both reactions they dismissed the possibility that this isomerization was due to alkyl- or acylcobalt carbonyls. The fact that Takegami *et al.* have found that branched-chain acylcobalt tetracarbonyls isomerize more readily than straight-chain acylcobalt tetracarbonyls would seem to fit in quite well with the results of Piacenti *et al.*, however, and suggests that the two findings may not be so irreconcilable as might at first appear (see Section II, B,2).

3. *Aldehydes and Alcohols*

Since formate esters are formed as a by-product of the hydrogenation of aldehydes, Marko (*94*) has tried hydroformylating propanol and hexahydrobenzyl alcohol, but obtained only minor amounts of the corresponding formate esters. He obtained a 35% yield of the formate esters, however, by hydroformylating the corresponding aldehydes. Possible mechanisms are considered in Section III, B.

III

HYDROGENATION AND HYDROGENOLYSIS

Dicobalt octacarbonyl was one of the earliest known compounds believed to be capable of activating molecular hydrogen in homogeneous solution (*48*). The hydrogenation of organic substrates in the presence of this catalyst has been described in several earlier reviews (*140a*, *158*). Reduction of olefins and aldehydes will be considered here.

A. Olefins

Hydrogenation is a competing reaction in the Oxo process but is not of importance, except for olefins that are branched, conjugated, or carry electronegative substituents. With propylene, cyclohexene, or a typical Fischer–Tropsch feedstock, less than 10% of saturated hydrocarbons were produced, but isobutene and other branched olefins gave as much as 65% saturated hydrocarbon as product (*41*). The effect of variation of the concentration of various reactants on the ratio of hydroformylation to hydrogenation, using α-methylstyrene as substrate, was investigated by Rudkovskii and Imyanitov (*132*). The ratio was found to be independent of catalyst concentration. Both reactions were first order in catalyst concentration and of an order greater than unity in α-methylstyrene concentration.

Hydroformylation of acrylonitrile (*75*) and of fluoroolefins (*133*) also suffer from hydrogenation as a serious side reaction.

Frankel *et al.* (*40*) have used dicobalt octacarbonyl as a catalyst for the hydrogenation of unsaturated fats and found it to be active at lower temperatures than iron carbonyl.

Marko (*91*) studied the effect of olefin structure on the ratio of hydroformylation to hydrogenation products, and concluded that the ratio declined with increasing branching of the olefin. This is not surprising in view of the known decrease in rate of hydroformylation with increased branching (*158*). He explained the effect of branching by the following reaction scheme:

$$\mathrm{RCo(CO)_4} \xrightleftharpoons{k_4} \mathrm{RCOCo(CO)_3} \xrightarrow{\mathrm{H_2}} \mathrm{RCHO + HCo(CO)_3} \qquad (49)$$

$$\mathrm{RCo(CO)_4} \xrightleftharpoons{k_5} \mathrm{CO + RCo(CO)_3} \xrightarrow{\mathrm{H_2}} \mathrm{RH + HCo(CO)_3} \qquad (50)$$

where k_5/k_4 apparently increases with increasing branching of R.

Evidence for the existence of the coordinatively unsaturated tricarbonyls has already been discussed. Equation (50) is similar to the corresponding decarbonylation of acylcobalt tetracarbonyls.

$$\mathrm{RCOCo(CO)_4} \xrightleftharpoons{k_6} \mathrm{RCOCo(CO)_3 + CO} \qquad (51)$$

This reaction was studied by Heck (*52*), who found that in the reaction of acylcobalt tetracarbonyls with triphenylphosphine, which proceeds via the acylcobalt tricarbonyl, the rate increases nearly two orders of magnitude as R goes from CH_3 to $(CH_3)_3C$. This steric acceleration of dissociation would be expected to affect k_5 to an even greater extent, thus explaining the increase of k_5/k_4 with increasing branching of R.

It should be noted, however, that the relation between branching of R and decarbonylation cannot alone be taken as evidence in favor of the mechanism of Eqs. (49) and (50). Such a relation could equally well fit other mechanistic explanations. Thus a similar relationship exists for the decarbonylation of acyl radicals (*151*).

Heck also examined the effect on k_6 of electronegative substituents on R and found a decrease rather than an increase in k_6. Thus the tendency for olefins bearing electronegative substituents to be hydrogenated cannot be explained on the preceding hypothesis. Increasing electronegativity in R would be expected to stabilize both alkyl–metal and acyl–metal bonds, but one would expect the effect to be greater for the alkyl. Thus the equilibrium

$$\mathrm{RM(CO)}_n + \mathrm{CO} \xrightleftharpoons[k_{-7}]{k_7} \mathrm{RCOM(CO)}_n \qquad (52)$$

should be displaced to the left with increasing electronegativity in R. This could explain the tendency for olefins with electronegative substituents to undergo hydrogenation rather than hydroformylation.

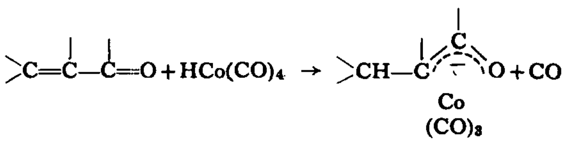
Some measurements have been made of the equilibrium constant for Eq. (52) for the case of manganese. Calderazzo and Cotton (*17*) have measured the value of the formation constant $K_7 = k_7/k_{-7}$ of the acylmanganese pentacarbonyls and found K_7 to vary in the order $R = CH_3CH_2$ (3300

$M^{-1}) > CH_3$ (366 M^{-1}) $> C_6H_5$ (66 M^{-1}); k_7 varied in a similar manner, $R = CH_3CH_2 > C_6H_5 \approx CH_3 \gg C_6H_5CH_2$, CF_3. Thus the tendency for styrene and fluoroolefins to be hydrogenated could result from either the thermodynamic or kinetic difficulty with which the corresponding alkylcobalt carbonyls undergo carbonylation.

Heck and Breslow (*63*) obtained evidence relating to Eq. (52) for the case of cobalt. They reacted a number of alkyl and acyl halides carrying functional groups with sodium cobalt tetracarbonylate under carbon monoxide. Normal acylcobalt carbonyls were readily formed except for the case of chloroacetonitrile, where a cyanomethylcobalt carbonyl was isolated. Apparently an α-nitrile group is sufficiently electronegative to stabilize the alkylcobalt carbonyl against carbonylation.

Unsaturated compounds containing oxygen functions, such as unsaturated aldehydes, ketones, esters and ethers might be expected to give a higher ratio of hydrogenation to hydroformylation than olefins. Goetz and Orchin (*43*, *44*) studied the reactions of unsaturated aldehydes, ketones, and ethers with cobalt hydrocarbonyl and found that hydrogenation occurred readily. Only the ethers gave more hydroformylation than hydrogenation products. Under similar conditions, Takegami *et al.* (*147*) reacted ethyl acrylate, *n*-butyl vinyl ether, and styrene with cobalt hydrocarbonyl and reported the hydrogenation product only in the case of styrene.

To account for the ready hydrogenation of unsaturated aldehydes and ketones, Goetz and Orchin proposed the formation of π-oxapropenyl derivatives.



$$>C{=}\overset{|}{C}{-}\overset{|}{C}{=}O + HCo(CO)_4 \rightarrow >CH{-}\overset{|}{C}\overset{\overset{|}{C}}{\cdots}O + CO \qquad \underset{(CO)_3}{Co} \qquad (53)$$

It was suggested that such derivatives would have unusual stability like the corresponding π-allyl complexes and would be further reduced by hydrocarbonyl rather than undergoing carbonylation. Heck (*63*) has, however, attempted the preparation of similar derivatives from chloroacetone and phenacyl bromide with sodium cobalt tetracarbonylate, Instead of finding unusually stable complexes he reported an unusual instability. It seems likely that in fact normal alkylcobalt carbonyls are formed, e.g.,

$$ClCH_2COCH_3 + NaCo(CO)_4 \rightarrow CH_3COCH_2Co(CO)_4 \qquad (54)$$

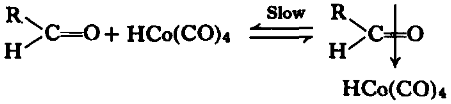
These are probably not sufficiently stable to be isolable as such, but probably carbonylate sufficiently more slowly than unsubstituted alkylcobalt carbonyls that decomposition competes with carbonylation.

B. *Aldehydes*

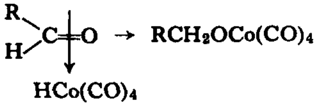
Another hydrogenation reaction of great importance in the Oxo synthesis is the hydrogenation of aldehydes to alcohols. Goetz and Orchin (*43*) demonstrated that many aldehydes are reduced to alcohols by reaction with cobalt hydrocarbonyl. The stoichiometric reaction may be written

$$RCHO + 2\,HCo(CO)_4 \rightarrow RCH_2OH + Co_2(CO)_8 \qquad (55)$$

The authors proposed the following steps:



$${}^{R}_{H}{>}C{=}O + HCo(CO)_4 \overset{Slow}{\rightleftharpoons} {}^{R}_{H}{>}\underset{\underset{HCo(CO)_4}{\downarrow}}{C{=}O} \qquad (56)$$



$${}^{R}_{H}{>}\underset{\underset{HCo(CO)_4}{\downarrow}}{C{=}O} \rightarrow RCH_2OCo(CO)_4 \qquad (57)$$

$$HCo(CO)_4 + RCH_2OCo(CO)_4 \xrightarrow{Fast} RCH_2OH + Co_2(CO)_8 \qquad (58)$$

Marko (*90*) investigated the catalytic hydrogenation of aldehydes and found a similar dependence on carbon monoxide pressure to that found for hydroformylation, in that the reaction had a maximum rate at a low partial CO pressure ($\sim$20 atm at 150° C). Above 32 atm partial pressure of CO the reaction followed the kinetic equation

$$d[ROH]/dt = k_8[R'CHO][Co][H_2][CO]^{-2}$$

Below 32 atm the rate fell off as cobalt metal was precipitated. Marko suggested a scheme similar to that of Orchin's.

$$HCo(CO)_3 + 2\,CO \rightleftharpoons HCo(CO)_4 + CO \rightleftharpoons HCOCo(CO)_4 \qquad (59)$$

$$RCHO + HCo(CO)_3 \rightleftharpoons \underset{\underset{HCo(CO)_3}{\downarrow}}{RCH{=}O} \rightleftharpoons RCH_2OCo(CO)_3 \qquad (60)$$

$$RCH_2OCo(CO)_3 + H_2 \rightarrow RCH_2OCoH_2(CO)_3 \rightarrow RCH_2OH + HCo(CO)_3 \qquad (61)$$

$$RCH_2OCo(CO)_3 + CO \rightarrow RCH_2OCo(CO)_4 \rightleftharpoons RCH_2OCOCo(CO)_3 \qquad (62)$$

$$RCH_2OCOCo(CO)_3 + H_2 \rightarrow HCOOCH_2R + HCo(CO)_3 \qquad (63)$$

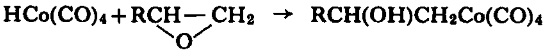
Aldridge and Jonassen (7) have also investigated the hydrogenation of aldehydes under hydroformylation conditions. Their reaction scheme differed in the following respects:

$$Co_2(CO)_8 + H_2 \rightleftharpoons 2\,HCo(CO)_4 \tag{64}$$

$$RCHO + HCo(CO)_4 \rightleftharpoons RCH(OH)Co(CO)_3 + CO \tag{65}$$

$$RCH(OH)Co(CO)_3 + HCo(CO)_4 \rightarrow RCH_2OH + Co_2(CO)_7 \tag{66}$$

Equation (65) differs from Eqs. (57) and (60) in the direction of addition of cobalt hydrocarbonyl to C═O. Evidence on this is conflicting. In favor of Eq. (65) is the fact that epoxides add cobalt hydrocarbonyl in the same sense



$$HCo(CO)_4 + RCH{-}CH_2\ (\text{—O—}) \rightarrow RCH(OH)CH_2Co(CO)_4 \tag{67}$$

The fact that formate esters are formed as a by-product of the reaction does not necessarily require Eq. (60) since they could equally well result from the reaction

$$HCOCo(CO)_4 + ROH \rightarrow HCOOR + HCo(CO)_4 \tag{68}$$

rather than via Eqs. (62) and (63). Formate esters are apparently formed by the hydroformylation of alcohols but in poorer yield than from the corresponding aldehydes (*94*). Carbonylation of a metal–oxygen bond as in Eq. (62) is rare, although cases are known [e.g., mercuric acetate (*49*, *58*)]. At the moment, then, there appears to be no convincing evidence either way, and it is conceivable that in fact both modes of addition occur.

Both Marko and Aldridge postulate tricarbonyl intermediates to account for the inverse dependence of rate on carbon monoxide pressure. Reaction of such intermediates with molecular hydrogen as in Eq. (61) is discussed in the section on coordinatively unsaturated intermediates.

Aldridge and Jonassen (7) have attempted to distinguish between the similar poisoning effects of thiophene and heavy metals on metal carbonyls and fresh metal surfaces. They concluded that Eq. (64) was heterogeneously catalyzed by cobalt metal. This is a point which is difficult to prove unequivocally, however. Attempts to vindicate the early assumption that the hydroformylation reaction is heterogeneously catalyzed (*5*, *6*) have received no further support in recent years.

IV

HYDROSILATION

A reaction closely related to hydrogenation which is catalyzed by dicobalt octacarbonyl or cobalt hydrocarbonyl under very mild conditions (0° C, atmospheric pressure) was recently described by Chalk and Harrod (*18*). The reaction involves the catalytic addition of a silicon hydride to an olefinic double bond as represented by Eq. (69).

$$RCH{=}CH_2 + R'_3SiH \rightarrow RCH_2CH_2SiR'_3 \qquad (69)$$

The following mechanism was suggested:

$$Co_2(CO)_8 + R_2SiH \rightarrow HCo(CO)_4 + R_3SiCo(CO)_4 \qquad (70)$$

$$HCo(CO)_n + RCH{=}CH_2 \rightarrow RCH_2CH_2Co(CO)_n \qquad (71)$$

$$RCH_2CH_2Co(CO)_n + R'_3SiH \rightarrow R'_3SiCH_2CH_2R + HCo(CO)_n \qquad (72)$$

In the absence of olefin, cobalt hydrocarbonyl was identified and demonstrated to react further with silicon hydride as in Eq. (73).

$$HCo(CO)_4 + R'_3SiH \rightarrow R_3SiCo(CO)_4 + H_2 \qquad (73)$$

Equation (70) together with Eq. (73) result in Eq. (74).

$$Co_2(CO)_8 + 2\ R_3SiH \rightarrow 2\ R_3SiCo(CO)_4 + H_2 \qquad (74)$$

Several silylcobalt carbonyls were isolated and shown to be formed according to the stoichiometry of Eq. (74). Since the silylcobalt carbonyls were found to be inactive as catalysts, it was concluded that catalyst deactivation resulted from Eq. (73). This was obviated by the use of an excess of olefin to facilitate Eq. (71).

Olefin isomerization was found to occur as a side reaction. This was presumed to occur via the alkylcobalt carbonyls formed by Eq. (71) as discussed in Section V and elsewhere.

Alkylsilane formation as in Eq. (72) might alternatively result from Eq. (75)

$$RCH_2CH_2Co(CO)_4 + R'_3SiCo(CO)_4 \rightarrow RCH_2CH_2SiR'_3 + Co_2(CO)_8 \qquad (75)$$

However, no evidence in support of this could be found from reactions of silylcobalt carbonyls with an equivalent of cobalt hydrocarbonyl in an olefin. Inclusion of an equivalent of silicon hydride in the latter reaction resulted in the formation of some alkylsilane derived from the silicon moiety of the silylcobalt carbonyl. This result was shown to arise from a facile exchange reaction as in Eq. (76), however.

$$R'_3SiCo(CO)_4 + R''_3SiH \rightleftharpoons R''_3SiCo(CO)_4 + R'_3SiH \qquad (76)$$

Triethylsilylcobalt carbonyl was formed by Eq. (74) even under high pressures of carbon monoxide (60 atm, 200° C) so that carbon monoxide insertion into a cobalt–silicon bond does not readily occur

$$(C_2H_5)_3SiCo(CO)_4 + CO \not\longrightarrow (C_2H_5)_3SiCOCo(CO)_4 \qquad (77)$$

In view of the stability of the cobalt–silicon bond, ascribed to *d–d* back-bonding, this result is not surprising.

Carbon monoxide was taken up, however, in the presence of olefins, and among the complex reaction products unsaturated alkoxysilanes predominated. It seems likely that these resulted from reactions such as the following:

$$C_2H_5COCo(CO)_n + (C_2H_5)_3SiH \rightarrow [C_2H_5COSi(C_2H_5)_3] + HCo(CO)_n \qquad (78)$$

$$[C_2H_5COSi(C_2H_5)_3] \xrightarrow[\gamma]{} C_3H_5OSi(C_2H_5)_3 \qquad (79)$$

V

ISOMERIZATION

The isomerization of epoxides is discussed in Section II, D,1. The isomerizations of olefins and of alkyl- and acylcobalt carbonyls have been considered as side reactions to hydroformylation but studies dealing principally with these reactions will now receive attention.

A. Olefins

A recent review (*106*) deals with the subject of olefin isomerization, which will therefore be dealt with only briefly here.

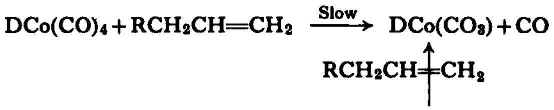
Orchin and Roos (*108*) examined the isomerization of allylbenzene by $HCo(CO)_4$ and $DCo(CO)_4$ at ambient temperature and pressure. Both $HCo(CO)_4$ and $DCo(CO)_4$ catalyzed isomerization to propenylbenzene at the same rate, and when $DCo(CO)_4$ was used as catalyst ~5% of the propenylbenzene produced was found to contain a deuterium atom. Hydroformylation of propylene with residual $DCo(CO)_4$, after an isomerization of allylbenzene, yielded RCDO with no detectable RCHO. The authors chose to reject a mechanism involving addition of D—Co to the olefinic double bond, on the grounds that the lack of an isotope effect indicated breaking of D—Co, or H—Co, was not the rate-determining step, and that only a relatively minor amount of deuterium was incorporated into the isomerized reaction product. Instead, the authors favored a mechanism expressed as

$$A + Co \rightleftharpoons Aco \qquad (80)$$

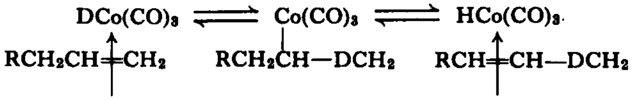
$$ACo + A \rightarrow A' + ACo \qquad (81)$$

where A = allyl benzene; Co = $HCo(CO)_4$; ACo = intermediate complex; and A′ = propenyl benzene.

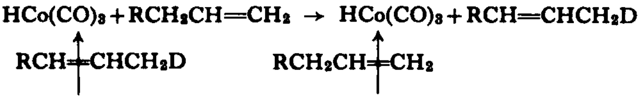
Others (*21*) subsequently pointed out that the results of Orchin and Roos are in fact in accord with a mechanism involving the reversible addition of H—Co to a double bond. They propose an S_N1 replacement of CO by olefin as the rate-determining step, a proposal in accord with the observed autocatalytic behavior of the reaction. The mechanism is written thus



$$DCo(CO)_4 + RCH_2CH{=}CH_2 \xrightarrow{\text{Slow}} \underset{\displaystyle RCH_2CH{=}CH_2}{\underset{\uparrow}{DCo(CO_3)}} + CO \qquad (82)$$



$$\underset{\displaystyle RCH_2CH{=}CH_2}{\underset{\uparrow}{DCo(CO)_3}} \rightleftharpoons \underset{\displaystyle RCH_2CH{-}DCH_2}{\underset{|}{Co(CO)_3}} \rightleftharpoons \underset{\displaystyle RCH{=}CH{-}DCH_2}{\underset{\uparrow}{HCo(CO)_3}} \qquad (83)$$



$$\underset{\displaystyle RCH{=}CHCH_2D}{\underset{\uparrow}{HCo(CO)_3}} + RCH_2CH{=}CH_2 \rightarrow \underset{\displaystyle RCH_2CH{=}CH_2}{\underset{\uparrow}{HCo(CO)_3}} + RCH{=}CHCH_2D \qquad (84)$$

(VIII)

The species (VIII), it is proposed, survives long enough to pass through an average of ~20 cycles of reactions analogous to Eqs. (83) and (84) before undergoing irreversible destruction. Such a process accounts satisfactorily for the observed incorporation of deuterium into ~5% of the propenylbenzene product and the lack of protium in the butyraldehydes prepared from the isomerization catalyst. It is worth noting that this amount of deuterium corresponds to between 10% and 15% of the deuterium present in the original $DCo(CO)_4$, and in view of the autocatalytic nature of the reaction [i.e., $DCo(CO)_4$ is not itself the catalyst], the interpretation proposed by Cramer and Lindsey seems highly plausible.

It has been observed that rapid isomerization accompanies the cobalt carbonyl-catalyzed hydrosilation of olefins (*18*). The reaction of equimolar amounts of a trisubstituted silane and dicobalt octacarbonyl has been shown to result in the formation of cobalt hydrocarbonyl (cf. Section IV). A very effective isomerization catalyst may be prepared by treatment of a solution of $Co_2(CO)_8$ in olefin (~0.01 M) with a silicon hydride in sufficient quantity to slightly exceed the cobalt carbonyl concentration.

The behavior of 1-heptene-3d_2 and 1-pentene-1d_1-2d_1 in the presence of such a catalyst was found to be very similar to that observed with a $RhCl_3 \cdot 3H_2O$ catalyst (*51*). The pertinent facts may be summarized as follows: (1) Migration of the double bond occurs in a stepwise fashion. [Such behavior was previously observed by Johnson (*72*) for the isomerization of 4-methyl-1-pentene under hydroformylation conditions.] (2) Coisomerization of 1-pentene and 1-heptene-3d_2 results in exchange of ~0.5 deuterium atoms per molecule of 1-heptene-3d_2 isomerized, the exchanged deuterium being distributed between all of the carbon atoms of the allylic system of the 2-pentene. Since the results obtained with the cobalt carbonyl/silane catalysts parallel so closely those obtained with rhodium complex catalysts, and little doubt remains that the latter operate through a metal alkyl intermediate, it seems very likely that such a mechanism is operative with the former catalyst.

B. *Alkylcobalt and Acylcobalt Carbonyls*

The isomerization of alkyl- and acylcobalt carbonyls is important in considering the products of the hydroformylation reaction and has been dealt with in part in Section II, A. Equations (9) and (10) give the most likely mechanism for the isomerization.

The isomerizations have been studied by Takegami *et al.* by reacting the isomeric alkyl or acyl halides with an alkali metal cobalt carbonylate (*142*, *148*, *149*).

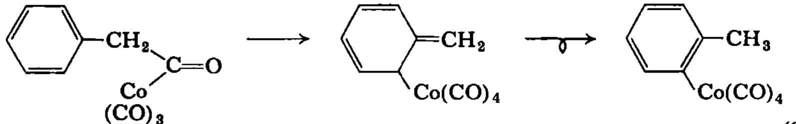
$$RX + KCo(CO)_4 \rightarrow RCo(CO)_4 + KX \tag{85}$$

$$RCOX + KCo(CO)_4 \rightarrow RCOCo(CO)_4 + KX \tag{86}$$

The products were isolated as esters by reaction of the acylcobalt carbonyls with an alcohol and iodine. In the case of the alkyl halides, carbon monoxide was normally absorbed, but under nitrogen, acylcobalt tricarbonyls must be formed. The reaction with alkyl halides was slow and some isomerization was noted using *n*-propyl iodide (formation of *n*-butyrates and isobutyrates). Absence of carbon monoxide "promoted" the isomerization. Isopropyl iodide gave no reaction. When ethyl α-bromopropionate was used, no isomerization was found at −25° C under carbon monoxide, but the isomerized product, diethyl succinate, was the major product at 25° C under carbon monoxide or nitrogen. Under the conditions of the experiments no isomerization of the alkyl halide itself was found.

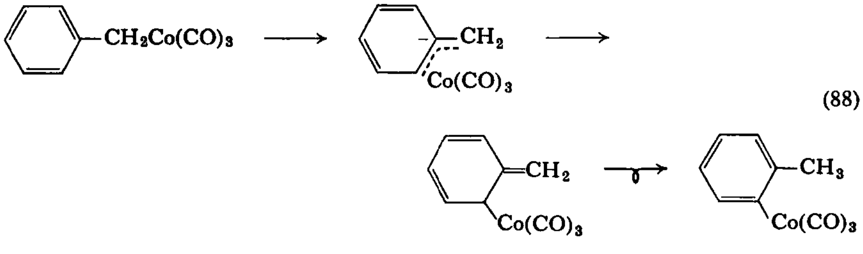
Acylcobalt carbonyls formed from acyl halides appear to isomerize less readily. No isomerization was found using isobutyryl bromide or *n*-butyryl chloride in nonpolar solvents such as hexane or benzene. Some isomerization was found with diethyl ether and ethyl acetate as solvents, again "promoted" by absence of carbon monoxide. Curiously, no isomerization was found in dioxane or tetrahydrofuran using *n*-butyryl chloride, but this could result from an inhibition period which appeared to be present for ethyl acetate. Isomerization occurred readily using isobutyryl bromide in these solvents. The extent of isomerization for the acylcobalt carbonyls derived from both *n*-butyryl and isobutyryl halides was about the same, ~50%. The carbon monoxide inhibition of the isomerization suggests that the reaction proceeds via the acylcobalt tricarbonyl while the promotion by coordinating solvents suggests that the dissociation of the tetracarbonyl may be a solvent-assisted S_N1 reaction (*96*).

A related isomerization, that of phenylacetylcobalt carbonyl to *o*-toluylcobalt carbonyl, has recently been studied (*143*). It also appears to proceed via a tricarbonyl but could not proceed via Eqs. (9) and (10). This rearrangement has much in common with the so-called "abnormal" reactions of benzyl Grignard and benzyllithium reagents to produce ortho-substituted products (*13*, *134*). It is possible that a cyclic intermediate similar to that postulated in the Grignard rearrangements may be involved, Eq. (87).



(87)

However, reaction via a π-benzyl intermediate[4] is perhaps a more likely probability [Eq. (88)].



(88)

This is similar to postulating the various resonance forms for the benzyl anion but does not so easily permit para products. Takegami found that this isomerization was strongly promoted by cobalt hydrocarbonyl. It would be interesting to know if this is also true of the isomerization of aliphatic acylcobalt carbonyls.

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[4] *Note added in proof:* A π-benzyl molybdenum carbonyl similar to that postulated in Eq. (88) has recently been synthesized (R. B. King and A. F. Fronzaglia, *J. Am. Chem. Soc.* **88**, 709, 1966).

VI

CARBOXYLATION

The reaction under consideration is typified by the formation of saturated carboxylic acids from olefins, carbon monoxide, and water. Other compounds have been used in place of olefins (alkyl halides, alcohols), and besides water, a variety of compounds containing "active" hydrogen may be employed. Thus, alcohols, thiols, amines, and acids give rise to esters, thioesters, amides, and acid anhydrides, respectively (*15*). If the olefin and the "active" hydrogen are part of the same molecule, three or four atoms apart, cyclizations may occur to produce lactones, lactams, imides, etc. The cyclizations are formally equivalent to carbonylations, however, and will be considered later.

Nickel carbonyl is the more widely known catalyst for the carboxylation reaction; dicobalt octacarbonyl has the disadvantage of giving side reactions (*15*). Dicobalt octacarbonyl has been used in the presence of tributyl phosphine for the reaction of ethylene, carbon monoxide, water, and ethanol. Besides ethyl acetate, acetaldehyde and diethyl ketone were found (*136*). Hydrogen has been found to increase the rate of reaction (*78*), presumably by the formation of cobalt hydrocarbonyl. However, this can lead to the formation of aldehydes, as in the reaction of acetyl bromide when an 89.4% yield of aldehyde was obtained in spite of the presence of water (*95*).

Heck (*59*) has suggested that the first step in the carboxylation reaction is the formation of cobalt hydrocarbonyl, which can be formed from dicobalt octacarbonyl and solvent (*55*). Alkylation and carbonylation then produce an acylcobalt carbonyl. Reaction of the acylcobalt carbonyl with the compound containing "active" hydrogen then regenerates cobalt hydrocarbonyl, e.g.,

$$RCOCo(CO)_4 + R'OH \rightarrow RCOOR' + HCo(CO)_4 \qquad (89)$$

Heck demonstrated Eq. (89) for a number of acylcobalt carbonyls, preparing them from the corresponding alkyl halide and sodium cobalt carbonylate. In the presence of bases, cobalt hydrocarbonyl regenerated cobalt carbonylate ion and a catalytic reaction resulted at atmospheric pressure and at temperatures from 0° to 100° C. Thus the following reaction was reported in 56% yield at 50° C:

$$B + C_8H_{17}I + CO + CH_3OH \xrightarrow{NaCo(CO)_4} C_8H_{17}COOMe + BH^+Cl^- \qquad (90)$$

The base (B) used was dicyclohexylethylamine. At the higher temperatures the isomeric products that one would expect from an isomerization of the acylcobalt carbonyls were formed (see Section II, A). Amines were also used in place of alcohols to give amides. Thus benzyl chloride reacted with carbon monoxide and aniline in tetrahydrofuran solution at 35° C in the presence of sodium cobalt carbonylate catalyst to give a 47% yield of phenylacetanilide.

$$C_6H_5CH_2Cl + CO + C_6H_5NH_2 \xrightarrow{NaCo(CO)_4} C_6H_5CH_2CONHC_6H_5 \qquad (91)$$

A catalytic carboxyalkylation can also occur if the acylcobalt carbonyl is formed from an epoxide and sodium cobalt carbonylate ion. This reaction is discussed in Section II, D,1,a.

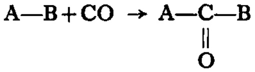
When nonconjugated dienes react with carbon monoxide and water in the presence of dicobalt octacarbonyl, saturated and unsaturated cyclic ketones are produced (*55*, *77*). This appears to be due to the formation of unsaturated acylcobalt carbonyls followed by cyclization, as discussed in Section II, B,3.

Acetylenes can also be carboxylated in the presence of dicobalt octacarbonyl. A patent (*105*) described the formation of acrylic and succinic acids from acetylene. Cyclopentanone was also formed in the presence of solvents (acetone, dioxane). Substituted succinic acids were formed from the corresponding substituted acetylenes.

VII

CARBONYLATION

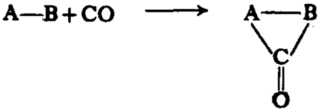
Two important kinds of carbonylation reaction may be catalyzed by cobalt carbonyls. The first kind involves the insertion of a carbonyl group into a σ-bond, thus,



$$A{-}B + CO \rightarrow A{-}\underset{\underset{O}{\|}}{C}{-}B \qquad (92)$$

Typical is the formation of formamides from amines. The authors are aware of no work in this area since the last review.

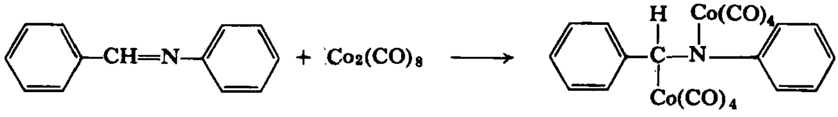
The second kind involves the cyclization of a linear molecule through a carbonyl bridge, thus,



The general question of ring closures catalyzed by metal carbonyls was recently the subject of an excellent review by Falbe (*33*). In general, such ring closures may be performed on substrates containing unsaturation three or four atoms removed from an "active" hydrogen atom. Known examples involve unsaturated C—C, C—N, and N—N bonds.

Falbe and co-workers have studied carbonylation of unsaturated amides to give imides (*34*), unsaturated amines to give lactams (*37*), and unsaturated alcohols to give lactones (*38*). Rosenthal and co-workers studied carbonylation of aromatic ketoximes, (*127*), phenylhydrazones (*131*), semicarbazones (*129*), azines (*129*), and nitriles (*128*) to produce phthalimidines. Horiie (*65*) has described the carbonylation of azobenzenes to give indazolones or 2,4-dioxo-1,2,3,4-tetrahydroquinazolines. Pritchard (*121*) and Murahashi *et al.* (*103*) have described the carbonylation of Schiff's bases to yield substituted phthalimidines.

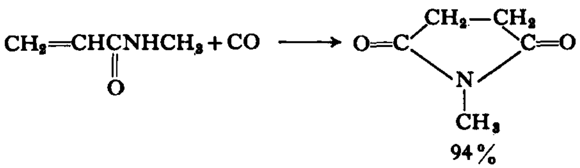
Sternberg and Wender (*140a*) reviewed several reactions such as these in 1959. At that time they proposed the homolytic addition of dicobalt octacarbonyl as the initiating step in the reaction, thus,



(94)

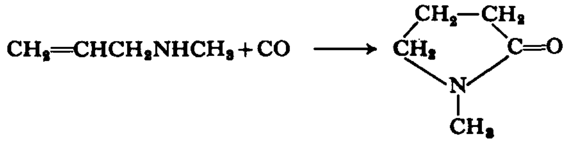
At the present time it seems more likely that *in situ* generated cobalt hydrocarbonyl is the species which adds to the unsaturated bond of the substrate (*33*).

Representative examples of these reactions are given in Eqs. (95)–(103).



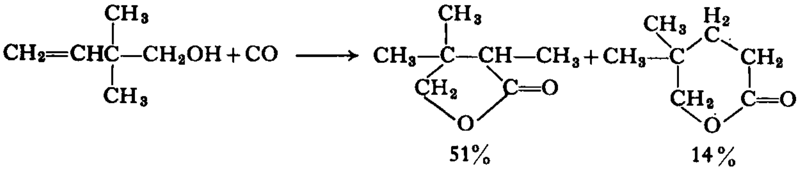
94%

(95)



78%

(96)



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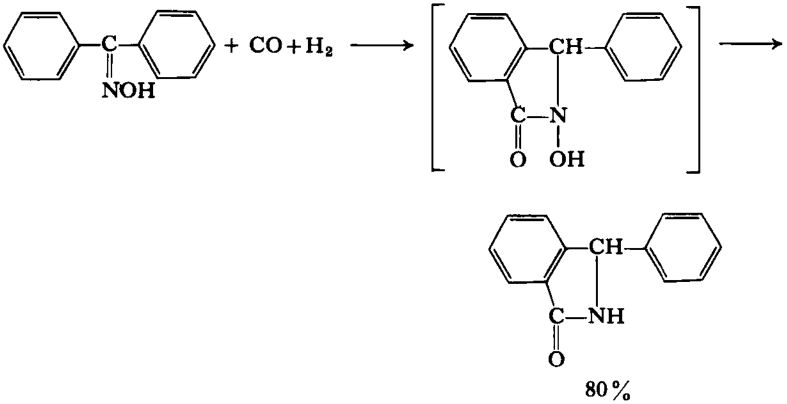

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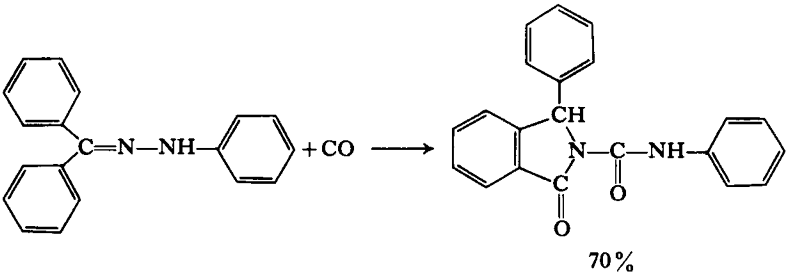

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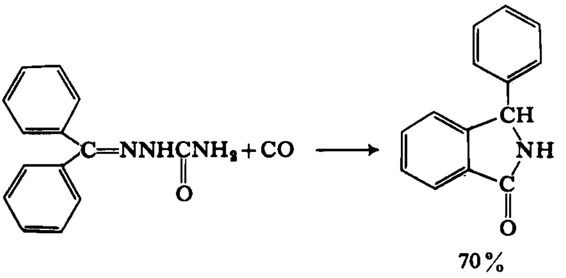
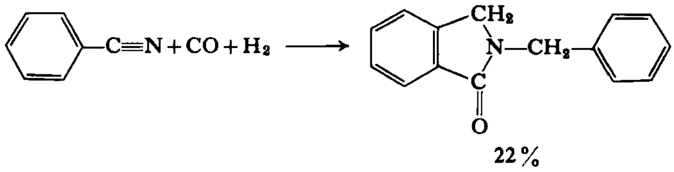


(100)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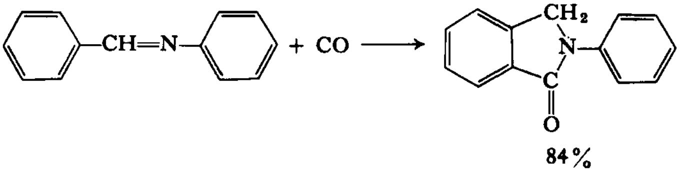
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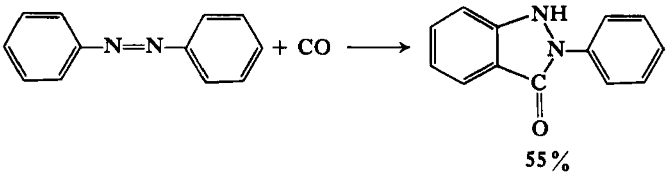
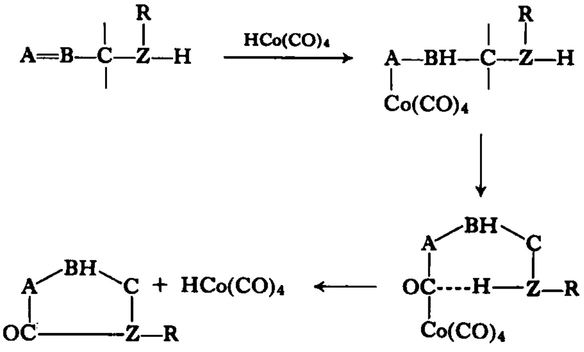

(103)

For greater detail of the influence of reaction conditions and substrate structures on yields and product distributions the original papers and a review (*33*) should be consulted.

All of these reactions may be considered as intramolecular carboxylations since the necessary alcohol or amine is already present within the unsaturated molecule. Falbe (*33*) has generalized the mechanism in terms of three steps, thus,

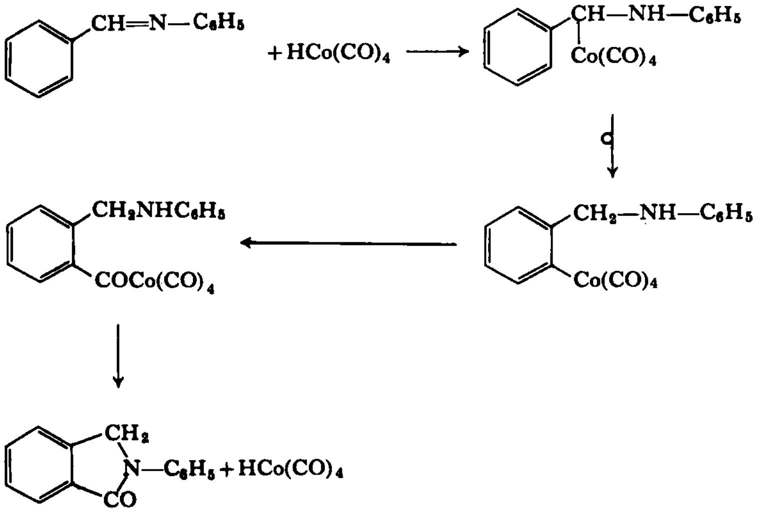

(104)

The last step represents an intramolecular nucleophilic lysis of the acylcobalt carbonyl, with the regeneration of cobalt hydrocarbonyl. Similar intermolecular reactions are discussed in the section on carboxylation. An example of intramolecular alcoholysis

(105)

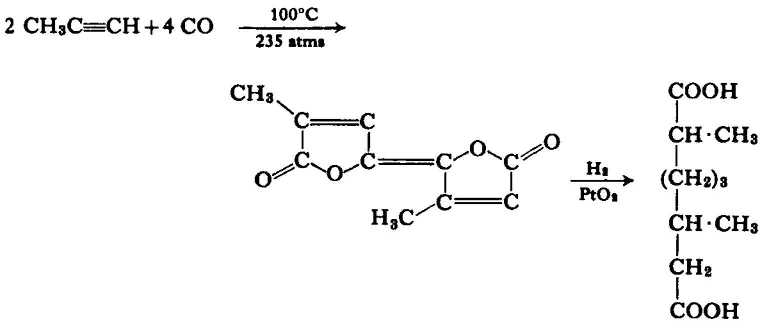
occurs at 0° C when the acylcobalt carbonyl formed from trimethylene oxide and cobalt hydrocarbonyl is reacted with dicyclohexylethylamine (*54*).

Equations (98)–(103) present some difficulty in rationalizing as intramolecular carboxylations. It would seem unlikely that an aromatic hydrogen would be capable of reacting with an acylcobalt carbonyl, although such a reaction has been postulated in the hydroformylation of eugenol (*42*). An alternative possibility, however, is suggested by the fact that σ-toluylcobalt carbonyl is formed when benzyl chloride is reacted with potassium cobalt carbonylate (*143*) (Section V, B). Thus Eq. (102) could result from the following steps:



(106)

The reaction of acetylenes with CO to produce octatrienediolides has been reported (*2a*). In the presence of dicobalt octacarbonyl in acetic anhydride/acetone solvent, propyne was found to react with CO to give dimethyloctatrienediolides. Hydrogenation of the latter yielded 2,6-dimethylsuberic acid.



(107)

The reaction product consisted of ~53% *trans*- and 38% *cis*-2,6-dimethyl-2,4,6-octatriene-1,4:5,8-diolide and ~9% of the 2,7-dimethyl analog.

VIII

POLYMERIZATION

Three types of reaction should be mentioned:

1. Cyclization of acetylenes to produce benzene derivatives (*65a*).
2. Polymerization of dienes.
3. Vinyl polymerization.

The first two appear to be catalyses occurring within the coordination shell of the metal, but little has yet been learned of their mechanisms. The latter is a free radical polymerization, the kinetics of which have been examined in some detail. Other metal carbonyls are effective to some extent in all three cases.

Otsuka *et al.* (*110, 112*) studied the polymerization of butadiene in the presence of an aged $Co_2(CO)_8/2\ MoCl_5$ catalyst. The product obtained was predominantly an atactic poly(1,2-butadiene), the 1,2-structure being favored by low reaction temperature (e.g., at 40° C, 97% 1,2; at 30° C, > 99% 1,2). Similar experiments with a $Ni(CO)_4/MoCl_5$ catalyst yielded a polymer with 85% *cis*-1,4-structure. The results of Otsuka *et al.* have been confirmed by Babitski and co-workers (*8*), who studied the polymerization of butadiene by a large number of binary catalysts, based on transition metal halide, transition metal carbonyl combinations. These systems are of interest as further examples of alkyl-free coordination polymerization catalysts for dienes (*9, 15a, 109*). Little is known of the origins of stereospecificity of these reactions.

Otsuka and co-workers (*111*) have also studied the polymerization of butadiene by a mixed $Co_2(CO)_8/(C_2H_5)_3$ Al catalyst. In an inert hydrocarbon solvent this catalyst results in a highly selective dimerization of 1,2-butadiene to give *trans*-3-methyl-1,4,6-heptatriene (~90% yield). However, in methylene chloride solvent the reaction proceeds to give a high molecular weight poly(butadiene) of high *cis*-1,4 content. During preparation of the catalyst, evolution of carbon monoxide was observed and the authors postulated a Co(0) weakly coordinated to aluminium alkyl and solvent as the polymerization site. Such reasoning must be considered highly speculative, particularly in the case of methylene chloride solvent, where alkyl–halogen exchange and oxidation of Co(0) are distinct possibilities.

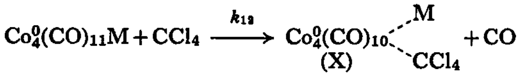
A related system is the three-component catalyst for polymerization of 1,3-butadiene (*81*). An aged mixture of $Co_2(CO)_8/AlCl_3$ (1:2) in benzene was reacted with a large excess of diethylchloroaluminum and butadiene to give a poly(butadiene) with ~98% *cis*-1,4 content. Tinyakova (*152*) found that a binary $Co_2(CO)_8/Al(C_2H_5)_2Cl$ catalyst polymerized 1,3-butadiene to a polymer of ~90% *cis*-1,4-content.

The carbonyl group does not appear to be of importance in the above catalysts since similar results may be obtained using cobalt halides in combination with aluminium alkyls (*81a*).

The synthetic aspects of coordination catalysis still receive far more attention than mechanistic aspects, and precious little can be said with assurance concerning the mechanisms of the foregoing polymerization reactions. Almost the opposite is true of the free radical initiation of vinyl polymerization by metal carbonyls. Bamford *et al.* (*10, 11*) have studied the kinetics of several such reactions and arrived at plausible interpretations of their results. The initiation of methyl methacrylate polymerization by tetracobalt dodecacarbonyl in the presence of carbon tetrachloride was studied in detail and the results were rationalized in terms of the following mechanism:

$$Co_4^0(CO)_{12} + M \underset{k_{10}}{\overset{k_9}{\rightleftharpoons}} \underset{(IX)}{Co_4^0(CO)_{11}M} + CO \tag{108}$$

$$(IX) \xrightarrow{k_{11}} \text{Inactive products} \tag{109}$$

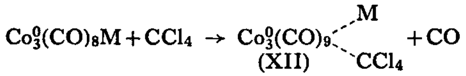


$$Co_4^0(CO)_{11}M + CCl_4 \xrightarrow{k_{12}} \underset{(X)}{Co_4^0(CO)_{10}}\begin{smallmatrix} \cdots M \\ \cdots CCl_4 \end{smallmatrix} + CO \tag{110}$$

$$(X) \rightarrow \underset{(XI)}{CO_3^0Co^1Cl(CO)_{10}M} + \underset{(or\ MCCl_3)}{\cdot CCl_3} \tag{111}$$

$$\text{(XI)} + \text{M} \rightarrow \text{Co}^{0}_{3}(\text{CO})_9\text{M} + \text{Co}^{I}\text{Cl(CO)M} \qquad (112)$$

$$\text{Co}^{0}_{3}(\text{CO})_9\text{M} \rightleftharpoons \text{Co}^{0}_{3}(\text{CO})_8\text{M} + \text{CO} \qquad (113)$$



$$\text{Co}^{0}_{3}(\text{CO})_8\text{M} + \text{CCl}_4 \rightarrow \underset{\text{(XII)}}{\text{Co}^{0}_{3}(\text{CO})_9\langle{}^{\text{M}}_{\text{CCl}_4}} + \text{CO} \qquad (114)$$

$$\text{(XII)} \rightarrow \underset{\text{(XIII)}}{\text{Co}^{0}_{2}\text{Co}^{I}\text{Cl(CO)}_7\text{M}} \qquad (115)$$

$$\text{(XIII)} + \text{M} \rightarrow \text{Co}^{0}_{2}(\text{CO})_6\text{MCo}^{I}\text{Cl(CO)M} \qquad (116)$$

On the assumption that all Co(O) species except $Co_4(CO)_{12}$ achieved a steady state by virtue of being more reactive than $Co_4(CO)_{12}$, the authors derived the following expression from Eqs. (108)–(116):

$$-\frac{dM}{dt} = \frac{2k_p[\text{M}]}{(\sqrt{k_t})^{1/2}}\left\{\frac{k_9 k_{12}[\text{M}][\text{Co}_4(\text{CO})_{12}][\text{CCl}_4]}{k_{11}+k_{10}[\text{CO}]+k_{12}[\text{CCl}_4]}\right\}^{1/2}$$

k_p and k_t are propagation and termination constants for free radical polymerization of methyl methacrylate and M is monomer concentration. All of the experimental observations could be rationalized in terms of this equation.

Although the acetylene derivatives $Co_2(CO)_6(C_6H_5C{\equiv}CCOOH)$ and $Co_3(CO)_9(H)(CH{\equiv}CC_6H_5)$ were also found to initiate polymerization in the presence of CCl_4, $Co_2(CO)_8$ was found to be not only inactive, but actually to inhibit polymerization in the presence of conventional free radical initiators. The unusual behavior of dicobalt octacarbonyl may be related to its greater reactivity. The reaction with carbon tetrachloride has been studied by Dent *et al.* (*22a*) and Ercoli *et al.* (*26a*) who isolated a complex $ClC\,[Co(CO)_3]_3$. This could arise from a series of C—Cl cleavage reactions followed by sterically induced decarbonylations.

$$\text{CCl}_4 + \text{Co}_2(\text{CO})_8 \rightarrow \text{Cl}_3\text{CCo(CO)}_4 + \text{ClCo(CO)}_4 \qquad (117)$$

$$\text{Cl}_3\text{CCo(CO)}_4 \rightarrow \text{Cl}_3\text{CCo(CO)}_3 + \text{CO} \qquad (118)$$

$$\text{Cl}_3\text{CCo(CO)}_3 + \text{Co}_2(\text{CO})_8 \rightarrow \text{CO} + \text{Cl}_2\text{C}[\text{Co(CO)}_3]_2 + \text{ClCo(CO)}_4 \qquad (119)$$

$$\text{Cl}_2\text{C}[\text{Co(CO)}_3]_2 + \text{Co}_2(\text{CO})_8 \rightarrow \text{CO} + \text{ClC}[\text{Co(CO)}_3]_3 + \text{ClCo(CO)}_4 \qquad (120)$$

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Redistribution Equilibria of Organometallic Compounds

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I

INTRODUCTION

The exchange of substituents between molecules or parts of molecules has been observed for many years. Probably one of the first such observations dates back to the 19th century when Ladenburg (*93*, *147*) detected the presence of a diphenylsilicon derivative in the reaction product of the alkylation of phenyltrichlorosilane with dialkylzinc. He concluded that this compound had formed as a result of "migration" of substituents between silicon atoms. In the following years many other examples of such behavior have been found and were termed variously as disproportionations, comproportionations, symmetrizations, dissymmetrizations, or metatheses. They have also been described in the literature as scrambling, exchange, substituent exchange, interchange, reorganization, distribution, and redistribution reactions. The latter term was introduced by Calingaert (*41–51*) who recognized the rôle of equilibria in these reactions and considered the statistics of sorting of the substituents, leading to the concept of randomness. In general, all these different terms, which are employed more or less interchangeably in chemistry, really describe the same phenomenon: chemical reactions in which two or more kinds of substituents exchange places with each other on one or more kinds of polyfunctional central atoms or moieties, with the exchange sooner or later reaching an equilibrium state. The various substituents and central moieties may be made up of a number of atoms; but under the experimental conditions employed, these atomic assemblages remain intact.

This review summarizes some earlier qualitative work as well as recent quantitative studies of redistribution equilibria and describes the principles underlying the mathematical treatment of such equilibria as well as the general implications of these equilibria with respect to general chemistry. In line with the general objective of the *Advances in Organometallic Chemistry* series, this article is limited to carbon–metal-bonded systems, metal hydrides, metal carbonyl compounds, metallocenes, and similar complexes. Excluded therefore are halogen-, sulfur-, nitrogen, and phosphorus-based systems. Various aspects of redistribution reactions were reviewed previously (*42*, *74*, *87*, *88*, *150*, *186*, *285*, *286*, *288*).

Most of the earlier data on redistribution reactions or equilibria reported in the literature are of more or less qualitative character. One of the exceptions is the work of Calingaert (*41–51*) where in a series of papers entitled "The Redistribution Reaction," the laws of probability were applied to a quantitative interpretation of the "random redistribution" of interchangeable substituents. In these studies, the respective redistribution products were determined quantitatively by fractional distillation of the equilibrated mixture. Although this method was fairly successful in the cases studied by Calingaert, there were many other systems to which it could not be applied due to too small boiling-point differences of the redistribution products or rapid rearrangement under the conditions of the distillation.

In addition, this procedure was quite tedious and time consuming. Therefore, in recent years when physical methods for assaying molecules in mixtures—methods such as nuclear magnetic resonance (NMR), gas chromatography, and others—have become available, a renaissance in the study of redistribution reactions has taken place. These methods allowed a rapid, quantitative, and precise determination of all of the reaction products present in a mixture. Also, equilibrium reactions could be carried out in much smaller sample sizes, thus permitting the study of exotic, hard-to-obtain compounds. Redistribution reactions—the kinetics as well as the equilibria—can now be measured directly in sealed NMR tubes. Furthermore, the relatively recent widespread availability to chemists of high-speed computers, in addition to these modern analytical tools, has facilitated the use of the appropriate mathematics even when highly complicated.

II

THEORY OF REDISTRIBUTION EQUILIBRIA

Of all the redistribution reactions in a single fluid phase, the scrambling of two kinds of *monofunctional* substituents about a given kind of central atom or nonexchangeable moiety is the simplest type. Such a case may be exemplified by the system QZ_ν vs QT_ν, where Q is the central atom or moiety Z and T the monofunctional exchangeable substituents, and ν the number of exchangeable sites on Q. The overall process merely is a rearrangement of covalent bonds, with the total number of σ bonds of any type remaining constant. However, other effects may also be quite significant—effects such as hybridization changes or nonbonding interactions, including steric factors and dipole interactions. A single phase is necessary in order to avoid shifting the equilibria by phase separation according to the Le Chatelier principle. Fluidity is required in order that the system remain homogeneous and that equilibration can proceed without being hindered by slow diffusion.

The above system becomes more complex when *more than two* monofunctional substituents are scrambled about the central moiety Q; e.g., in systems QZ_ν vs QY_ν vs QT_ν. Monofunctional substituents Z and T may also be scrambled between several kinds of central atoms or moieties, e.g., *two kinds*, Q and M. Such systems may be described by QT_ν vs MZ_μ, where ν and μ are the number of exchangeable sites on Q and M, respectively. Systems consisting of more than two monofunctional exchangeable substituents and more than two participating central atoms are probably too complex to be studied experimentally at the present time.

Not only may monofunctional substituents be redistributed on polyfunctional groups (*simple compounds*) but polyfunctional substituents may also be employed (*families of compounds*). Of course, if all of the groups which are scrambling are polyfunctional, only infinite network polymers and complicated fused ring systems may result and, as yet, suitable techniques have not been developed for study of such systems when amorphous. When monofunctional and difunctional substituents are sorted on a polyfunctional moiety, a large number of molecular structures are possible ranging from the simple structures in which all of the sites of the polyfunctional moiety are filled by monofunctional substituents through molecules of increasing complexity to the most complicated structures in which the polyfunctional moieties are held together by difunctional or bridging substituents.

A. Redistribution Equilibria of Simple Compounds

1. Systems QZ_ν vs QT_ν

If we consider a single kind of central atom or moiety, Q, exhibiting a functionality of ν (ν is the number of exchangeable sites) on which two kinds of substituents may be exchanged, and denote these substituents by T and Z, there are $(\nu+1)$ possible reaction products of the formula $QZ_iT_{\nu-i}$, where $i=0, 1, 2, 3, \ldots, \nu$. The system thus contains the molecules QT_ν, $QZT_{\nu-1}$, $QZ_2T_{\nu-2} \ldots QZ_{\nu-2}T_2$, $QZ_{\nu-1}T$, and QZ_ν, in which only Q—Z and Q—T bonds redistribute. For the sake of simplicity, these molecules will be represented by the respective symbols $z_0, z_1, z_2, \ldots, z_{\nu-2}, z_{\nu-1}, z_\nu$.

a. *Equilibrium Constants.* The resulting equilibria may be treated in terms of the following set of general equations corresponding to $i=1, 2, 3, \ldots, (\nu-1)$:

$$2\, z_i \rightleftarrows z_{i-1} + z_{i+1} \tag{1}$$

Accordingly, redistribution equilibria of the type described by Eq. (1) are characterized by $(\nu-1)$ equilibrium constants of the following form:

$$K_i = [z_{i-1}][z_{i+1}]/[z_i]^2 \tag{2}$$

with i having any integer value between 0 and ν, i.e., $1, 2, \ldots, (\nu-1)$.

Any other reaction equation or equilibrium constant in such systems can be derived from Eqs. (1) and (2).

All the equilibrium constants K_i and an overall composition parameter R defined as

$$R \equiv [Z]/[Q] = [z_1]+2[z_2]+3[z_3]+\ldots+\nu[z_\nu] \tag{3}$$

when

$$[z_0]+[z_1]+[z_2]+\ldots+[z_\nu] = 1 \tag{4}$$

are sufficient to completely describe the chemical composition of the system at equilibrium.

Although the values of K_i will depend on the nature of Q, Z, T, and ν, there is, for each ν, a special situation, the "ideal random case," where the sorting of the substituents about the central atom follows the laws of random statistics. For this case, the Z and T substituents become arranged about the Q in a completely random fashion irrespective of other substituents which are attached to Q. The K_i values for the ideal random case may be derived mathematically. If it is assumed that the Z/T atom ratio is p/q (with $p+q=1$), the probability P of having a central atom Q with i Z substituents and $(\nu-i)$ T substituents in the ν sites subject to redistribution is

$$P_\nu^{(i)} = \frac{\nu!}{i!(\nu-i)!}p^i \cdot q^{(\nu-i)} \tag{5}$$

Values thus obtained may be substituted in Eq. (2) for the calculation of $K_{i(\mathrm{rand})}$. It turns out that the p and q terms drop out and a numerical value for K_i is obtained.

TABLE I

RELATIVE DISTRIBUTION OF MOLECULES FOR THE IDEALLY RANDOM CASE FOR TWO EXCHANGING SUBSTITUENTS ON ONE TYPE OF CENTRAL MOIETY AT THE OVERALL COMPOSITION $R=\nu/2$

Number of sites for exchange, ν	Relative abundance of molecules								
	z_0	z_1	z_2	z_3	z_4	z_5	z_6	z_7	z_8
0	1								
1	1	1							
2	1	2	1						
3	1	3	3	1					
4	1	4	6	4	1				
5	1	5	10	10	5	1			
6	1	6	15	20	15	6	1		
7	1	7	21	35	35	21	7	1	
8	1	8	28	56	70	56	28	8	1

Although this mathematical approach is rather involved, the random values of K_i can easily be obtained by considering that, when $R = \nu/2$ (as many Z substituents as T substituents in the overall system), the distribution of the various molecules upon random redistribution is given by the binominal series, as illustrated in Table I. By using Eq. (2), the corresponding K_i values may be calculated quite easily and are given in Table II.

TABLE II

EQUILIBRIUM CONSTANTS FOR THE IDEALLY RANDOM REDISTRIBUTION OF TWO KINDS OF SUBSTITUENTS ON A CENTRAL MOIETY

Number of sites for exchange, ν	Value of K_i						
	K_1	K_2	K_3	K_4	K_5	K_6	K_7
2	1/4						
3	1/3	1/3					
4	3/8	4/9	3/8				
5	2/5	1/2	1/2	2/5			
6	5/12	8/15	9/16	8/15	5/12		
7	3/7	5/9	3/5	3/5	5/9	3/7	
8	7/16	4/7	5/8	16/25	5/8	4/7	7/16

With the use of these equilibrium constants, the composition of the system at random distribution equilibrium, i.e., the relative amounts of each species present at equilibrium at any overall composition, may be plotted against the overall composition parameter R. The resulting graphs are shown in Fig. 1.

Considering the random case as a reference point, we may term equilibria for which K_i is different from $K_{i(\text{rand})}$ as "nonrandom" cases, with K_i assuming "smaller than random" or "larger than random" values. If the values of the equilibrium constants K_i are smaller than random, the equilibrium concentrations of the "mixed" species, i.e., molecular species containing both substituents Z and T, is larger than expected for random distribution. Thus at infinitely small values of K_i, the maxima of the curves in Fig. 1 grow to the 100% level with the equilibrium concentrations of the species containing just one kind of substituent diminishing accordingly. On the other hand, if the values of K_i are larger than the random value, the equilibrium concentrations of the "mixed" species become smaller than at random equilibrium and consequently that of the species containing just one kind of substituent becomes larger. At extremely large values of K_i, the mixed species are nonexistent and the curves of Fig. 1 degenerate to two diagonal lines representing the "unmixed" species.

Computer programs (*106*, *107*) have been developed to facilitate the calculation of weighted average equilibrium constants and their standard error from the experimental data and the error estimation between the

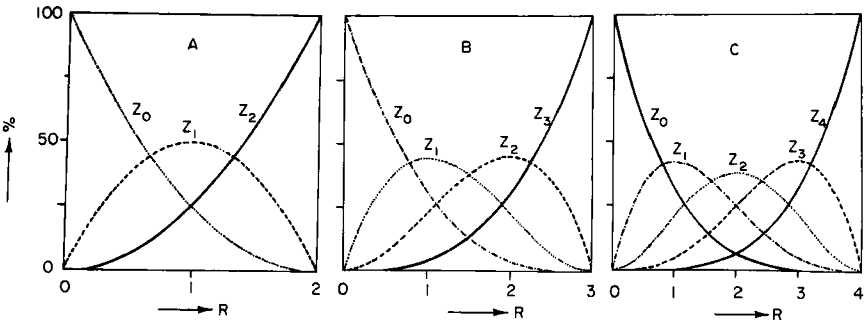


FIG. 1. Equilibrium distribution of molecules for the ideal random case in systems QZ_ν vs QT_ν as a function of the composition parameter R. A, $\nu=2$; B, $\nu=3$; C, $\nu=4$.

overall composition as determined from the reactants and from the analytically determined product ratios. Another procedure has been worked out for calculating the amounts of the various component molecules z_i in a mixture of a given overall composition when the equilibrium constants are known.

b. *Thermodynamics of Redistribution Reactions.* The formation of each of the components z_i [i being an integer from 1 to $(\nu-1)$] from the "unmixed" species z_0 and z_ν can be represented by the chemical reactions

$$(\nu-i)z_0+iz_\nu \rightarrow \nu z_i \tag{6}$$

to which corresponds a set of equilibrium constants

$$K_{fi} = [z_i]^\nu/\{[z_0]^{(\nu-i)}[z_\nu]^i\} \tag{7}$$

These equilibrium constants K_{fi} can also be derived from the K_i constants; e.g., for $\nu=3$, it can be shown that $K_{f1}=1/(K_1^2\cdot K_2)$ and $K_{f2}=1/(K_1\cdot K_2^2)$.

Consequently, it is possible to calculate the free energy of formation of the species z_i from the two end members z_0 and z_ν, as follows:

$$\Delta F = \Delta H - T\Delta S = -(RT/n)\ln K_{fi} \tag{8}$$

For the ideal random case, the ΔH term is zero, thus giving the following equation for the free energy:

$$(\Delta F)_{\text{rand}} = -T(\Delta S)_{\text{rand}} = -(RT/n)\ln(K_{fi})_{\text{rand}} \tag{9}$$

or

$$(\Delta S)_{\text{rand}} = (R/n)\ln(K_{fi})_{\text{rand}} \tag{10}$$

with the term $(\Delta S)_{\text{rand}}$ being the entropy of mixing.

One is generally interested in the enthalpies of scrambling reactions since these may be measured thermochemically and thus brought into relationship with equilibrium constants. Real scrambling equilibria, however, deviate more or less from the ideal random case. And, in order to be able to calculate enthalpies, it is assumed that for large values of the enthalpy, $(\Delta S)_{\text{real}} \approx (\Delta S)_{\text{rand}}$. Accordingly, we may now estimate the enthalpy of a "real" scrambling reaction.

$$\Delta H = \Delta F + T\Delta S \tag{11}$$

$$\Delta H = -(RT/n)\ln(K_{fi})_{\text{real}} + (RT/n)\ln(K_{fi})_{\text{rand}} \tag{12}$$

$$\Delta H = -(RT/n)\ln[(K_{fi})_{\text{real}}/(K_{fi})_{\text{rand}}] \tag{13}$$

There are special cases (*231*)—particularly where $(\Delta F_{\text{real}} - \Delta F_{\text{rand}})$ is less than 1 or 2 kcal—where the approximation of Eq. (13) is extremely poor due to differences in solvation of the various species, aggregation or clumping of certain molecules, or other factors leading to abnormal entropies.

2. *Systems* QZ_ν *vs* QY_ν *vs* QT_ν

When three different monofunctional substituents Z, Y, and T redistribute on the ν sites of the central moiety Q, a large number of compounds is possible. To give an example, for $\nu = 3$, a total of ten different compounds may be expected: Three compounds with three identical substituents attached to Q, six with two different substituents, and one with three different substituents.

A plot used to conveniently describe such a system is a triangular prism. The equilateral base of this prism is shown in Fig. 2, with the points drawn to correspond to the composition of each of the ten compounds.

To fully describe the overall system, seven equilibrium constants must be used: Two for each of the three subsystems involving only two of the three different exchangeable substituents (systems represented by each of the three sides of the triangle, i.e., QZ_3 vs QY_3, QZ_3 vs QT_3, and QY_3 vs QT_3) and one constant determining the concentration of the compound QZYT. Three equally simple equilibria may be written to relate QZYT to the other species [Eqs. (14)–(16)]

$$2\,QZYT \rightleftarrows Z_2YQ + YT_2Q \tag{14}$$

$$2\,QZYT \rightleftarrows Z_2TQ + Y_2TQ \tag{15}$$

$$2\,QZYT \rightleftarrows ZY_2Q + ZT_2Q \tag{16}$$

Thus, the equilibrium constant derived from any of these reactions may be used to complete the definition of the system. Any of the three reactions of

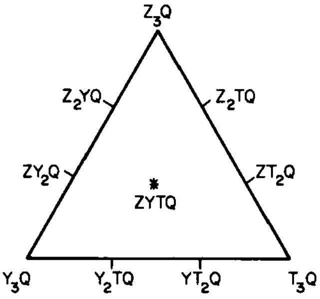


FIG. 2. Base triangle of the three-dimensional graph representing the system QZ_3 vs QY_3 vs QT_3.

Eqs. (14)–(16) represent a redistribution equilibrium similar to the case where two different substituents exchange between two sites and may be treated accordingly. Furthermore, two *R* values are required to describe the overall composition in a mixture of this system.

Generally speaking, the study of systems with three or more kinds of monofunctional substituents exchanging on a central moiety offers considerable experimental difficulties. So far, only one such case, the system (*292*) $SiCl_4$ vs $Si(OCH_3)_4$ vs $Si[N(CH_3)_2]_4$ has been investigated quantitatively. However, several qualitative reports have appeared which indicate the complexity of the equilibria, e.g., in systems such as PCl_3 vs PBr_3 vs PI_3 (*90*) or $SnCl_4$ vs $SnBr_4$ vs SnI_4 (*40*). Semiquantitative studies of equilibria in the systems (*45*) $(CH_3)_4Pb$ vs $(C_2H_5)_4Pb$ vs $(n\text{-}C_3H_7)_4Pb$ and $(CH_3)_4Pb$ vs $(n\text{-}C_3H_7)_4Pb$ vs $(\text{iso-}C_3H_7)_4Pb$ have been performed by distillation separation. Redistribution on silicon involving the four substituents CH_3, C_2H_5, n-C_3H_7, and n-C_4H_9 has been studied by gas chromatography and 29 of the 35 expected species were resolved (*232*).

3. *Systems QT_ν vs MZ_μ*

a. ***Equilibrium Constants.*** When the T substituents of the compound QT_ν are scrambled with the Z substituents of the compound MZ_μ a total of $(\nu+\mu+2)$ molecular species may result. Again letting the symbol z_i stand for the compounds $QZ_iT_{\nu-i}$ and z'_i for the compounds $MZ_iT_{\mu-i}$, it is seen that there are $(\nu+1)$ compounds of the type z_i and $(\mu+1)$ compounds of the type z'_i. As pointed out previously, a minimum of $(\nu-1)$ equilibrium constants are required to represent scrambling equilibria involving Z and T substituents between molecules of the type z_i and $(\mu-1)$ for the molecules of the type z'_i. Generally, these $(\nu+\mu-2)$ constants are chosen (*291*) to be of the following form:

$$K_{i(Q)} = [z_{i-1}][z_{i+1}]/[z_i]^2 \tag{17}$$

$$K_{i(M)} = [z'_{i-1}][z'_{i+1}]/[z'_i]^2 \tag{18}$$

In addition, there is one other equilibrium constant, an intersystem constant, necessary to relate the system of z_i molecules with that of the z'_i molecules. Although this constant, K_I, may be written in a number of ways, the following format has been chosen for this constant since this is the form which is most readily evaluated from existing compilations of thermodynamic data:

$$K_I = \{[z_0]^\mu [z'_\mu]^\nu / ([z_\nu]^\mu [z'_0]^\nu)\}^{1/x} \tag{19}$$

where $x=1$; unless $\mu=\nu$, when $x=\mu=\nu$.

b. ***Evaluation of the Equilibrium Constants.*** Due to the generally encountered nonrandom character of the distribution of Z and T on the two different central moieties, often one or more of the end members of the series $(z_0, z_\nu, z'_0$, and $z'_\mu)$ is present in undetectable amounts. It is therefore not possible to obtain an accurate value of K_I by direct substitution of analytical data into Eq. (19). However, it is feasible to calculate the missing data from the $(\nu-1)$ $K_{i(Q)}$ and the $(\mu-1)$ $K_{i(M)}$ equilibrium constants which in turn can be evaluated from the experimental data or from a separate study of the z_i or z'_i system. By use of a computer program, weighted-average equilibrium constants are obtained which may then be employed to calculate the theoretical distribution for any given R value in either system. These R values are obtained from the experimental data, since for the compounds based on the central moiety Q,

$$R_{(Q)} = \sum_i (\nu - i)[z_i] / \sum [z_i] \tag{20}$$

and for the system based on the central moiety M,

$$R_{(M)} = \sum_i (\mu - i)[z_i'] / \sum_i [z_i'] \tag{21}$$

By this means, a value of K_I for each experiment is obtained. The deviation of the average of these values for a set of experiments is obtained by taking the square root of the sum of the squares of the deviation of the individual values from the average.

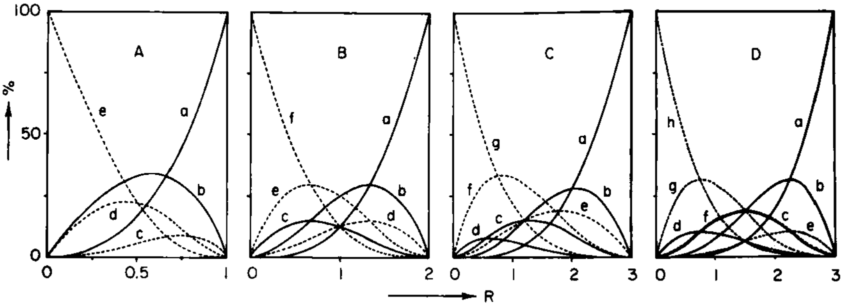


FIG. 3. Theoretical equilibrium curves in systems QZ_ν vs MT_μ for K_I and K_i having the values for ideal random distribution as a function of $R \equiv [T]/([Q]+[M])$. The solid lines represent the compounds $MZ_{\mu-i}T_i$ and the broken lines the $QZ_{\nu-i}T_i$ compounds. A, $\nu=2, \mu=1$, a=MT, b=MZ, c=QT_2, d=QTZ, and e=QZ_2; B, $\nu=\mu=2$, a=MT_2, b=MZT, c=MZ_2, d=QT_2, e=QTZ, and f=QZ_2; C, $\nu=2$, $\mu=3$, a=MT_3, b=MT_2Z, c=MTZ_2, d=MZ_3, e=QT_2, f=QZT, and g=QZ_2; D, $\nu=\mu=3$, a=MT_3, b=MT_2Z, c=MTZ_2, d=MZ_3, e=QT_3, f=QT_2Z, g=QTZ_2, and h=QZ_3.

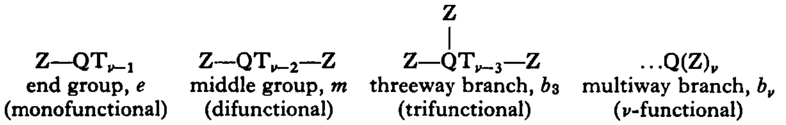
The overall composition of a mixture in such a system is characterized by two parameters: One to determine the relative amount of Z and T in the mixture, $R \equiv [T]/([Q]+[M])$ and one to determine the relative amount of Q and M, $R' \equiv [Q]/([Q]+[M])$. A computer program (*106*) has been developed which permits the calculation of the relative amounts of all species present at equilibrium from the set of constants $K_{i(Q)}$, $K_{i(M)}$, and K_I for any overall composition defined by the two parameters R and R'.

Similar to the graphs shown in Fig. 1, curves describing the distribution at equilibrium of all participating species as a function of the overall composition may be drawn. Variously shaped sets of curves are obtained depending on the numerical values of the sets of equilibrium constants and the number of sites for exchange on the two central moieties (*183*, *195*, *291*). A few examples of such curves are shown in Fig. 3. These graphs represent the case for "ideal random" distribution of Z and T between Q and M as well as on either Q or M. Considerably different curves result when K_{I} deviates from the random value $K_{\mathrm{I(rand)}} = 1$ and when the constants $K_{i(\mathrm{Q})}$ and $K_{i(\mathrm{M})}$ are nonrandom also.

B. Redistribution Equilibria in Families of Compounds

In the theoretical approach thus far, the substituents Z and T which exchange places on the central moiety were monofunctional. There is no reason, of course, why the exchanging substituents in this scheme cannot be di- or polyfunctional.

Let us again consider Q as a central atom or moiety of the functionality ν, T as a monofunctional exchangeable substituent, and Z one-half of a difunctional (bridging) atom or group such as $O_{1/2}$, $S_{1/2}$, or $(NR)_{1/2}$, or simply "half" of a bond to another Q atom. Then the $(\nu + 1)$ kinds of species of the general formula $QZ_iT_{\nu-i}$ resulting from exchange of Z and T on the central moiety are no longer simple molecules (except for $i = 0$) but parts of molecules which are termed building units. The functionality of each building unit is dependent on i and ranges from 0 for the *neso* molecule, QT_ν—a term taken from silicate chemistry meaning a small "island" structure (from the Greek word for island) which in equilibrium chemistry denotes the smallest member of a family of compounds—and the building units given below to a most-branched unit.



$$\begin{array}{cccc} Z{-}QT_{\nu-1} & Z{-}QT_{\nu-2}{-}Z & Z{-}\overset{\overset{\displaystyle Z}{|}}{Q}T_{\nu-3}{-}Z & \ldots Q(Z)_\nu \\ \text{end group, } e & \text{middle group, } m & \text{threeway branch, } b_3 & \text{multiway branch, } b_\nu \\ \text{(monofunctional)} & \text{(difunctional)} & \text{(trifunctional)} & (\nu\text{-functional}) \end{array} \qquad (22)$$

This most-branched building unit (multiway branch) in a system having the functionality ν is also termed the "zeugotatic" compound.

1. *Equilibrium Constants in Ring-Free Systems*

Similar to the treatment of equilibria in systems involving monofunctional substituents only, the equilibria resulting from scrambling of Z and T on a central moiety Q are described by $(\nu - 1)$ equilibrium constants. The set of equilibrium constants of the form of Eq. (2)—but now involving building units in molecules which are noncyclic or do not contain rings—fully desscribe the distribution of building units in the ring-free portion of a system for which the "reorganizational heat order" (*159*) is equal to 1. These equilibrium constants for $i = 1$, 2, and 3 thus may be written in the following form:

$$K_1 = [neso][\text{middles in chains}]/[\text{ends}]^2 \tag{23}$$

$$K_2 = [\text{ends}][\text{threeway branches}]/[\text{middles in chains}]^2 \tag{24}$$

$$K_3 = [\text{middles in chains}][\text{fourway branches}]/[\text{threeway branches}]^2 \tag{25}$$

with the amount of building units expressed in units of concentration.

For systems having a central moiety Q with only three exchangeable sites, $\nu = 3$, the ring-free portion of the system is determined by only two equilibrium constants, K_1 and K_2; for $\nu = 2$, by one constant, K_1.

In this treatment of families of compounds (i.e., "polymeric" systems), the infinite number of equilibrium constants involving all of the variously sized molecules is thus replaced by a much smaller number of equilibrium constants involving parts of molecules. Although the equilibrium constants of Eqs. (23)–(25) may have nonrandom values, the resulting building units $QZ_iT_{\nu-i}$ are generally randomly arranged into ring-free molecular structures. This is the situation for a reorganizational heat order, ρ, of unity. For higher values of ρ, it is necessary to employ more equilibrium constants involving larger blocks of building units. In such cases, due to overlapping of these blocks, there is no longer stoichiometric additivity, since a given atom may be part of several overlapping blocks or building units. The reorganizational heat order is a measure of the smallest sized block of building units in the ring-free part of the system from which any larger assemblage is randomly composed.

When the ring-free portion of a system is random with respect to the sorting of atoms or other smaller exchangeable units, ρ is zero. In this case, monofunctional substituents interchange randomly with pieces of chains so that for the class of "heteropolymers" (*124*) there is no energetic distinction between the monofunctional substituents and the bridging atoms with respect to scrambling interchanges and for "homopolymers" (*124*), the chain atoms are not thermodynamically distinguishable from the substituents in a sorting process.

2. *Ring–Chain and Ring–Ring Equilibrium Constants*

For the sake of simplicity, the following discussion will be limited to systems composed exclusively of *neso* molecules, end, and middle groups.

If we denote a monofunctional building unit by *e* (end group) and a difunctional unit by *m* (middle group), the equilibria involving all molecules including the *neso* molecule are summarized in the following general equations:

$$2e \rightleftarrows neso + m_{\text{chain}} \tag{26}$$

$$em_k e + em_j e \rightleftarrows em_{k+i} e + em_{j-i} e \tag{27}$$

$$em_q e \rightleftarrows em_{q-r} e + m_r \tag{28}$$

Equation (26) describes the scrambling of substituents to form building units and Eq. (27) deals with the chain–chain equilibria; i.e., the reactions whereby the size distribution of the chains is established. For $\rho = 1$, i.e., random sorting of building units, the equilibrium constant of this equation is equal to unity (*89*). The third reaction, Eq. (28), deals with equilibria between chain molecules and cyclic molecules of ring size *r*. In contrast to Eqs. (26 and 27), the latter equilibrium is concentration-dependent, with the amount of ring molecules at equilibrium increasing with increasing dilution.

By a similar statistical reasoning whereby it has been demonstrated that the equilibrium constant of Eq. (27) is unity, the equilibrium constant of Eq. (28) may be shown (*159*) to have the following form for $\rho = 1$:

$$K_r^\circ = \frac{[\text{Middles in the } r\text{-sized rings}]}{(1+D)\{V_2 + (R/2)(V_0 - V_2)\}} \left[\frac{[\text{ends}] + 2[\text{chain middles}]}{2[\text{chain middles}]}\right]^r \tag{29}$$

In the above equation, D is the dilution expressed in volumes of diluent per volume of neat sample, V_0 and V_2 are the molar volumes in liters per mole of the *neso* and a middle group, repectively, R is the overall mole ratio [T]/[Q] and all bracketed concentrations are measured in terms of mole fractions of the total building units.

When there are ring molecules of several sizes, these are related by ring–ring constants defined by Eq. (30)

$$K_{r,\,(r-1)}^{\circ\circ} = (K_r^\circ)^{(r-1)}/(K_{(r-1)}^\circ)^r = [[m_r]^{(r-1)}/[m_{(r-1)}]^r]\,V[\text{liter/mole}] \tag{30}$$

where $[m_r]$ denotes the mole fraction of middle groups in the ring molecule of the size r and $[m_{(r-1)}]$ those in rings of the size $(r-1)$, and V is the molecular volume of a middle group. When the various ring–chain constants of the form of Eq. (29) are known, the ring–ring constants of the form of Eq. (30) may be calculated. Alternatively, a system may be fully described by one ring–chain constant and a full set of ring–ring constants.

3. *Determination of Rings*

Often ring structures cannot be determined directly and must be calculated or estimated by difference. Since middle groups present in simple rings are effectively removed from the chain population, the presence of simple rings should make the observed amount of short-chain molecules larger than the amount calculated on the assumption of no cyclic molecules. Within the reliability of the approximation that $\rho \leqslant 1$, it is therefore possible to estimate the amount of simple ring molecules from the deviation of the observed amount of a short-chain molecule, such as the dichain from that calculated on the basis of no rings. Equilibrium constants for the exchange of the constituent atoms between building units truly apply only to the ring-free portion of the molecules and the presence of simple cyclic molecules can be shown to cause a continuous increase in the apparent value of such equilibrium constants as the amount of bridging units is increased with respect to the monofunctional substituents. Correcting this increase by subtracting middle groups present in the simple cyclic molecules so as to give a constant value for the equilibrium constant represents a method for estimating the amount of rings when they cannot be measured directly by the analytical procedure.

The exact mathematical derivations of the equations in this section have been obtained by using Graph Theory (*23*). The ring–chain problem has also been treated from a statistical-mechanical viewpoint (*149*).

III

EXPERIMENTAL METHODS

Fractional distillation and crystallization were the separation methods used in earlier studies of redistribution reactions. Quantitative equilibrium data were obtained first by Calingaert over a quarter of a century ago from an equilibrated mixture of tetraethyllead and tetramethyllead. Fractional distillation showed that, in addition to the starting materials, all three of the expected redistribution products were found in amounts corresponding to random interchange of methyl and ethyl groups on lead.

In many cases, however, distillation is not suitable for studying redistribution equilibria since the high temperatures involved may cause continuous reorganization of substituents so that the lowest boiling compound is regenerated as quickly as it is removed from the mixture by distillation. This usually results in complete decomposition of the mixed compounds to yield—provided good rectification—the two compounds having only one kind of substituents attached to the central atom or moiety. This indicates that in such cases where the rate of reorganization is of the same order of magnitude as the rate of distillation, the amounts of the various species present in the equilibrium mixture will have to be determined by physical methods, which do not involve separations.

A. *Nuclear Magnetic Resonance*

High-resolution NMR is a method particularly well suited for this purpose. At the present time, the nuclei most frequently used for quantitative measurement are ^{1}H, ^{31}P, and ^{19}F. Other nuclei, although having spin 1/2, such as ^{29}Si, ^{13}C, ^{14}N, ^{115}Sn, ^{117}Sn, ^{119}Sn, ^{203}Tl, ^{207}Tl and others, are ill-suited for the quantitative assay of a mixture of redistribution products because of their low natural abundance and the thus resulting weak signals. However, newly developed methods of NMR signal averaging seem to make the use of the NMR signals of these nuclei more attractive. Another way to utilize the NMR activity of these nuclei perhaps may lie in isotopic enrichment. Nuclei having spins larger than 1/2 and/or a quadrupole moment, such as ^{11}B (spin 3/2), ^{23}Na (spin 3/2), ^{27}Al (spin 5/2), and others, give rise to much broader line widths and spin multiplets and thus are of only limited interest with respect to quantitative NMR work.

Hence, for practical purposes, redistribution equilibria are studied best by observing the ^{1}H or ^{19}F signals of substituents attached directly or via one or more other atoms to the central atom, rather than the signals of the central atoms, as is done in phosphorus chemistry by ^{31}P NMR. The resonance of a substituent having NMR-active nuclei will have a different chemical shift for different combinations of other substituents on a given central atom. The substituent observed by NMR may or may not participate in the exchange processes. Suitable monofunctional substituents which as such may remain intact under normal redistribution conditions and do not give unduly complicated spectra due to spin–spin interaction are H, CH_3, $C_6H_5CH_2$, $ClCH_2$, CH_3O, CH_3S, $(CH_3)_2N$, $(CH_3)_3C$, $(CH_3)_3Si$, F, F_3C, and similar groups.

Since the NMR measurements of equilibrated systems are performed on single-phase liquids or solutions, the resulting data correspond to a total analysis of all of the components in the system under study.

B. Interpretation of NMR Spectra

There are a series of aids for the interpretation of NMR spectra of equilibrated redistribution mixtures. Spectra of systems involving equilibria in simple compounds, of course, are easier to correlate than those of families of compounds.

1. *Simple Systems*

The type of spectra obtained in these systems and the methods employed for their interpretation will be discussed using the equilibria in the system (*195*) CH_3GeCl_3 vs CH_3SiBr_3, which is of the type QZ_3 vs MT_3, as an example.

When mixtures of CH_3GeCl_3 with CH_3SiBr_3 are allowed to stand for several days at room temperature, exchange of chlorine with bromine atoms occurs, with the methyl groups remaining firmly attached to the respective germanium or silicon atoms. The following eight compounds are to be expected from scrambling of chlorine with bromine atoms between the methylsilicon and methylgermanium moieties: CH_3GeBr_3, CH_3GeBr_2Cl, $CH_3GeBrCl_2$, CH_3GeCl_3, CH_3SiBr_3, CH_3SiBr_2Cl, $CH_3SiBrCl_2$, and CH_3SiCl_3. Proton NMR spectra of the methyl resonances in such equilibrated mixtures are shown in Fig. 4 and are seen to exhibit up to eight different resonances (in addition to satellites due to spin–spin coupling of the protons with ^{29}Si) depending on the overall composition of the mixture.

The problem of assigning these various resonances to their respective chemical structures may be solved either by preparing all eight compounds in reasonably pure form and measuring their shifts or more easily from the following rationale: First, since the starting materials were CH_3GeCl_3 and CH_3SiBr_3, the shifts of these two compounds are known and correspond to resonances D and E, respectively, in Fig. 4. Since successive substitution of bromine for chlorine will have the same effect on the chemical shift of the protons of

$$CH_3Ge\lessdot \text{ or } CH_3Si\lessdot$$

and since peaks D and E lie toward the middle of the spectrum, it seems reasonable to ascribe peaks A through D to the methylgermanium compounds ranging from the tribromide to the trichloride. Furthermore, the presence of a pair of satellites (e through h in Fig. 4) encompassing the more intense peaks in the series E through H gives strong evidence that these represent silicon compounds. This evidence is borne out by the fact that the areas of the satellites relative to those of their main peaks, as well as the satellite–main peak spacing in cycles per second, are equal for both satellites and correspond to the expected spin–spin splitting of the hydrogens of methyl groups bonded to ^{29}Si atoms.

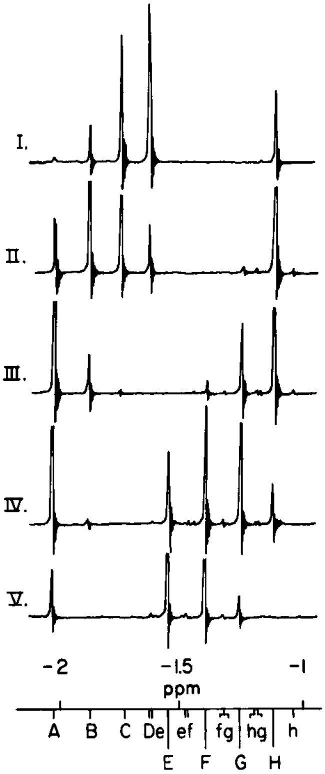


FIG. 4. Proton NMR spectra of equilibrated samples of CH_3GeCl_3 and CH_3SiBr_3 at various $R \equiv Cl/(Si+Ge)$ and $R' \equiv Si/(Si+Ge)$ ratios. I, $R=2.48$, $R'=0.16$; II, $R=2.02$, $R'=0.33$; III, $R=1.44$, $R'=0.52$; IV, $R=0.94$, $R'=0.69$; V, $R=0.44$, $R'=0.85$.

An independent check of these assignments is obtained from the material balance. Thus, on the assignments established in the preceding paragraph for the eight observed resonances, we find that the overall ratio $R \equiv Cl/(Si+Ge)$ varies from spectrum I to V of Fig. 4 in the sequence 2.49 (2.44), 2.02 (1.98), 1.44 (1.41), 0.94 (0.90), 0.44 (0.44), where the first numbers listed result from the stoichiometry of the starting materials and the following numbers in parentheses are calculated from the relative NMR peak areas. Good agreement is also observed for the $R' \equiv \mathrm{Si}/(\mathrm{Si}+\mathrm{Ge})$ values from the reagents and from the NMR analyses. This strongly supports the given peak assignments, and it has been found generally that the application of the material balance requirement to the interpretation of a stoichiometrically related series of NMR patterns is a powerful tool for making or confirming NMR assignments.

2. *Families of Compounds*

Assignments of NMR resonances obtained from families of compounds at equilibrium to specific structure-building segments appear to be somewhat more complicated than in the previous case. But here also methods have been devised which permit an unequivocal assignment and which will be discussed in the following sections.

a. *General Considerations.* In the NMR spectra of families of compounds resonances generally appear in clusters, which indicates that these peaks represent moieties of the same functionality in different chemical environment. The separation between the various clusters is often much greater than that between individual peaks within a cluster. In addition, assignments may be based on the order of appearance of new NMR resonances when increasingly larger amounts of a compound A are equilibrated with compound B. Furthermore, the maximization of the peak areas at certain compositions when comparing a series of spectra of samples composed of varying ratios of starting materials or their increase or decrease with varying overall composition is utilized in assigning NMR peaks. In many cases, the ratio of the areas of two or more peaks remains constant over the total range of overall compositions. Peaks exhibiting such a fixed area relationship generally are readily assignable to certain simple molecules or molecular segments. Also kinetic data serve as a source of information for peak assignments. A point to bear in mind is the fact that in sealed tubes where no phase separation occurs, the overall composition must remain fixed from start to finish of a kinetic experiment. In many scrambling reactions peaks appear, reach a maximum area, and then disappear at a given overall composition, whereas at another composition this particular peak may be seen at equilibrium conditions. After assigning all of the resonances, one may check the validity of the assignments by material-balance calculations. For a single-phase liquid, the correct assignment will give an acceptable material balance at any stage of the redistribution reaction, at equilibrium as well as when approaching equilibrium. In addition, the arrangement of building units into molecules at equilibrium may be described by a set of equilibrium constants, as shown in Section II, B. These constants may be used to calculate a theoretical distribution as a function of the overall composition and good agreement of experimental with calculated data is a final confirmation of the veracity of the interpretation of the spectra obtained at equilibrium.

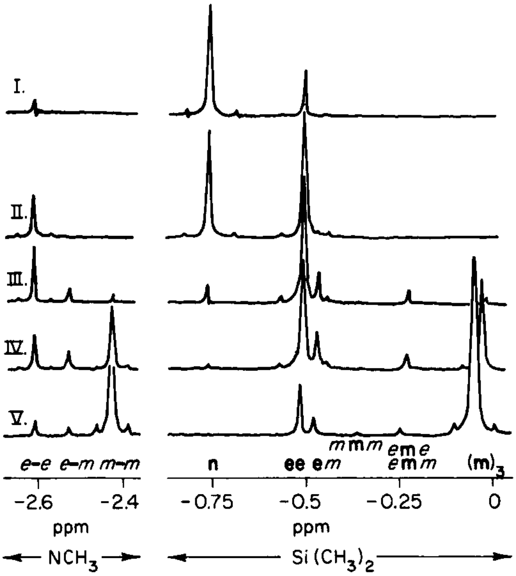


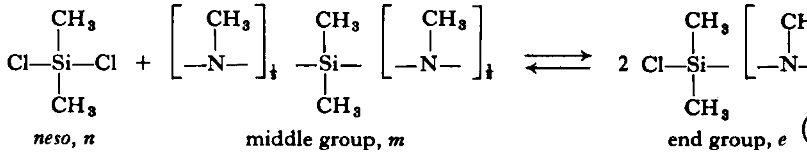
FIG. 5. Proton NMR spectra of equilibrated samples of $(CH_3)_2SiCl_2$ and $[(CH_3)_2SiNCH_3]_3$ for various $R \equiv Cl/Si$ ratios. I, $R=1.80$; II, $R=1.36$; III, $R=0.99$; IV, $R=0.56$; V, $R=0.16$.

b. *The System* $(CH_3)_2SiCl_2$ *vs* $[(CH_3)_2SiNCH_3]_3$. The assignment of NMR resonances to specific building units or segments of molecules is demonstrated for the equilibria in the family of chloro-terminated polydimethyl(*N*-methyl)silazanes (*289*).

When dimethyldichlorosilane is mixed in various proportions with nonamethylcyclotrisilazane, $[(CH_3)_2SiNCH_3]_3$, redistribution of chlorine atoms with bridging methylimino groups on the dimethylsilicon moiety occurs. The proton NMR spectra of such equilibrated mixtures, shown in Fig. 5, display two distinct regions of peaks, one in the range of -2.3 to -2.7

and the other in the range of 0 to -0.9 ppm, relative to tetramethylsilane. Comparison with the spectra of the starting materials shows that the downfield groups of resonances correspond to hydrogen atoms in the $CH_3N\!<$ bridging moiety, whereas the upfield group of peaks is attributable to the $(CH_3)_2Si\!<$ moiety.

The redistribution reaction involving exchange of chlorine atoms with bridging NCH_3 groups can be written in terms of structure-building units, as follows:



$$\mathrm{Cl{-}Si(CH_3)_2{-}Cl} + \left[-\mathrm{N(CH_3)}-\right]_{\frac{1}{2}} -\mathrm{Si(CH_3)_2}- \left[-\mathrm{N(CH_3)}-\right]_{\frac{1}{2}} \rightleftharpoons 2\ \mathrm{Cl{-}Si(CH_3)_2}-\left[-\mathrm{N(CH_3)}-\right]_{\frac{1}{2}} \qquad (31)$$

Obviously when a small amount of nonamethylcyclotrisilazane is added to dimethyldichlorosilane, the reaction product will be all or nearly all the end–end molecule, $ClSi(CH_3)_2N(CH_3)Si(CH_3)_2Cl$, which from the vantage point of methyl groups on the methylimino-bridging groups may be abbreviated as *e—e*, but from the vantage point of the methyl groups on silicon as **ee**. These *e—e* and **ee** resonances exhibit relative areas of 1:4, respectively, as expected, since there are in this molecule one CH_3 group on the nitrogen and four CH_3 groups on the two silicon atoms.

As seen in the spectra of Fig. 5, the chemical shift of the hydrogens of a dimethylsilicon moiety is not only affected by the substitution of a methylimino bridge by a chlorine atom on that particular silicon atom but also by such substitution on a neighbouring silicon atom bonded to the given dimethylsilicon moiety. As a result of this secondary effect, in the region where end-group resonances occur (-0.48 to -0.51 ppm), two kinds of end groups are seen: An end group bonded to another end group (-0.51 ppm) and an end group bonded to a middle group (-0.48 ppm). Likewise, to the same degree of structure resolution, one should see at least three resonances for the hydrogens of the dimethylsilicon moieties bearing a pair of methylimino bridges in the middle-group region (-0.06 to -0.37 ppm). The corresponding three arrangements are ***eme***, ***emm***, and ***mmm***, with the a priori possibility of several ***mmm*** resonances corresponding to middle groups in chains and different-sized rings.

Similarly one should also be able to "see in depth" into the molecule from the hydrogens of each methylimino bridge. If the chemical shift of these hydrogen atoms is sensitive to the substitution of a methylimino bridge by a chlorine atom on each of the silicon atoms bridged by this group, three kinds of resonances should be seen, *e*—*e*, *e*—*m*, and *m*—*m*, where the boldface bond refers to the methylimino bridge.

In addition to the 1:4 ratio of the *e*—*e* and *ee* peak areas, there are a number of other quantitative relationships between resonance areas. For example, there must always be a 1:2 relationship between the areas of the *e*—*m* and *em* peaks. Furthermore, material-balance calculations must agree with the peak assignments. These requirements, in addition to the ones discussed in the previous paragraph, lead to an unambiguous structural assignment of the NMR spectra and thus a correct mathematical description of the system.

C. Other Methods

A method that has found considerable use in the study of redistribution equilibria is gas chromatography, which is applicable in cases where the rate of redistribution is slow compared to the retention times of the redistribution products. Gas chromatography has been utilized in studying the redistribution equilibria in systems involving ester–ester interchanges (*189, 290*) such as $CH_3Si(OCH_3)_3$ vs $CH_3Si(OC_2H_5)_3$ and $(CH_3)_2Si(OCH_3)_2$ vs $(CH_3)_2Si(OC_2H_5)_2$, as well as in the system $Sn(C_2H_3)_4$ vs $SnCl_4$ (*220*) and many alkyl–alkyl exchanges on Group IV elements (*232*).

Additional methods which so far have been of only limited interest for the quantitative study of redistribution equilibria are mass spectrometry (*313*), Raman (*68*), and infrared (*110*) spectroscopy. It can be visualized that methods such as microwave spectroscopy, thin-layer chromatography, or Mössbauer spectroscopy may be of interest in the near future.

D. Computer Programs

The evaluation of experimental equilibrium data is most conveniently performed using some of the available computer programs in FORTRAN IV for the IBM-7040 (*106*). For the equilibria in simple systems, programs have been written by L. C. D. Groenweghe which calculate weighted-average equilibrium constants and their standard errors from experimental data (Program P0050), compute the theoretical distribution of components at equilibrium for given compositions from given equilibrium constants

(Program P0049), determine intersystem equilibrium constants from experimental data (Program P0091), or calculate the theoretical distribution of equilibrium products in mixed systems from the intersystem constant and the supporting equilibrium constants (Program P0216).

The study of complicated scrambling equilibria involving the reorganization of monofunctional and difunctional substituents on a given kind of atom or atom group requires the use of considerable sophistication in the computer routines used for data reduction. A single general-purpose computer program (Program P0085) is available which will handle essentially the full range of specific cases to be encountered in these scrambling studies. This program combines into a single entity the computation of weighted-average constants in the presence of ring structures and the calculation of the theoretical molecular composition of equilibrated mixtures corresponding to a given overall stoichiometry. In addition, it selects and computes the concentration of a wide variety of atomic groupings by using structure codes and obtains a fit-figure indicating the agreement between the computed values and the experimentally obtained concentrations. Also, trial-and-error procedures have been incorporated as a systematic search routine (e.g., fitting the number of units in rings to the experimentally obtained distribution of chain structures).

IV

RATES AND MECHANISMS OF REDISTRIBUTION REACTIONS

Although a large amount of speculation has been published (e.g., Lockhart, *150*) concerning the mechanisms of redistribution reactions, there are surprisingly few studies devoted to kinetic measurements which are adequate for establishing the mechanism. It has generally been assumed that the exchanges are bimolecular and proceed through a four-center activated complex. The rates of redistribution reactions may vary greatly depending on the nature of the central atoms or moieties and the exchanging substituents. As a rule of thumb, redistributions involving a first-row element as the central atom generally proceed more slowly than those of second-row elements, and the latter are slower than those of a third- or fourth-row element. Also, exchanges involving carbon–metal bonds are much slower than exchanges involving halogen, sulfur, oxygen, or nitrogen bonds to the metal.

A. Slow Reactions

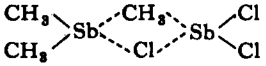
Redistributions occurring at moderate rates may be studied by any of the conventional means. However, NMR has become a very convenient method since the reactions may be performed directly in sealed NMR tubes which are inserted into the thermostated probe of the NMR spectrometer. Although a great number of qualitative statements or semiquantitative data regarding rates of redistribution reactions are found in the literature, only a few systems have been studied quantitatively (*298*).

1. *Simple Systems*

Initial rate measurements of the system trimethylantimony vs antimony trichloride indicate the following first-step reaction to be first order in each component:

$$(CH_3)_3Sb + SbCl_3 \rightarrow (CH_3)_2SbCl + CH_3SbCl_2 \qquad (32)$$

Second-order rate constants were obtained at 72° C ($6.7 \pm 0.5 \times 10^{-5}$ liter/mole sec) and 100° C ($5.3 \pm 0.5 \times 10^{-4}$ liter/mole sec) from which an activation enthalpy of 18 kcal and entropy of -25 e.u. were calculated. These values are consistent with a mechanism involving the formation of the four-center transition state given below:



(33)

The relatively large negative activation entropy is in agreement with values observed for other bimolecular reactions believed to involve two sites for attachment in the transition state (*240, 296*). Also in the system $Ti[N(CH_3)_2]_4$ vs $Ti(tert\text{-}C_4H_9O)_4$, the rate law is first order in each component with a mechanism involving the formation of a rigid four-center transition state similar to the antimony case (*298*).

Another example is the catalytic disproportionation of methylchlorosilanes. Based on a thorough kinetic study (*313*), any mechanism will have to take into account the following facts: (a) The rate is a linear function of the $AlCl_3$ concentration; (b) the reaction is first order in chlorosilanes; (c) the rate equations must reduce to equilibrium constants K_1, K_2, or K_3 [Eqs. (99)–(101)] when the change in concentration with time is zero; (d) substantially all the aluminum chloride is associated in some manner with the chlorosilanes.

A most reasonable mechanism which fits all these requirements is the following: The reaction $(CH_3)_2SiCl_2 + AlCl_3 \rightarrow (CH_3)_2SiCl_2 \cdot AlCl_3$ goes to completion before either one of the reactions $(CH_3)_2SiCl_2 + (CH_3)_2SiCl_2 \cdot AlCl_3 \rightleftarrows (CH_3)_3SiCl + CH_3SiCl_3 \cdot AlCl_3$ and $CH_3SiCl_3 \cdot AlCl_3 + (CH_3)_2SiCl_2 \rightleftarrows CH_3SiCl_3 + (CH_3)_2SiCl_2 \cdot AlCl_3$ start to take place. The latter reaction, which merely involves the transfer of aluminum chloride from one silane to another, must be very much more mobile than the preceding reaction where rupture and formation of both silicon–carbon and silicon–chlorine bonds are involved. Very probably the aluminum chloride is attached to the chlorine of the chlorosilane. This weakens the Si—Cl bond and when a collision occurs with another chlorosilane molecule, the two silicons exchange $AlCl_4^-$ and CH_3^- or $AlCl_4^-$ and Cl^-. Since halogens attached to silicon exchange quite easily, only a relatively few collisions will have the correct orientation to permit rupture of an Si—C bond to give the methyl interchange. This high degree of necessary orientation implies a low entropy of activation.

These few studies make it appear very likely that mechanisms involving four-center transition states will be common in redistribution reactions. However, it is not yet possible to predict a mechanism on an a priori basis.

2. *Families of Compounds*

Somewhat more complex are rate and mechanism studies in families of compounds. Here one of the starting compounds is a polymer structure, such as a cyclic or high-polymer species. The latter is equilibrated with the species bearing the monofunctional substituents (i.e., the *neso* molecule). This is exemplified in the equilibration of dimethyldichlorosilane with octamethylcyclotetrasiloxane to give an equilibrium mixture of α,ω-dichloropolydimethylsiloxanes (*191*). The reaction of the two components in the mole ration of 4:1 at 200° C in the presence of catalytic amounts of aluminum chloride was studied by proton NMR. The curves shown in Fig. 6 were obtained from the various NMR peaks assigned to specific molecular segments. The prominent feature of this figure is the observation that the amount of the cyclic tetramer decreases quite rapidly and the curves corresponding to the four- and five-membered chains go through shallow maxima. From the fact that the resonance corresponding to middle groups in long chains was the first to maximize, it is concluded that the first process to occur in the mixture is the reaction of Eq. (34)

$$j(\text{4-ring}) \rightarrow \text{long chains or large rings} \tag{34}$$

The maximum of the resonance for the five-membered chain shows that the following reaction is also occurring:

$$\textit{neso} + \text{4-ring} \rightarrow \text{5-chain} \tag{35}$$

The rapid decrease of the concentration of the long chains or large rings, after they have maximized, is probably due to the reaction of Eq. (36)

$$\textit{neso} + \text{long chains or large rings} \rightarrow \text{shorter chains} \tag{36}$$

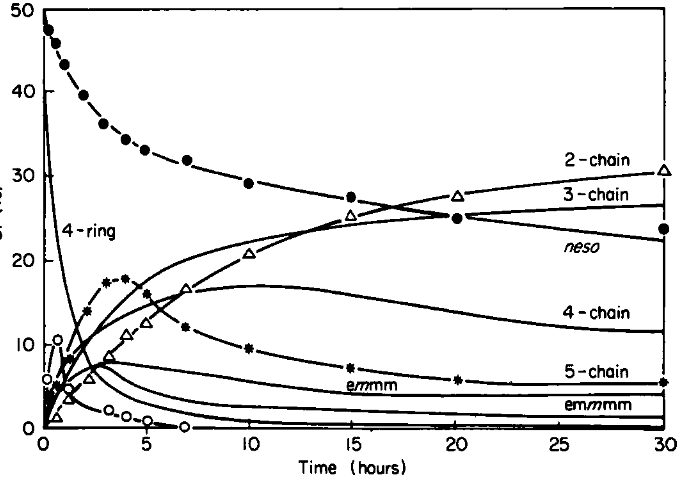


FIG. 6. Variation with time of the distribution of total silicon present in various molecules or building units during equilibration (*191*) at 200°C of a mixture of 1 mole of dichlorodimethylsilane with ¼ mole of octamethylcyclotetrasiloxane using 0.5 wt % $AlCl_3$ as catalyst. To avoid confusion, experimental points are shown only for the *neso* compound (●), the dichain (△), the pentachain (*), and the large molecules (big rings or long chains) (○).

Later, the amount of five-membered chains decreases by further attack by the *neso* compound, according to Eqs. (37) and (38)

$$\text{5-chain} + \textit{neso} \rightarrow \text{2(3-chain)} \tag{37}$$

$$\text{5-chain} + 3\ \textit{neso} \rightarrow \text{4(2-chain)} \tag{38}$$

After more than 25 hours under the above experimental conditions, equilibrium is reached with the molecules exchanging parts with each other in a state of dynamic equilibrium.

B. Mathematical Treatment of Simple Redistribution Kinetics

Assuming second-order kinetics, the entire redistribution process has been treated in terms of $\nu(\nu-1)$ second-order rate constants corresponding to all nontrivial bimolecular exchange processes (*287*). Scrambling of two kinds of monofunctional substituents, Z and T, on a central atom, Q, of functionality ν, results in $(\nu+1)$ molecules having the generic formula $QZ_iT_{\nu-i}$, where i is an integer ranging from 0 to ν. Again, the short-form notation for the molecules $QZ_iT_{\nu-i}$ is used by calling them z_i and their molar concentration $[z_i]$.

From all possible equations involving exchange of substituents, the only kinetically significant ones must be those which give exchange of one Z for one T at a time. Thus, the general equation for second-order exchange is

$$z_i + z_j \overset{k_{ij}}{\underset{k_{(j+1)(i-1)}}{\leftrightarrows}} z_{i-1} + z_{j+1} \tag{39}$$

where the subscript of the second-order rate constant k_{ij} refers to the molecule on which a Z substituent is replaced by a T substituent. Some of these k_{ij} constants relate to impossible restrictions and therefore must be zero. When z_0 is involved in the substituent-interchange process, it can only contribute T substituents so that all rate constants of the form k_{0j} equal zero but those of the form k_{i0} have finite values. Likewise, z_ν can only contribute a Z substituent so that all equilibrium constants of the form $k_{i\nu}$ must be zero. When $i=j+1$, the rate constant k_{ij} is set to zero since this situation corresponds to trivial reactions in which the products are identical to the reactants, as shown by the following equation:

$$z_{j+1} + z_j \xrightarrow{k_{ij} \text{ for } i=j+1} z_j + z_{j+1} \tag{40}$$

The second-order rate constants can now be written in a matrix form, in which the trivial or disallowed reactions form a pattern. Since, as explained above, k_{0j} and $k_{i\nu}$ represent impossible reactions, the first row and νth column of the matrix must be composed of zeros. This is also true for the first off-diagonal, $k_{(j+1)j}$, for any process except an isotope-exchange reaction since, as shown above, the products are identical to the reactants.

$$\begin{array}{cc|cccccc}
 & z_j & 0 & 1 & 2 & 3 & 4 & 5 \\
\hline
z_i & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 & 1 & 0 & k_{11} & k_{12} & k_{13} & k_{14} & 0 \\
 & 2 & k_{20} & 0 & k_{22} & k_{23} & k_{24} & 0 \\
 & 3 & k_{30} & k_{31} & 0 & k_{33} & k_{34} & 0 \\
 & 4 & k_{40} & k_{41} & k_{42} & 0 & k_{44} & 0 \\
 & 5 & k_{50} & k_{51} & k_{52} & k_{53} & 0 & 0
\end{array} \quad \text{for } \nu = 5 \tag{41}$$

The rate constants are so defined that a constant $k_{\alpha\beta}$ has $k_{(\beta+1)(\alpha-1)}$ as the rate constant for the reverse reaction. This means that the rate constants for the fore and back reactions must lie at an equal distance taken symmetrically from either side of the all-zero off-diagonal of the matrix. From inspection of the matrix, it can be seen that there are $\nu(\nu-1)$ different rate constants for second-order interchanges leading to chemically different molecules.

In order to calculate the change in the amount of a certain molecule z_i with time, it is necessary to consider all reactions of the form of Eq. (39) which contain z_i.

When this is worked out in a general form, the following typical set of equations is obtained for $\nu = 4$, with $[\dot{z}_i]$ standing for the rate of change of the amount of the molecules z_i with time.

$$\begin{aligned}[\dot{z}_0] = {} & -k_{20}[z_2][z_0] - k_{30}[z_3][z_0] - k_{40}[z_4][z_0] + k_{11}[z_1]^2 + k_{12}[z_1][z_2] \\ & + k_{13}[z_1][z_3]\end{aligned} \tag{42}$$

$$\begin{aligned}[\dot{z}_1] = {} & -2\,k_{11}[z_1]^2 - k_{12}[z_1][z_2] - k_{31}[z_3][z_1] - k_{41}[z_4][z_1] - k_{13}[z_1][z_3] \\ & + k_{22}[z_2]^2 + k_{23}[z_2][z_3] + 2\,k_{20}[z_2][z_0] + k_{30}[z_3][z_0] + k_{40}[z_4][z_0]\end{aligned} \tag{43}$$

$$\begin{aligned}[\dot{z}_2] = {} & -k_{20}[z_2][z_0] - 2\,k_{22}[z_2]^2 - k_{23}[z_2][z_3] - k_{12}[z_1][z_2] - k_{42}[z_4][z_2] \\ & + k_{30}[z_3][z_0] + k_{33}[z_3]^2 + k_{11}[z_1]^2 + 2\,k_{31}[z_3][z_1] + k_{41}[z_4][z_1]\end{aligned} \tag{44}$$

$$\begin{aligned}[\dot{z}_3] = {} & -k_{30}[z_3][z_0] - k_{31}[z_3][z_1] - 2\,k_{33}[z_3]^2 - k_{13}[z_1][z_3] - k_{23}[z_2][z_3] \\ & + k_{40}[z_4][z_0] + k_{41}[z_4][z_1] + k_{12}[z_1][z_2] + k_{22}[z_2]^2 + 2\,k_{42}[z_4][z_2]\end{aligned} \tag{45}$$

$$\begin{aligned}[\dot{z}_4] = {} & -k_{40}[z_4][z_0] - k_{41}[z_4][z_1] - k_{42}[z_4][z_2] + k_{13}[z_1][z_3] + k_{23}[z_2][z_3] \\ & + k_{33}[z_3]^2\end{aligned} \tag{46}$$

The $\nu(\nu+1)$ rate constants needed to define the second-order kinetics of simple scrambling can be reduced in half by use of the $(\nu-1)$ equilibrium constants needed to define the system at equilibrium. Generally it is easier to obtain good equilibrium constants than to measure adequate rate constants.

This kinetic scheme, in which all forward and back reactions are second order, has been programmed in FORTRAN IV for an IBM-7040 computer, using a Calcomp No. 570 digital plotter for plotting mechanically the data points and experimental curves (*17*). This program is so arranged that the input data are a suggested set of rate constants and/or equilibrium constants to be used as a basis for the search procedure employed to find best-fit values of these constants with respect to the experimental kinetic data.

C. Rapid Reactions

NMR spectroscopy may be used advantageously to investigate rapidly equilibrating systems where the individual components cannot be separated by conventional separations methods due to fast exchange of substituents. If the exchange of substituents between different environments occurs at the exchange rate $1/\tau$, where τ is the average time between exchanges, and the exchange rate is large with respect to $(\nu_A^\circ - \nu_B^\circ)\tau^{-1} > 10(\nu_A^\circ - \nu_B^\circ)$, the spectrum will consist of a single peak centered at a position midway between ν_A° and ν_B°.

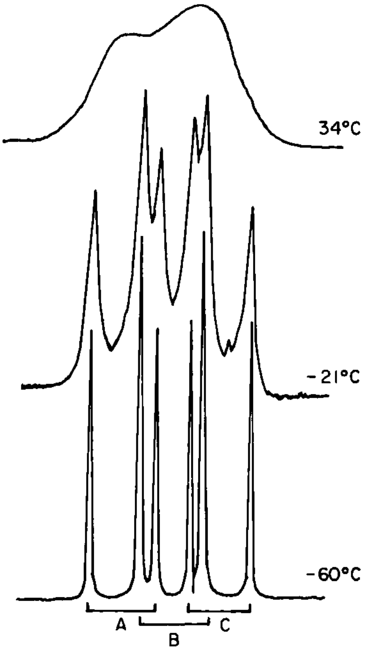


FIG. 7. Proton NMR spectra of an equimolar mixture of CH_3PCl_2 and CH_3PBr_2 at various temperatures. A, CH_3PBr_2, $\delta = -2.78$ ppm, $J_{HCP} = 20$ cps; B, CH_3PClBr, $\delta - 2.53$ ppm, $J_{HCP} = 18.8$ cps; C, CH_3PCl_2, $\delta = -2.29$ ppm, $J_{HCP} = 17.5$ cps.

The transition region between slow and fast exchange has been described (*111*, *112*, *162*) for the above case by solution of modified Bloch equations that take into account the possibility of exchange between the various environments. It can be shown that as the lifetime increases, the original sharp single peak broadens, and resolves into two broad peaks which on further increase of the lifetime sharpen into two individual resonances.

Other equations for the calculations of lifetimes are suitable only for that part of the transition region in which separate resonances are observed and only if the separations are large with respect to the line width.

Very rapid exchange leads to complete collapse of the spectrum to a single resonance. An additional method may be applied here to calculate lifetimes from the line widths of the single resonances (*188*, *236*).

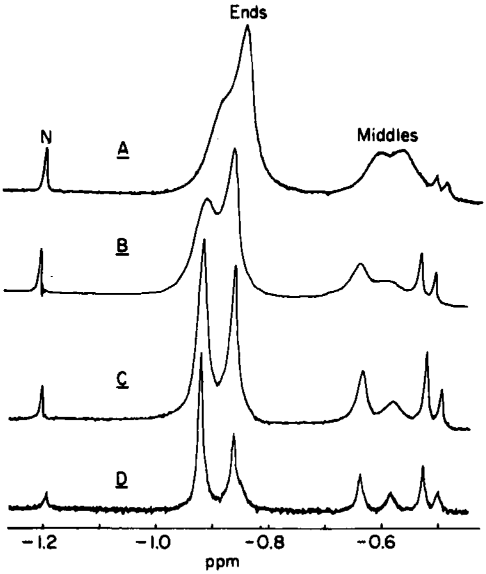


FIG. 8. Proton NMR spectra of an equilibrated sample in the system $(CH_3)_2GeCl_2$ vs $[(CH_3)_2GeO]$ of the composition $R \equiv Cl/Ge = 0.72$ at various dilutions. A, neat liquid; B, diluted with three parts; C, 15 parts; and D, 63 parts of carbon tetrachloride (v/v).

An example of rapid exchange of substituents in a simple system is shown in Fig. 7 for an equilibrated mixture of CH_3PCl_2 and CH_3PBr_2 (*184*). As the temperature is decreased, the rate of exchange of halogen atoms diminishes, thus sharpening the individual proton NMR signals.

Rapid exchange has also been observed in families of compounds as shown in Fig. 8 for the exchange of bridging oxygen with chlorine atoms on dimethylgermanium moieties in α,ω-dichloropolydimethylgermoxanes

(*193*). Details of this rapidly occurring exchange process are discussed in Section V, D,2,g.

V

REDISTRIBUTIONS IN COMPOUNDS OF MAIN GROUP ELEMENTS

In discussing redistribution reactions from a general point of view, it should be noted that these reactions are equilibrium reactions with the equilibrium constants being a quantitative measure for the randomness or nonrandomness of the exchange processes. Therefore, the expression of this equilibrium state in terms of equilibrium constants will be emphasized throughout this review although a surprisingly large number of more-or-less qualitative statements may be found in the literature in which reference is made to the term redistribution or its synonyms. Obviously, it is neither practical nor possible to list each of these qualitative reports concerning substituent exchange observed in connection with preparative or other studies in the course of more than 100 years of organometallic research. Therefore, only limited space will be devoted to the latter type of data.

Limited space also will be devoted to the many instances of qualitative experimental evidence for substituent-exchange equilibria between two kinds of central moieties in favor of quantitative studies of this type. Excluded from the scope of this review will be isotope-exchange equilibria and electron-exchange reactions.

Before reviewing in detail redistribution equilibria in the chemistries of the various elements, it is appropriate to ask why the study of such equilibria is significant with respect to chemistry in general. Such redistribution reactions are often utilized for synthetic purposes and information about the corresponding equilibria will provide information regarding the maximum yield to be expected. Knowledge of the rates of reequilibration of compounds prepared by this method will guide the decision as to the conditions for separating the respective compounds from their coredistribution products and whether they will remain stable upon storage at ambient temperature. On the negative side, scrambling reactions often will complicate separations of mixtures, lead to unreliability in elucidation of structures by degradation or synthesis and cause many preparations of supposedly pure compounds to consist of mixtures of molecules at or near equilibrium with respect to exchange of substituents or parts.

A. Group I

1. *Lithium Alkyls*

One would generally assume that redistribution reactions involving organometallic compounds of Group I—if they occur—should be trivial as far as the formation of new products is concerned. Colligative measurements in hydrocarbon solutions established that alkyllithium compounds in these solvents are associated to electron-deficient tetramers or hexamers (*35*). There does not seem to be any indication for the existence of an equilibrium between variously sized species. Lithium alkyls having more highly branched alkyl groups, such as tert-C_4H_9 and $(CH_3)_3SiCH_2$, appear to form tetramers whereas, for the methyl and *n*-butyl derivatives, hexamer species seem to prevail.

Two kinds of such associated species, when exchanging alkyl groups between each other, should indeed result in chemically new species. Evidence for such exchanges was obtained from proton as well as ^{7}Li NMR spectra of hydrocarbon solutions of mixtures of ethyllithium and tert-butyllithium (*297*). The exchange of alkyl groups between polymeric organolithium molecules proceeding according to Eq. (47)

$$(C_2H_5Li)_n + (\text{tert-}C_4H_9Li)_m \rightleftarrows p(C_2H_5Li)_{n/q}(\text{tert-}C_4H_9Li)_{m/t} \qquad (47)$$

results in novel compounds which are believed to be electron-deficient polymers, where m and n are small numbers such as 4 or 6. From proton NMR spectra of these systems, it appears that if ethyl groups exist in different environments, exchange must be rapid compared to the relaxation time. Corroborating this observation, it was found that intermolecular exchange of ethyl groups between bonding sites in toluene solutions of ethyllithium in the absence of tert-butyllithium at 30° C occurs at exchange times of the order of 0.1 second or larger. In basic solvents, intermolecular exchanges in alkyllithium compounds proceed much more easily than in hydrocarbon solvents (*36*).

Compared to the lithium alkyls, the carbon–metal bond in the corresponding sodium and potassium compounds is more polar and thus the lower alkyl derivatives are no longer soluble in hydrocarbons nor are they volatile (*262*). Therefore, little has been done to elucidate any exchange reactions in which they might participate.

2. *Transmetalation Equilibria of Lithium Alkyls*

The exchange of organic groups between an organolithium compound and an organic derivative of a heavy metal, such as HgR_2, TlR_3, SnR_4, PbR_4,

SbR_3, or BiR_3, has been used as a route to prepare novel organolithium compounds. Although first described by Schlenk and Holtz (*256*), the scope of this reaction and its preparative applications were investigated rather recently (*266–272*). According to the general equilibrium reaction

$$SnR_4 + i\, C_6H_5Li \rightleftarrows i\, LiR + SnR_{4-i}(C_6H_5)_i \tag{48}$$

new organolithium compounds were first prepared with the insolubility of either one of the two products—depending on the solvent in which the reaction was performed—being the main driving force for the completion of the reaction. Based on Eq. (48), the following new organolithium compounds, LiR, were prepared: R ≡ vinyl, allyl, methallyl, perfluorovinyl, cyclopropyl, and stereoisomer isopropenyls. The equilibrium nature of the reaction of Eq. (48) was established by performing the experiment in solvents in which reactants as well as products were soluble. Semiquantitative studies indicate that the equilibrium of Eq. (49) is shifted to the right. For example, at equilibrium were found,

$$(n\text{-}C_4H_9)_3SnCH{=}CH_2 + C_6H_5Li \rightleftarrows (n\text{-}C_4H_9)_3Sn(C_6H_5) + CH_2{=}CHLi \tag{49}$$

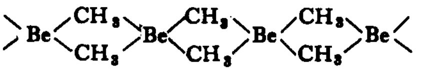
when approached from the right side, 76% tri-*n*-butylphenyltin as well as 63% vinyllithium (determined by its reactions with acetone to give dimethylvinylcarbinol) and 12% tri-*n*-butylvinyltin. The reverse reaction, starting with phenyllithium and tri-*n*-butylvinyltin gave in addition to 75% tri-*n*-butylphenyltin, about 5% tri-*n*-butylvinyltin.

B. *Group II*

Of the organometallic compounds of Group II elements, undoubtedly the chemistry of the magnesium compounds is best known. By contrast, the remaining elements in this group have received less attention and it is only recently that more information on organo derivatives of beryllium and, to lesser extent, of calcium, strontium, and barium has become available. Therefore, most of the observations regarding redistribution equilibria have been of more or less qualitative nature.

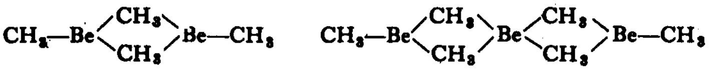
1. *Beryllium*

Dimethylberyllium, which at room temperature exists as a solid, high polymer having three-center electron-deficient bonds, may enter reversible equilibria with low polymers.



(50)

From a study of the pressure dependence of the vapor density, it is concluded that the vapor contains monomer, dimer, trimer, and higher polymers which are in equilibrium with each other (*62*). At 180° C, the saturated vapor consists of 41% monomer, 44% dimer, and 14% trimer. The following structures have been proposed for the dimer and trimer in the vapor state:



(51)

Equilibrium constants have been calculated from the vapor pressure and vapor density data obtained in this study. The constants of the following form:

$$K_D = p_{\text{dimer}}/p^2_{\text{monomer}} \ (\text{atm}^{-1}) \tag{52}$$

$$K_T = p_{\text{trimer}}/p^3_{\text{monomer}} \ (\text{atm}^{-1}) \tag{53}$$

have been determined in the range from 160° to 200° C with the temperature dependence of these two constants given by

$$\log K_D = 10.92 - 5325/T \tag{54}$$

$$\log K_T = 10.3 - 9970/T \tag{55}$$

From the facts of the formation of beryllium dialkyls by the continuous heating of alkylberyllium halides and of the formation of the latter when beryllium dialkyls are treated with beryllium halides (*99*), the following equilibrium was suggested (R = alkyl, X = halogen):

$$R_2Be + BeX_2 \rightleftarrows 2\ BeRX \tag{56}$$

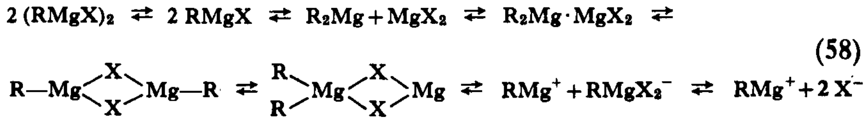
However, recently by using $^7BeBr_2$, it was shown (*69*) that no isotopic exchange was found to occur between diphenylberyllium and beryllium bromide. Thus it appears that an equilibrium of the form of Eq. (56) is not established and the findings are represented best by the formulation given below:

$$R_2Be + BeX_2 \rightleftarrows R_2Be \cdot BeX_2 \tag{57}$$

There is also evidence for equilibria involving the exchange of an alkyl group with OR, NR_2, and SR groups (*63*).

2. *Magnesium*

Discussions and speculations regarding the nature of the Grignard reagents and the equilibria in Grignard solutions have been the subject of many communications (*294*). There is no doubt that halogens and alkyl groups attached to magnesium do undergo exchange reactions in solution. It has been generally accepted that mixtures of dialkylmagnesium and magnesium halide after equilibration essentially are equivalent to Grignard reagents prepared from metallic magnesium and alkyl halide. Summarising the numerous studies regarding the structure of the Grignard reagent and considering the exchange equilibrium point of view, there are probably a great many species in equilibrium with each other. The existing experimental evidence is best represented by the assumption of an extended solution equilibrium involving monomer, dimer, and higher as well as ionic species.



$$2\,(\mathrm{RMgX})_2 \rightleftarrows 2\,\mathrm{RMgX} \rightleftarrows \mathrm{R_2Mg}+\mathrm{MgX_2} \rightleftarrows \mathrm{R_2Mg\cdot MgX_2} \rightleftarrows$$

(58)

$$\mathrm{R{-}Mg}\overset{\mathrm{X}}{\underset{\mathrm{X}}{\diamond}}\mathrm{Mg{-}R} \rightleftarrows \overset{\mathrm{R}}{\underset{\mathrm{R}}{>}}\mathrm{Mg}\overset{\mathrm{X}}{\underset{\mathrm{X}}{\diamond}}\mathrm{Mg} \rightleftarrows \mathrm{RMg^{+}}+\mathrm{RMgX_2^{-}} \rightleftarrows \mathrm{RMg^{+}}+2\,\mathrm{X^{-}}$$

The concentrations of the various species depend on the overall concentration, the nature of the solvent, the organic groups R, the halogen, and perhaps many other factors. The monomeric species seem to predominate at low concentrations, with strongly donating solvents, and for bromides and iodides. Dimeric species (and higher polymers) are favored by high concentrations, weakly donating solvents, and for chlorides. Aryl derivatives generally are more associated than alkyl derivatives. The concentration of the ionic species is always low.

Regarding the rate of scrambling of alkyl groups and halogens on magnesium, it has been observed that phenyl groups in mixtures of diphenylmagnesium and phenylmagnesium halide in ether, using isotopically labeled phenyl groups, undergo rapid exchange (*275*). In the proton NMR spectra of Grignard reagents, no ^{25}Mg—^{1}H coupling has been observed for the α-methylene protons, suggesting rapid exchange of alkyl groups between different sites (*294*).

An equilibrium involving substituent exchange between magnesium dialkyls and magnesium dialkoxides recently has been postulated in order to explain stereoselectivity of certain Grignard reduction reactions (*64*).

3. *Calcium, Strontium, Barium*

Organic compounds of these three elements are less readily available and thus less well known than those of beryllium (*18*). Although a great deal of effort has been spent in the preparation of Grignard analogs of these elements and their reactions with organic compounds, their exchange equilibria have not been studied. However, exchange of alkyl groups has been observed in mixtures of diethylstrontium or diethylbarium with tetraphenyltin. No exchange was observed with the tetraphenyl derivatives of silicon, germanium, and lead (*97*).

C. Group III

One of the characteristic features of the organometallic chemistry of Group III elements is the readily and rapidly occurring exchange of substituents bonded to the metal atom. Such exchanges undoubtedly proceed via dimer four-center transition states involving electron-deficient bonding. In the course of preparative studies, many such exchange equilibria have been uncovered and subsequently have frustrated many synthetic chemists wishing to study reactions and physical properties, such as vapor pressure, of "pure" compounds. Although many of these observations were of purely qualitative nature, recent efforts have shed considerable light on the mechanism of such exchanges, the mean average lifetimes that a substituent is bonded to a specific central atom, and the extent to which equilibrium is established.

1. *Boron*

a. *Diborane–Borine Equilibrium.* By an indirect method, a reliable estimate (*21*) has been made of the equilibrium constant for the dissociation of diborane into borine groups given in Eq. (59). At 155° C and 1 atm, the degree of dissociation of diborane

$$2\,BH_3 \rightleftarrows B_2H_6 \qquad (59)$$

as computed from the equilibrium constant, K, listed in Table III is of the order of 10^{-5}. Clearly, the equilibrium concentrations of borine are too small to be detected by the usual physical technique.

A study of the exchange of boron between isotopically normal diborane and ^{10}B-enriched diborane (*273*) showed that exchange is quite rapid at room temperature, the rate being of the same order of magnitude as the deuterium exchange between diborane and hexadeuterodiborane (*160*). Both exchange processes rely on equilibria of the type of Eq. (59).

TABLE III

EQUILIBRIUM CONSTANTS AND EQUILIBRIUM PRESSURE OF BORINE FOR THE REACTION $2\ BH_3 \rightleftarrows B_2H_6$

T, (°K)	K (atm^{-1})	p_{BH_3} (atm)
273°	1.7×10^{18}	$1.5 \times 10^{-9}\ P_{atm}^{1/2}$
300°	8.6×10^{15}	$2.2 \times 10^{-8}\ P_{atm}^{1/2}$
373°	2.3×10^{11}	$4.1 \times 10^{-6}\ P_{atm}^{1/2}$
473°	2.5×10^{7}	$2.0 \times 10^{-4}\ P_{atm}^{1/2}$

b. *Exchange of Boron–Hydrogen with Boron–Halogen Bonds.* Boron trichloride and diborane in the gas phase react to form chloroboranes according to the equilibrium reaction given below (*136*). Although a number of equi-

$$BCl_3 + B_2H_6 \rightleftarrows B_2H_5Cl + BHCl_2 \tag{60}$$

librium reactions may be written, Eq. (60) is the simplest type which conforms to the experimental finding that upon equilibration, there is no change in the total number of moles of gas. Monochlorodiborane and dichloroborane, identified by their infrared spectra, apparently are the only redistribution products in addition to the starting materials.

The two redistribution products, monochlorodiborane and dichloroborane, could be isolated by low-temperature gas chromatography (*216*). Monochlorodiborane, although comparatively stable for a short time at room temperature, slowly reequilibrates, exchanging chlorine and hydrogen atoms as shown in Fig. 9. During the disproportionation according to Eq. (61)

$$6\ B_2H_5Cl \rightleftarrows 5\ B_2H_6 + 2\ BCl_3 \tag{61}$$

a secondary reaction of BCl_3 with unreacted B_2H_5Cl leads to the presence of $BHCl_2$ in the final equilibrium mixture. The reaction is extremely slow, reaching equilibrium only after 70 hours. Also dichloroborane reequilibrates slowly at room temperature with the first step proceeding according to Eq. (62)

$$5\ BHCl_2 \rightleftarrows B_2H_5Cl + 3\ BCl_3 \tag{62}$$

and with final formation of diborane and boron trichloride, according to the overall reaction

$$6\ BHCl_2 \rightleftarrows B_2H_6 + 4\ BCl_3 \tag{63}$$

The equilibrium constant for the reaction of Eq. (63) has been determined for the equilibrium in the gas phase as well as in the liquid, both at 0° C (*215*).

$$K_{liq} = [B_2H_6][BCl_3]^4/[BHCl_2]^6 = 12.5 \times 10^3 \tag{64}$$

$$K_{gas} = p_{(B_2H_6)}p^4_{(BCl_3)}/p^6_{(BHCl_2)} = 872.3\ \text{atm}^{-1} \tag{65}$$

The system B_2H_6–BCl_4 has also been studied in ethers as solvent by infrared and ^{11}B NMR spectroscopy (*32, 227*). Only dichloroborane etherate has been detected as sole redistribution product.

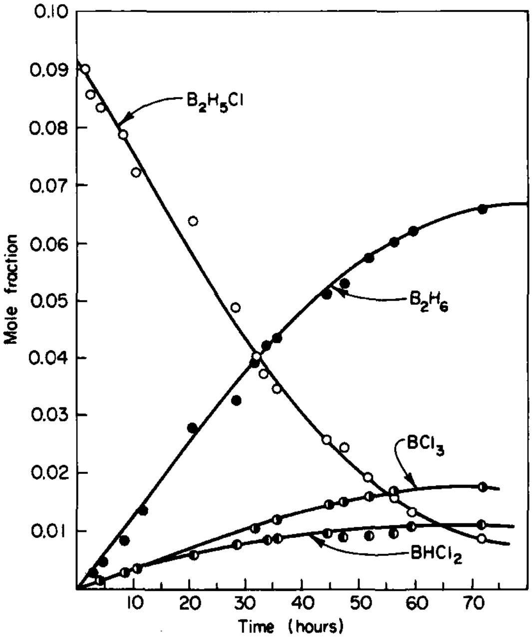


FIG. 9. Reequilibration of monochlorodiborane in nitrogen at 760 mm at 35° C.

Also difluoroborane, BHF_2, has been found to reequilibrate slowly at room temperature (*65*).

c. *Exchange of Boron–Hydrogen with Boron–Oxygen Bonds.* An extensive investigation of the gas-phase disproportionation of dimethoxyborane (*282*) described earlier by Burg and Schlesinger (*39*) resulted in the stoichiometry

$$6\ (CH_3O)_2BH \rightleftarrows B_2H_6 + 4\ (CH_3O)_3B \tag{66}$$

The reaction has been found to be heterogeneous and of apparent second order. 1,3,2-Dioxaborolane, $(CH_2O)_2BH$, disproportionates also quite easily at room temperature into diborane and $(CH_2O)_2BOCH_2CH_2OB(OCH_2)_2$, probably by the same mechanism (*245*).

d. *Exchange of Boron–Hydrogen Bonds with Boron–Sulfur Bonds.* Various alkylthioboranes have been found to disproportionate on standing or upon heating at moderately elevated temperature (*212*). An apparent polymer of the composition $(RS)_3B_2H_3$ ($R=C_2H_5$) upon standing gives $(RS)_3B$ and $(RSBH_2)_3$. Another compound, $(RS)_2BH$ ($R=n\text{-}C_4H_9$), upon standing disproportionates also into a mixture of $(RS)_3B$ and $(RSBH_2)_3$.

e. *Exchange of Boron–Hydrogen with Boron–Carbon Bonds.* When diborane is mixed with trimethylborane at room temperature, as a result of interchange of hydrogen atoms with methyl groups, all five possible methyldiboranes, $B_2H_{6-n}(CH_3)_n$ (where $n=1, 2, 3$, or 4) are obtained, including the isomeric dimethyl compounds (*257*, *261*).

$$(6-n)\ B_2H_6 + 2n\ B(CH_3)_3 \rightleftarrows 6\ B_2H_{6-n}(CH_3)_n \tag{67}$$

Not more than four alkyl groups can be accommodated in the diborane structure, thus preserving the essential hydrogen bridge. At low temperatures, the exchange rate is sufficiently slow as to allow isolation of the various species by fractional condensation.

Approximate equilibrium constants for the gas-phase reaction at 300°*K* have been determined for the trimethylborane–diborane exchange from equilibrium experiments and from thermodynamic data (*164*, *261*) with the computed constants listed in parentheses in Eqs. (68)–(71).

$$K = [1{,}1\text{-}(CH_3)_2B_2H_4][B_2H_6]/[CH_3B_2H_5]^2 = 2.8 \qquad (3.1) \tag{68}$$

$$K = [(CH_3)_3B_2H_3]^2[B_2H_6]/[1{,}1\text{-}(CH_3)_2B_2H_4]^3 = 2.7\times10^{-4} \qquad (5.2\times10^{-4}) \tag{69}$$

$$K = [(CH_3)_4B_2H_2]^3[B_2H_6]/[(CH_3)_3B_2H_3]^4 = 6.7\times10^{-3} \qquad (3.5\times10^{-3}) \tag{70}$$

$$K = [(CH_3)_3B]^2[B_2H_6]^5/[CH_3B_2H_5]^6 = \ldots \qquad (\sim10^{-12}) \tag{71}$$

1,2-Dialkyldiborane is obtained by the reversible disproportionation of the monoalkylated diborane (*283*).

$$2\ CH_3B_2H_5 \rightleftarrows B_2H_6 + (CH_3BH_2)_2 \tag{72}$$

The equilibrium constant for the latter reaction is

$$K = [B_2H_6[(CH_3BH_2)_2]/[CH_3B_2H_5]^2 = 7.01\times10^{-2} \tag{73}$$

Also equilibria in higher *n*-alkyldiboranes and phenylboranes have been investigated (*175*, *259*, *305*).

The kinetic stabilities of the methyldiboranes are in the order 1,2-di$\gg$ 1,1-di$>$tri$>$mono$>$tetra. Studies of the partial disproportionation of tetramethyldiborane reveal that whereas equilibration is complete in about 30 minutes at 40° C the time required at 0° C is 24 hours or more, which explains why the methyldiboranes can be isolated at low temperatures (*151*).

f. *Exchange of Boron–Carbon Bonds with Boron–Carbon Bonds.* Trialkylboranes and triarylboranes do not exchange hydrocarbyl groups at room temperature, a behavior which is in contrast to the analogous aluminum compounds (*139*). Therefore, purified mixed trialkylboranes below 100° C are stable compounds (unless the alkyl group is α-branched, e.g., isopropyl) having constant boiling points (*116*). This is probably due to the fact that trialkylboranes do not associate to form dimers as is well known for trialkylaluminum compounds (*19*, *279*). However, rapid alkyl group exchange is observed in mixtures of trialkylboranes and trialkylaluminum, with the latter promoting the interchange of alkyl groups by its tendency to form electron-deficient mixed dimers as intermediates (*139*).

$BR_3 + AlR'_3 \rightleftharpoons$

$\rightleftharpoons R_nBR'_{3-n} + R'_nAlR_{3-n}$ (74)

Thus the aluminum trialkyls act as catalyst for the alkyl exchange and indeed it has been reported that small amounts of trialkylaluminum catalyze the exchange of alkyl groups in a mixture of BR_3 and BR_3' (*140*, *141*).

$$BR_3 + BR_3' \rightleftharpoons \sum R_nB\,R'_{3-n} \tag{75}$$

The exchange equilibrium of Eq. (75) is also catalyzed by compounds containing boron–hydrogen bonds, such as $(CH_3)_4B_2H_2$ (*140*, *141*).

Above 100° C, thermal redistributions were observed in the trialkylborane systems involving also isomerization of primary alkyl groups to secondary alkyl groups and subsequent equilibration of the primary and secondary alkyl groups on the boron atoms (*115*, *141*, *171*).

g. *Exchange of Boron–Carbon Bonds with Boron–Halogen Bonds.* Heating of a trialkylborane with a trihaloborane under pressure results in the redistribution of alkyl and halogen groups with the rate of this reaction

$$R_3B + BX_3 \rightleftharpoons R_2BX + RBX_2 \tag{76}$$

depending on the nature of the substituent groups. In the presence of certain BH-containing substances (e.g., B_2H_6 or $R_nB_2H_{6-n}$) trialkyl and triarylboranes react with trihaloboranes according to Eq. (76) at room temperature (*141a, 141b*). After removal of the catalyst the products may be isolated by distillation. In view of these results it is very probable that the reported rapid disproportionation of dichloromethylborane and chlorodimethylborane into the starting materials upon distillation may be due to trace amounts of catalyst (*307*). For $R = C_2H_5$ or C_4H_9 and $X = Cl$ or F, equilibrations have been performed by heating the reactants according to Eq. (*76*) at a temperature of 200° C for 4 hours and isolation of the resulting products by distillation under reduced pressure. The reported data have been used to calculate equilibrium constants of the form (*37*)

$$K_1 = [R_3B][RBX_2]/[R_2BX]^2 \tag{77}$$

$$K_2 = [BX_3][R_2BX]/[RBX_2]^2 \tag{78}$$

For $R = C_2H_5$ and $X = Cl$, the values of the equilibrium constants were $K_1 = 5.3$ and $K_2 = 1.5$. For $R = n\text{-}C_4H_9$ and $X = Cl$, $K_1 = 5.3$ and $K_2 = 0.06$; For $R = n\text{-}C_4H_9$ and $X = F$, $K_1 = 4.3$ and K_2 could not be determined. Similar redistributions have also been performed with boron trifluoride etherate (*176*). The reaction of Eq. (76) has been utilized as a general method for the preparation of various alkylhaloboranes. Thermal disproportionation studies of these products have been reported (*168*).

h. *Exchange of Boron–Carbon Bonds with Boron–Oxygen Bonds.* Quantitative studies of the exchange of phenyl groups with methoxyl groups in the system $B(C_6H_5)_3$ vs $B(OCH_3)_3$ were performed at 200° C and the equilibrium distribution of products determined by the proton NMR signals of the methoxyl groups (*122*). The reported values of the equilibrium constants

$$K_1 = [B(C_6H_5)_2(OCH_3)][B(OCH_3)_3]/[B(C_6H_5)(OCH_3)_2] = 0.5 \tag{79}$$

$$K_2 = [B(C_6H_5)_3][B(C_6H_5)(OCH_3)_2]/[B(C_6H_5)_2(OCH_3)] = 0.19 \tag{80}$$

indicate that the equilibria are close to the random case. The exchange of B—C with B—O bonds is also catalyzed by BH-containing substances (*141a*) with the rate of exchange, in addition, depending on the number of B—O bonds in the molecule.

The facile exchange of boron–carbon with boron–oxygen bonds has been applied to the synthesis of trialkylboroxines from trialkylboranes and anhydrous boric acid (*115*).

$$R_3B + B_2O_3 \rightleftarrows (RBO)_3 \tag{81}$$

The resulting trialkylboroxines disproportionate reversibly into trialkylborane and boric oxide upon heating above 200° C (*166*). The method was later improved based on the equilibrium of Eq. (82)

$$[(RO)BO]_3 + BR'_3 \rightleftarrows (R'BO)_3 + B(OR)_3 \tag{82}$$

with the driving force of the reaction in the case of higher alkylboranes being the removal of the low-boiling trimethoxyborane.

i. *Exchange of Boron–Carbon Bonds with Boron–Sulfur Bonds.* Evidence for a facile exchange is obtained from a report where it is stated that upon vacuum sublimation of trimeric methylboron sulfide, trimethylborane and boron sulfide were obtained (*308*).

j. *Exchange of Boron–Carbon Bonds with Boron–Nitrogen Bonds.* Exchange equilibria in the system $B(C_6H_5)_3$ vs $B[N(CH_3)_2]_3$ resulting in the exchange of phenyl groups with dimethylamino groups have been found to occur at 200° C (*122*). The equilibrium situation as determined by quantitative NMR spectroscopy of the dimethylamino group in the compounds $B(C_6H_5)_n[N(CH_3)_2]_{3-n}$ resulted in the following equilibrium constants:

$$K_1 = [B(C_6H_5)_2(NMe_2)][B(NMe_2)_3]/[B(C_6H_5)(NMe_2)_2]^2 = 0.2 \tag{83}$$

$$K_2 = [B(C_6H_5)_3][B(C_6H_5)(NMe_2)]_2/[B(C_6H_5)_2(NMe_2)]^2 = 0.003 \tag{84}$$

The fact that the equilibrium constant corresponding to the disproportionation of $(C_6H_5)_2B[N(CH_3)_2]$ according to Eq. (84) is approximately a 100-fold smaller than the equivalent constant for $C_6H_5B[N(CH_3)_2]_2$ shows that the arrangement of one dimethylamino group per boron atom is about 4.3 kcal more stable than the arrangement in which there are two such groups.

k. *Other Exchange Reactions on Boron.* Readily occurring halogen–halogen exchange has been established in binary mixtures of boron trihalides (*150*). Rapid exchange of chlorine and bromine has also been observed by ^{11}B NMR in mixtures of $C_6H_5BCl_2$ and $C_6H_5BBr_2$ with the B—C bond remaining intact and not participating in the exchange process (*84*). From the appearance of a single NMR line in the mixtures and the lack of appreciable broadening of this line, the maximum lifetime of an exchanging species was estimated to be 10^{-2} second. A mass spectrometric study of the equilibria in the systems RBX_2 vs BY_3, where $R = CH_3$, C_2H_5, or $CH_2{=}CH$ and X and Y were F and Cl, and systems R_2BX vs BY_3 also indicate rapid interchange of halogens without affecting the B—C bond. The existence of the species RBXY in the equilibrium mixtures was clearly established (*30*).

Exchange involving boron–halogen bonds and boron–oxygen bonds has been observed in the synthetically important reactions for the preparation of alkyldihaloboranes from alkylboroxines and boron trihalides (*165*, *167*, *169*).

$$(RBO)_3 + 2\,BX_3 \rightleftarrows 3\,RBX_2 + B_2O_3 \tag{85}$$

Rapid exchange of boron–oxygen bonds with boron–oxygen bonds in alkylalkoxyboranes has been observed on fractional distillation (*177*) and by proton NMR (*170*). In mixtures of diisobutylmethoxyborane with isobutyldiethoxyborane upon equilibration diisobutylethoxyborane, isobutylethoxymethoxyborane, and isobutyldimethoxyborane were observed. A minimum of 0.3 second for the mean lifetime for the methoxy groups on the two sites was calculated for room temperature.

Exchange of boron–oxygen bonds with boron–sulfur bonds has been investigated (*178*) in the systems described by Eqs. (86)–(89), where X and Y are oxygen or sulfur,

$$3\ \mathrm{RB(XR')_2} + 2\ \mathrm{B(YR'')_3} \rightleftarrows 3\ \mathrm{RB(YR'')_2} + 2\ \mathrm{B(XR')_3} \tag{86}$$

$$3\ \mathrm{R_2B(XR')} + \mathrm{B(YR'')_3} \rightleftarrows 3\ \mathrm{R_2B(YR'')} + \mathrm{B(XR')_3} \tag{87}$$

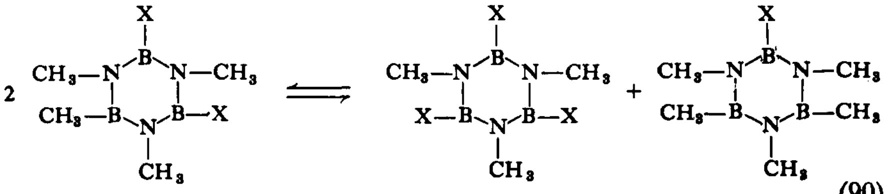
$$\mathrm{RB(XR')_2} + \mathrm{R'''B(YR'')_2} \rightleftarrows \mathrm{RB(YR'')_2} + \mathrm{R'''B(XR')_2} \tag{88}$$

$$\mathrm{R_2B(XR')} + \mathrm{R_2'''B(YR'')} \rightleftarrows \mathrm{R_2B(YR'')} + \mathrm{R_2'''B(XR')} \tag{89}$$

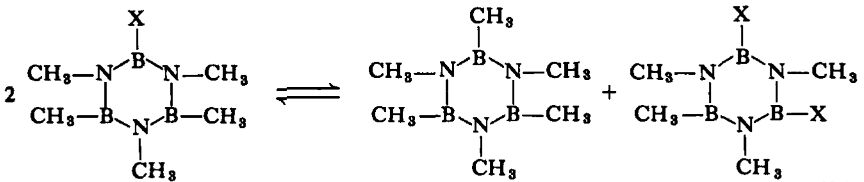
The equilibrium nature of these reactions has been established and by removing the most volatile component from the mixture—thus shifting the equilibrium—the synthetic aspect of these equilibria has been utilized.

1. *Exchange of Substituents in Borazines*

Redistribution of substituents bonded to boron atoms in the borazine ring molecule has been studied by analyzing equilibrated mixtures by vapor-phase chromatography (*224*). Mixtures of *B*-trichloroborazine and hexamethylborazine when heated at temperatures between 175° and 250° C exchange chlorine atoms and methyl groups attached to boron atoms in the borazine ring. The methyl groups bonded to nitrogen do not exchange under these conditions. These exchange reactions may be treated formally as exchanges of substituents between "trifunctional" borazine moieties, $(\text{—BNCH}_3)_3$. Thus the equilibria require a set of two equilibrium constants derived from the following two equations:



(90)



(91)

For X = Cl and M = (—BNCH$_3$)$_3$, the corresponding equilibrium constants for 250° C were calculated from three sets of data

$$K_1 = [MX_3][MX(CH_3)_2]/[MX_2CH_3]^2 = 0.13 \tag{92}$$

$$K_2 = [M(CH_3)_3][MX_2CH_3]/[MX(CH_3)_2]^2 = 0.13 \tag{93}$$

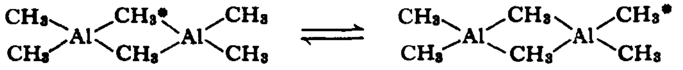
For the same system at 350° C, the values were $K_1 = 0.13$ and $K_2 = 0.22$, indicating in both cases nonrandom equilibrium distribution of chlorines and methyl groups in the borazines.

Exchange of hydrogen and methyl groups between *N*-trimethylborazine and hexamethylborazine was found to occur in the same temperature region as for the *B*-trichloro system; however, equilibrium was not reached. Hydrolysis experiments of pentamethylborazine isomers (*293*) showed that in each of the independent pyrolyses of the pentamethylborazine isomers, redistribution products were formed as a result of interchange of substituents only among like skeletal atoms.

The mechanisms of these exchange reactions as well as of the related exchanges with boron halides, tris(dialkylamino)boranes, and boron alkyls has been interpreted to proceed through a four-center transition state (*255, 258, 260*).

2. *Aluminum*

a. ***Exchange of Aluminum–Carbon Bonds with Aluminum–Carbon Bonds.*** The temperature dependence of the proton NMR spectrum of [Al(CH$_3$)$_3$]$_2$ in cyclohexane as presented in Fig. 10 shows a sharp singlet at room temperature and two resonances with a 1:2 ratio of areas at temperatures below ~ −50° C (*237*). This is interpreted in terms of exchange processes involving terminal and bridging methyl groups (*214*). From line-width measurements, the average lifetime, τ, that a methyl group spends at a particular position has



(94)

been calculated; at $-50°$ C, τ has a value of 1.3×10^{-1} second; at $-10°$ C, $\tau = 2.8 \times 10^{-4}$ second. A similar temperature dependence has also been observed in the proton NMR spectra of triethylaluminum (*276*), tri-*n*-propyl, and other trialkyls of aluminum (*119*, *120*). Exchange in these systems has also been detected by other methods, such as cryoscopy, calorimetry, IR, and Raman spectroscopy (*138*).

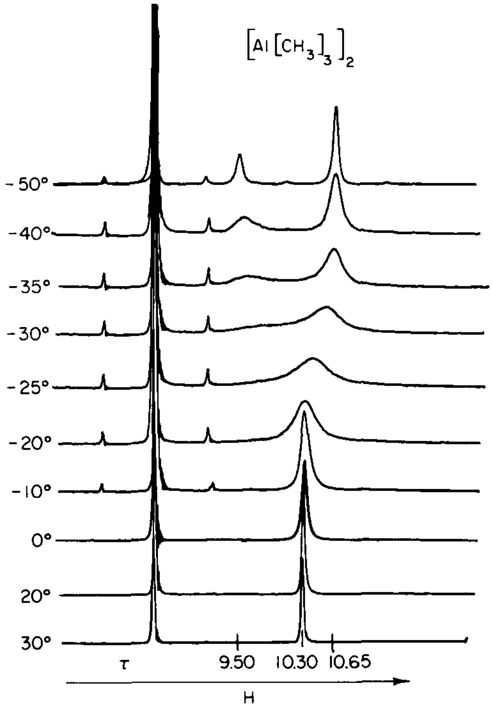


FIG. 10. Temperature dependence of the proton NMR spectrum of $[Al(CH_3)_3]_2$ in solution in cyclopentane.

When any two kinds of aluminum trialkyls are mixed, the alkyl groups undergo rapid exchange to produce mixed aluminum trialkyls (*118*, *120*, *237*, *316*). These usually cannot be isolated in pure form, as the energy of association of forming bridged species is generally very similar for the unmixed aluminum trialkyls. An equally rapid exchange of alkyl with aryl groups has been observed in mixtures of aluminum trialkyls and triphenylaluminum (*209*). Such exchanges have been studied by proton as well as

^{27}Al NMR spectroscopy (*234*). The exchange reactions are also fast in ether, but about 10^4 times slower in pyridine. In the latter solvent, a mixture of trimethylaluminum and triethylaluminum requires about 4 hours at 40° C for a 50% equilibration (*207*). From proton NMR measurements in pyridine, the following equilibrium constants were found for the exchange of phenyl with methyl groups (*209*),

$$K = [(CH_3)_3Al][(CH_3)(C_6H_5)_2Al]/[(CH_3)_2(C_6H_5)Al]^2 = 0.05 \tag{95}$$

$$K = [(C_6H_5)_3Al][(CH_3)_2(C_6H_5)Al]/[(CH_3)(C_6H_6)_2Al]^2 = 0.1 \tag{96}$$

indicating nonrandom exchange. However, random distribution was observed for exchange of methyl with ethyl groups on aluminum.

b. *Exchange of Aluminum–Carbon Bonds with Aluminum–Halogen Bonds.* Alkylaluminum halides in the liquid and dissolved state are dimers with halogen bridges. An equimolar mixture of dialkylaluminum halide and alkylaluminum dihalide equilibrates to a statistical distribution of dihalide, monohalide, and "sesquihalide"; $R_2Al_2X_4 : R_3Al_2X_3 : R_4Al_2X_2 = 1:2:1$ (*29*). Proton NMR measurements show that equilibration occurs very rapidly. At room temperature in mixtures of methylaluminum chlorides, only one proton signal is seen, the shift of which lies between that of the pure compounds CH_3AlCl_2 and $(CH_3)_2AlCl$. Below room temperature, the signal splits into two resonances corresponding to the two types of terminal methyl groups in the dimers. The average lifetime of a species in such solutions at room temperature was estimated to be 0.01 second (*207*). Similar observations were also made for the ethyl derivatives (*29*, *276*). Equilibrations of alkylaluminum halides in ether as solvent are also fast, whereas in stronger basic solvents, such as in pyridine, exchange proceeds more slowly. For the exchange in ether as solvent, the half-life of a given species was estimated to lie in the range of 10^{-1} to 10^2 second (*206*). Equilibria of methylaluminum chlorides with Lewis bases have been studied by proton NMR and infrared spectroscopy (*311*, *312*).

c. *Exchange of Aluminum–Carbon Bonds with Aluminum–Oxygen Bonds.* Exchange of alkyl groups for alkoxyl groups occurs in mixtures of trimethylaluminum and aluminum alkoxides. With aluminum ethoxide and aluminum isopropoxide, rapid reaction occurs in benzene (*207*). In mixtures of dimethylaluminum methoxide and trimethylaluminum, the observation of both methyl NMR peaks for trimethylaluminum and dimethylaluminum alkoxide (or phenoxide) indicates that the exchange of methyl groups with each other as well as with alkoxyl groups is not as extremely fast as in the halides. Lifetimes of the order of 0.1 to 0.5 second have been estimated (*120*, *121*, *205*, *208*).

In a detailed study of the reaction of trimethylaluminum with aluminum isopropoxide in the mole ratio 1:2 in benzene, NMR indicated that initially a 1:1 mixture of dimethylaluminum isopropoxide and aluminum isopropoxide was obtained, with the reaction being completed in 1 minute at 40° (*207*). Further reaction of the dimethylaluminum isopropoxide to give methylaluminum diisopropoxide was extremely slow even at 85° C.

From these studies it is evident that the rates of distribution depend greatly on the nature of the alkoxyl groups and the number of alkyl groups bonded to aluminum.

d. *Other Redistributions on Aluminum.* Exchange of phenyl groups and hydrogen atoms has been observed and the resulting phenylaluminum hydrides were characterized (*281*). Apparently exchange reactions in this system are quite slow. From a phase-diagram study of the system $NaAlH_4$ vs $NaAl(C_2H_5)_4$, evidence was obtained for the exchange of hydrogen with ethyl groups in the complex (*137*). Maxima in the diagram indicated the presence of the compositions $NaAl(C_2H_5)_3H$ and $NaAl(C_2H_5)_2H_2$, but no evidence was obtained for $NaAl(C_2H_5)H_3$. Mixtures of $NaAl(C_2H_5)_4$ with $NaAl(CH_3)_4$ have only one eutectic at the 1:1 mole ratio (*315*). In spite of this, however, there seems to be no reason why the formation of complexes with a mixture of alkyl groups should not occur.

Exchange of halogen with hydrogen atoms on aluminum is also quite rapid since solutions of aluminum hydride and aluminum chloride readily form hydridoaluminum halides (*302*). The ether and trialkylamine addition compounds disproportionate upon distillation or sublimation (*10*, *306*).

In addition to the redistributions discussed above which involve exchanges on aluminum atoms only, there is a great deal of literature available on the exchange reactions of aluminum alkyls with halides, oxides, and alkoxides of other elements which undoubtedly are also equilibrium reactions. These, however, have found great interest as methods for the syntheses of organometallic compounds in general (*129*, *130*). It appears that the equilibria in these systems lie almost completely at the side of the alkyl compound of the other element.

Quantitative studies have been reported for the distribution of pairs of different alkyl groups between aluminum and boron, defined by the constant of Eq. (97) where al = 1/3 Al and b = 1/3 B.

$$K = [\text{alR}][\text{bR}']/[\text{alR}'][\text{bR}] \qquad (97)$$

For $R = C_2H_5$ and $R' = n\text{-}C_4H_6$, the equilibrium constant of Eq. (97) is near unity, indicating completely random distribution of R and R′ between Al and B (*139*). For $R = CH_3$ and $R' = n\text{-}C_4H_9$, the constant K is ~ 12, indicating a preference of the methyl groups for aluminum. For $R = C_2H_5$ and $R' = \text{iso-}C_4H_9$, the constant K is ~ 3.5, which suggests that ethyl groups prefer to be associated with aluminum relative to isobutyl groups.

3. *Gallium*

Relatively few organic compounds of gallium have been described, indicating that gallium chemistry is still in a stage where most of the progress is achieved by synthetic work rather than through study of reactions and physical properties.

Gallium trialkyls, although monomers in the vapor state and in solution, undergo rapid self-exchange of alkyl groups in solution (*211*, *226*). In agreement with the monomolecular nature of trimethylgallium (*213*), its single-proton NMR signal remains virtually unaffected by changes in temperature and dilution. For trivinylgallium, a dimeric structure has been established in solution and in the pure liquid (*226*). However, proton NMR spectra indicate that the three vinyl groups are equivalent, thus suggesting rapid equilibration between terminal and bridging vinyl groups.

Alkylgallium halides have been prepared by halogen alkyl exchange and were found to be dimers in the vapor (*61*, *78*). The phenyl derivatives have been found to be dimeric in solution and it has been suggested that internal coordination takes place through halogen bridges.

4. *Indium*

Indium resembles gallium much more than thallium in its organic derivatives. Very little is known about exchange reactions involving organometallic indium compounds. Trimethylindium, a monomer in the gas phase and a tetramer in benzene (*61*), appears to be susceptible to self-exchange of methyl groups. It is hoped that redistribution studies involving indium compounds will be initiated in the near future.

5. *Thallium*

Rapid exchange is occurring at room temperature in methylene chloride or toluene solutions of trimethyl- or triethylthallium as evidenced by the collapse of the ^{205}Tl, ^{203}Tl, —^{1}H spin–spin multiplets, seen at −60° to −100° C, upon increase in the temperature. This exchange is concentration-and solvent-dependent and involves interchange of alkyl groups between two monomeric trialkylthallium molecules (*153*). Mixtures of trimethyl and triethylthallium in dichloromethane when cooled to − 85° C give additional proton resonance lines attributable to the mixed alkyls, $Tl(CH_3)_2(C_2H_5)$ and $Tl(CH_3)(C_2H_5)_2$.

A detailed study of the rate of exchange in solutions of trimethylthallium (*154*) gave the following values for the mean lifetime, τ, of a methyl group on a thallium nucleus in a given spin state (at 26° C, in seconds, with the molarity and solvent given in parentheses): 0.54×10^{-3} (1.22, deuterobenzene); 3.86×10^{-3} (0.74, trimethylamine); 3.25×10^{-3} (1.65, dimethyl ether). These data show that the exchange in the basic solvents is slower than in benzene, a fact which may be attributed to weak complex formation between the solvent and the trimethylthallium.

Also phenyl groups in triphenylthallium undergo rapid intermolecular exchange with the average lifetime of a phenyl group attached to a specific thallium atom being more than 0.05 second in trimethylamine solution and less than 3×10^{-4} second in dimethyl ether or deuterobenzene.

In the system $Tl(CH_3)_3$ vs $Tl(CH{=}CH_2)_3$, rapid exchange of alkyl groups was observed. It was estimated that the exchange rate of methyl groups in a solution 1 *M* in thallium at 26° C was about 30 times faster than for a solution of trimethylthallium of the same concentration. Since the thallium proton coupling of the vinyl group could not be seen, the vinyl exchange rate must be much more rapid than the methyl group exchange. This is explained in terms of stabilization of the transition state due to resonance hybrid structures involving the vinyl group and, alternatively, due to donation of the π electrons of the double bond into the vacant *p* orbitals of the thallium.

Additional observations of exchange equilibria involving organometallic thallium compounds are the rapidly occurring exchange reactions reported for mixtures of triphenylthallium and *n*-butyllithium and the halogen–phenyl interchange observed when solutions of phenylthallium dichloride are boiled.

$$2\,C_6H_5TlCl_2 \rightleftarrows (C_6H_5)_2TlCl + TlCl_3 \qquad (98)$$

D. Group IV

1. *Silicon*

Reactions involving the exchange of substituents attached to silicon have been studied most extensively (*186*). Many monofunctional substituents bonded to silicon undergo redistribution reactions quite readily under relatively mild conditions. There are, however, a few exceptions where rather drastic conditions have to be applied in order to initiate reorganization of substituents, such as the exchange reactions involving making and breaking of silicon–carbon bonds. Hence it is feasible to carry out two kinds of redistribution reactions on silicon. Under relatively mild conditions, exchange processes proceed which do not involve cleavage of silicon–carbon bonds, thus preserving a methylsilicon moiety or dimethylsilicon moiety while the other substituents on silicon are readily undergoing redistribution. Under much more severe conditions, the redistribution processes include all four substituents attached to silicon including the carbon-bonded ones. This observation permits one to obtain information on the exchange equilibria of NMR-inactive substituents on an NMR-inactive nucleus, such as silicon, by simply observing the exchange equilibria of the same substituents on the NMR-active "methylsilicon" or "dimethylsilicon" moiety under conditions where these moieties remain intact.

a. *Exchange of Silicon–Carbon with Silicon–Carbon Bonds.* Incidental observations (*147*), such as the detection of a diphenylsilicon compound in the reaction product of the alkylation of $C_6H_5SiCl_3$ with $Zn(CH_3)_2$ were the forerunners of the work of Calingaert on the $AlCl_3$-catalyzed redistribution of tetraethyl- and tetrapropylsilane (*47*) (Table IV). In this study, the proportions of the resulting ethylpropylsilanes were in agreement with the amounts calculated for the ideal random distribution. The *n*-propyl group

TABLE IV

CONSTANTS FOR SUBSTITUENT EXCHANGE ON SILICON[a]

Z	T	K_1	K_2	K_3	Temperature (°C)
C_2H_5	n-C_3H_7[b,c]	0.694	0.315	0.454	180°
CH_3	Cl[d]	—	0.025	0.013	350°
Ideal randomness		0.375	0.444	0.375	

[a] The constants are defined by Eqs. (99–101).

[b] Equilibrium constants were calculated from the single set of data given in Calingaert *et al.* (*47*).

[c] $AlCl_3$ catalyst, equilibrium reached in less than 5 hours.

[d] $AlCl_3$ catalyst, equilibrium reached in less than 15–20 hours; analysis by mass spectrometry (*313*).

does not rearrange during this reaction (*94*). In another study (*246*) dealing with the catalyzed redistribution of two kinds of alkyl groups on silicon, the disproportionation of ethyltrimethylsilane has been investigated with regard to catalytic effects of various Lewis acids. Also effects of cocatalysts, solvents, and temperature on the rate have been studied and a mechanism is discussed. Earlier it was shown (*125*) that ethylphenylsilanes undergo redistribution of ethyl and phenyl groups when heated above 300° C. However, no efforts were made in the latter two studies to describe quantitatively the equilibrium aspects of these reactions. Aluminum-chloride-catalyzed redistributions of methylalkylsilanes, $(CH_3)_nSiR_{4-n}$, with R ranging from ethyl to *n*-dodecyl and including also α-branched isopropyl and β-branched isobutyl groups have been studied by gas chromatography (*232*). These equilibria were found to be random exchanges; however, equilibrium constants which would have given evidence for the influence of the chain length of R were not determined. In the same study, redistributions of the type R_4Si vs R'_4Si vs R''_4Si and R_4Si vs R'_4Si vs R''_4Si vs R'''_4 Si are reported. The retention times generally varied linearly with the number of carbon atoms. Rate studies in these systems were also performed.

Mixtures of alkylsilanes corresponding to random distribution were also obtained (*264*) by the action of mixed organometallic reagents, $LiC_2H_5+LiC_3H_7$, on silicon tetrachlroide.

b. *Exchange of Silicon–Carbon with Silicon–Hydrogen Bonds.* Exchange reactions involving phenyl groups and hydrogen atoms bonded to silicon (*22*) were observed when diphenylsilane, $(C_6H_5)_2SiH_2$, or phenylsilane, $C_6H_5SiH_3$, were heated in the presence of metallic sodium in decalin. More recently, it was observed (*217*) that redistribution of phenyl groups and hydrogen atoms on silicon occurs on exposure to ultraviolet radiation at 70° to 130° C or on warming to 130° C with a variety of peroxy or azo initiators or in the presence or absence of a platinum catalyst at 100–300° C (*98*). The reported data do not permit a conclusion as to whether equilibrium was reached. The same type of redistribution has been found (*277*) to occur at room temperature when aluminum chloride is used as a catalyst. The only products identified in the latter case were silane, SiH_4, and tetraphenylsilane, which is to be expected since the reaction was performed in an open system with the silane being removed continuously in a stream of nitrogen. This resulted in a shift of the equilibrium according to Le Chatelier toward producing additional volatile silane and leaving tetraphenylsilane in the reaction flask.

c. *Exchange of Silicon–Carbon with Silicon–Oxygen Bonds.* The interchange of phenyl groups and alkoxyl groups on silicon has been shown to be promoted by sodium or the alkoxide ion (*247*). Phenyltrimethoxysilane forms tetramethoxysilane and products containing more than one phenyl group attached to silicon when heated at 200° C in the presence of catalytic amounts of sodium. Alkyl groups have also been found to undergo disproportionation with alkoxyl groups but higher temperatures are required. Methyltriethyoxysilane when heated with small amounts of sodium at 250° C essentially gave equimolar amounts of dimethyldiethoxysilane and tetraethoxysilane. Methyltrimethoxysilane reorganized to give a mixture of all of the methylmethoxysilanes except tetramethylsilane. Due to side reactions and formation of nonvolatile residues in these redistribution reactions, the reported quantitative data are not necessarily equilibrium data. Also studied was the redistribution of allyl (*13*) and crotyl (*13*) groups with ethoxyl groups—reactions which proceed smoothly in the presence of sodium at reflux temperature.

d. *Exchange of Silicon–Carbon with Silicon–Halogen Bonds.* Of considerable commercial importance is the redistribution of methyl groups and chlorine atoms on silicon, since the group of chemicals obtained in this reaction is used for the preparation of silicones (*24*). This redistribution reaction proceeds between 250° to 450° C in the presence of aluminum chloride as catalyst (*249*). Also studied were the kinetics and the equilibria of the reaction, with the nonrandom equilibrium constants listed in Table IV (*313*). The equilibration reactions for the determination of K_1 were too slow

$$K_1 = [SiZ_2T_2][SiT_4]/[SiZT_3]^2 \tag{99}$$

$$K_2 = [SiZ_3T][SiZT_3]/[SiZ_2T_2]^2 \tag{100}$$

$$K_3 = [SiZ_4][SiZ_2T_2]/[SiZ_3T]^2 \tag{101}$$

to be measured. Equilibrium concentrations of the products were determined by mass spectrometry. A mechanism for the exchange reactions is postulated which assumes complexing of aluminum chloride with the methylchlorosilane, resulting in a weakened silicon–chlorine bond. In a secondary reaction, the complex exchanges the tetrachloroaluminate group for a methyl or chloro group from another methylchlorosilane.

Tetraalkylsilanes also undergo redistribution reactions with silicon tetrafluoride (*128*) when heated in an autoclave at 300° to 400° C. Phenyl groups (*225*) redistribute readily with chlorine atoms on silicon when the reaction is being carried out at 300° to 400° C in the presence or absence of catalysts such as aluminum chloride.

e. *Exchange of Silicon–Hydrogen with Silicon–Halogen Bonds.* The redistribution of hydrogen and halogen atoms attached to silicon is one of the most facile ones to effect. Trifluorosilane (*26*), SiF_3H, disproportionates even at liquid nitrogen temperature and the other fluorosilanes, $SiFH_3$ and SiF_2H_2, are also readily redistributed (*80*). Diiododisilane (*81*), SiI_2H_2, has been found to redistribute readily without any catalyst. However, catalysts such as aluminum chloride (*278*, *301*) or amines (*15*) are required to effect hydrogen–chlorine interchanges. Redistribution of silanic hydrogen with chlorine without participation of carbon ligands attached to silicon may be effected by aluminum chloride (*27*, *75–77*, *95*, *301*) under mild conditions. As aluminum chloride is also an effective catalyst for the redistribution of silanic hydrogen with alkyl or aryl groups (*27*), the catalyst concentration and the temperature must be controlled carefully. Other catalysts are dialkylcyanamides, nitriles (*14*, *16*, *229*, *233*), pyridine (*230*), amides, tertiary phosphines, and tetraalkylammonium salts (*299*, *300*). Equilibrium constants are listed in Tables V and VI.

f. *Exchange of Silicon–Hydrogen with Silicon–Oxygen Bonds.* Alkoxyl groups are similar to halogens in their ability to interchange with hydrogen atoms in silanes (*93*) in the presence of basic catalysts such as sodium metal, sodium ethoxide (*12*), or lithium methoxide (*299*).

g. *Exchange of Silicon–Oxygen Bonds with Silicon–Oxygen Bonds.* Alkoxyl–alkoxyl group exchange occurs when two alkoxysilane (*28*) derivatives are heated together at 150° C for 16 hours. Thus when the pairs of compounds $ClCH_2CH_2Si(OCH_3)_3$ and $ClCH_2CH_2Si(OC_3H_7)_3$, or $ClCH_2CH_2Si(OCH_3)_3$ and $ClCH_2CH_2Si(OC_4H_9)_3$, or $ClCH_2CH_2Si(OCH_3)_3$ and $ClCH_2CH_2Si(OC_5H_{11})_3$, or $ClCH_2CH_2Si(OC_2H_5)_3$ and $ClCH_2CH_2Si(OC_4H_9)_3$ were heated, the mixed esters were obtained in addition to unchanged starting materials.

A study of the alkoxyl–alkoxyl group exchange (*145*) on the dimethylsilicon moiety between dimethyldiethoxysilane and dimethyldi-*sec*-butoxysilane, the latter prepared from optically active *sec*-butanol, showed that the optical activity was retained in the product

$$(CH_3)_2Si(OC_2H_5)[OCH(CH_3)(C_2H_5)].$$

This indicates that such reactions involve cleavage of Si—O bonds and not C—O bonds under these experimental conditions. For quantitative data, see Tables V and VI.

TABLE V

EQUILIBRIUM CONSTANTS FOR SUBSTITUENT INTERCHANGE ON THE METHYLSILICON MOIETY

Z	T	K_1[a]	s_1[b]	K_2[c]	s_2[b]	Temperature (°C)	Equilibrium reached	References
Cl	Br[d]	0.434	0.016	0.400	0.015	120°	< 20 hours	*195*
Cl	I	0.451	0.054	0.289	0.030	460°	< 0.5 hours	*91*
Cl	H	0.475	0.049	0.041	0.006	100°	< 2.3 hours	*180*
Cl	OCH_3	0.018	0.001	0.042	0.002	150°	< 12 hours	*290*
Cl	OC_6H_5	0.183	0.040	0.221	0.044	150°	< 163 days	*192*
Br	OCH_3	0.013	0.001	0.058	0.002	25°	< 13 days	*180*
Br	OC_6H_5	0.277	0.016	0.380	0.020	150°	< 27 days	*192*
Cl	SCH_3	0.118	0.063	0.162	0.086	120°	< 156 hours	*192*
Br	SCH_3	0.041	0.003	0.086	0.005	120°	< 7 days	*192*
Cl	$N(CH_3)_2$	5×10^{-4}	6×10^{-4}	5×10^{-4}	7×10^{-4}	25°	< 3 hours	*290*
Br	$N(CH_3)_2$	1.6×10^{-4}	5.7×10^{-4}	1.4×10^{-3}	0.9×10^{-3}	120°	< 5 hours	*192*
OCH_3	OC_2H_5	0.26	0.01	0.32	0.01	150°	< 7 days	*290*
OCH_3	$N(CH_3)_2$	0.40	0.05	0.30	0.04	120°	< 40 hours	*290*
Ideal randomness		0.333		0.333				

[a] $K_1 = [CH_3SiZ_2T][CH_3SiT_3]/[CH_3SiZT_2]^2$.

[b] Standard error.

[c] $K_2 = [CH_3SiZ_3][CH_3SiZT_2]/[CH_3SiZ_2T]^2$.

[d] From the data given by Kumada (*146*): $K_1 = 0.680$; $K_2 = 0.367$; for the system (*146*) $C_2H_5SiCl_3$ vs $C_2H_5SiBr_3$; $K_1 = 0.384$; $K_2 = 0.278$.

TABLE VI

EQUILIBRIUM CONSTANTS FOR SUBSTITUENT INTERCHANGE ON THE DIMETHYLSILICON MOIETY

Z	T	K_1[a]	s_1[b]	Temperature (°C)	Equilibrium reached	References
Cl	Br	0.305[c]	0.026	120°	<85 hours	*199*
Cl	I	0.404[d,e]	0.029	480°	<3 hours	*91*
Cl	H	0.098	0.007	100°	<23 hours	*181*
Cl	CH_3COO	0.340	0.029	120°	<8 days	*181*
Cl	NC	0.216	0.012	25°	<3 hours	*200*
Cl	NCO	0.282[f]	0.012	120°	<20 hours	*200*
Cl	NCS	0.307	0.028	120°	<23 hours	*200*
Br	NC	0.191	0.025	25°	<3 hours	*200*
Br	NCO	0.382	0.066	120°	<20 days	*200*
NC	NCS	0.421	0.097	72°	<160 hours	*200*
NCO	NCS	0.222	0.027	25°	<100 hours	*200*
Cl	OCH_3	0.010	0.002	120°	<8 hours	*290*
Cl	OC_6H_5	0.164	0.011	150°	<17 days	*181*
Br	OCH_3	6.4×10^{-3}	1.1×10^{-3}	120°	<0.5 hours	*291*
Br	OC_6H_5	0.135	0.010	150°	<190 hours	*181*
NCO	OCH_3	0.058	0.010	120°	<20 hours	*200*
OC_2H_5	OCH_3	0.28	0.03	150°	<7 days	*290*
Cl	SCH_3	0.178	0.017	120°	<100 hours	*291*
Br	SCH_3	0.049	0.006	120°	<46 hours	*291*
NC	SCH_3	0.014	0.006	72°	<8 days	*200*
NCS	SCH_3	0.244	0.046	25°	<90 hours	*200*
OCH_3	SCH_3	2.92	0.51	120°	<24 hours	*291*
Cl	$N(CH_3)_2$	1.5×10^{-4}	1.6×10^{-4}	25°	<3 minutes	*290*
Br	$N(CH_3)_2$	4.2×10^{-4}	4.2×10^{-4}	120°	<15 hours	*181*
OCH_3	$N(CH_3)_2$	0.22	0.06	120°	<40 hours	*290*

[a] $K_1 = [(CH_3)_2SiZ_2][(CH_3)_2SiT_2]/[(CH_3)_2SiZT]^2$.

[b] Standard error.

[c] The single set of data in (*146*) gives $K_1 = 0.381$.

[d] Calculated from the set of data in (*91*).

[e] For the system (*91*) $(C_2H_5)_2SiCl_2$ vs $(C_2H_5)_2SiI_2$: $K_1 = 0.337$.

[f] The single set of data in (*91*) gives $K_1 = 0.250$.

h. *Exchange of Silicon–Oxygen Bonds with Silicon–Halogen Bonds.* Studies regarding the symmetrization of methylethoxychlorosilanes were undertaken by Andrianov (*6*) and co-workers. The quantitative data in Table V on the system $CH_3Si(OCH_3)_3$ vs CH_3SiCl_3, indicate, however, that equilibrium was not attained by the former authors.

The halogen–alkoxyl exchange reaction on the dialkylsilicon moiety has been studied by Kumada (*146*), who heated equimolar amounts of $(CH_3)_2SiCl_2$ with $(CH_3)_2Si(OC_2H_5)_2$ for 35 hours at 180° C and upon distillation obtained 76.2% $(CH_3)_2SiCl(OC_2H_5)$. This agrees quite well with the values calculated from the equilibrium constant in Table VI for the corresponding methoxy system. Similarly, 81.9% of $(C_2H_5)_2SiCl(OC_2H_5)$ was obtained from an equimolar mixture of diethyldichlorosilane and diethyldiethoxysilane upon heating for 40 hours at 200° C. On the other hand, it is reported by Andrianov (*7*) that refluxing of $(CH_3)(C_2H_5)SiCl(OC_2H_5)$ in a fractionating column for 50 hours gave only 0.24% of methylethyldichlorosilane, indicating that under these conditions, equilibrium has not been reached. [See also the early work of Friedel and Crafts (*92*).]

i. *Exchange of Silicon–Halogen Bonds with Silicon–Halogen Bonds*. The aluminum-bromide-catalyzed exchange of chlorine and bromine atoms on the methylsilicon and ethylsilicon moiety was studied by Kumada (*146*). The composition of the reaction product was determined by fractional distillation and the data obtained in this work were employed to calculate equilibrium constants which are in good agreement with the data obtained in this laboratory (*195*). Feinberg and Rochow (*83*) found that $CH_3SiBrCl_2$ does not rearrange in the absence of metals or metal chlorides upon refluxing for 43 hours but basic solvents, such as ether and amines, promote redistribution.

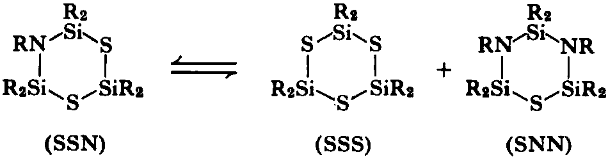
j. *Other Exchanges on Silicon*. In Tables V and VI, additional equilibrium constants are presented for the interchange of pairs of silicon–element bonds not mentioned above. It is interesting to note that pseudohalogen groups with respect to redistribution equilibria with other substituents act in a manner similar to the halogens (*200*). One of the few cases in which the equilibrium constant is larger than the random value (note that the constants in Table V and VI are either close to random or smaller than random) is the system involving exchange of OCH_3 with SCH_3 groups. In this system, the mixed type of compound, $(CH_3)_2Si(OCH_3)(SCH_3)$, at equilibrium is less favored than the dimethoxy or dimethylthio compounds.

Extreme nonrandom behavior was observed for the exchange of halogens with dimethylamino groups. A kinetic study of the latter exchange revealed that equilibrium is reached in a series of consecutive reactions of different rates. Alkoxyl-dimethylamino exchanges are, for all practical purposes, random exchanges.

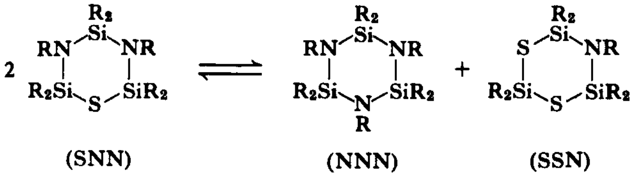
k. *Equilibria in Cyclic Silicon Compounds*. When mixtures of hexamethylcyclotrisilthiane, $[(CH_3)_2SiS]_3$, and nonamethylcyclotrisilazane,

$[(CH_3)_2SiNCH_3]_3$, are heated at 120° C for several days, exchange of bridging sulfur atoms and bridging methylimino groups takes place (*198*, *201*). At equilibrium, therefore, four types of hexatomic ring compounds must be considered, the two starting materials and two rings containing sulfur as well as nitrogen. Proton NMR was used to determine quantitatively the equilibrium concentration of the components.

The equilibria involving hexatomic ring molecules may be fully represented by the equations of reactions (102) and (103), with the methyl group being denoted by R.



(102)



(103)

In addition, under the same conditions, tetramethylcyclodisilthiane (SS), is also present in measurable amounts in the equilibrated system. The set of equilibrium constants describing this system is given in Table VII.

TABLE VII

EQUILIBRIUM CONSTANTS IN THE SYSTEM $[(CH_3)_2SiS]_3$ vs $[(CH_3)_2SiNCH_3]_3$[a]

	At 120° C	At 25° C
$K_{3SSN}^{\circ\circ} = \frac{[SSS][SNN]}{[SSN]^2}$	0.32 ± 0.02	0.34 ± 0.02
$K_{3SNN}^{\circ\circ} = \frac{[NNN][SSN]}{[SNN]^2}$	0.98 ± 0.05	0.90 ± 0.04
$K_{3S,2S}^{\circ\circ} = \frac{[SSS]^2}{[SS]^3}$ [liters/mole]	$1.3 \times 10^2 \pm 20$	$3.6 \times 10^3 \pm 0.7 \times 10^3$

[a] Weighted average values and their standard deviations.

1. *Scrambling Equilibria between Two Moieties of Silicon*

Equilibrations involving redistribution of monofunctional substituents Z and T between pairs of methylsilicon moieties,

$$CH_3Si\underset{\diagdown}{\overset{\diagup}{-}},(CH_3)_2Si\underset{\diagdown}{\overset{\diagup}{}},\ \text{and}\ (CH_3)_3Si-,$$

proceed well below the temperature where methyl groups directly attached to silicon participate in the exchange processes (*196*, *197*, *202*, *299*, *300*). The equilibria generally are characterized by an intersystem constant relating the distribution of Z and T between the two different moieties of silicon and the set of equilibrium constants of the form of Eq. (19) to relate the distribution of Z and T on each of the silicon moieties separately. The intersystem equilibrium constants are summarized in Table VIII.

The general conclusions drawn from these data are that there exists a definite preference of a substituent for a specific silicon moiety as indicated by the large deviations of the intersystem constants from the random value $K_{\text{I(rand)}} = 1.0$. Considering the pair chlorine–bromine, it is seen that at equilibrium in each case, the chlorine atoms tend to associate with the silicon moiety bearing the lesser amount of methyl groups. On the other hand, in relation to the other substituents in Table VIII [OCH_3, SCH_3, $N(CH_3)_2$, H], chlorine as well as bromine atoms prefer to be linked to the silicon moiety bearing the larger number of methyl groups.

Theoretical considerations of the enthalpy of the reactions represented by the intersystem constants based on the bond-energy approach show that the values of ΔH assuming only σ-bond contributions differ considerably from the ΔH values that were calculated from the intersystem constant according to Eq. (13). These differences are attributable to π-bonding effects which, therefore, appear to be the major driving force for the nonrandom equilibrations described by the data in Table VIII.

m. *Scrambling Equilibria between Moieties of Silicon and Germanium.* Intersystem equilibrium constants determined in a similar manner as described in the previous section are summarized in Table IX for the exchange of pairs of monofunctional substituents between moieties of silicon and germanium (*195*, *199*, *204*, *291*). Considering a pair of halogen atoms, the intersystem equilibrium constants in Table IX indicate that in each case the halogen which is higher in the Periodic Table is preferentially attached to the silicon moiety while the halogen lower in the Table goes with the germanium moiety. For the two systems involving isocyano groups, reversal of the preference is seen when going from chlorine to bromine. Whereas the

TABLE VIII

INTERSYSTEM EQUILIBRIUM CONSTANTS FOR THE METHYLSILICON SYSTEMS AT 120° C

Z	T	$K_I' = \frac{[MeSiT_3]^2[Me_2SiZ_2]^3}{[MeSiZ_3]^2[Me_2SiT_2]^3}$	$K_I'' = \frac{[MeSiT_3][Me_3SiZ]^3}{[MeSiZ_3][Me_3SiT]^3}$	$K_I''' = \frac{[Me_2SiT_2][Me_3SiZ]^2}{[Me_2SiZ_2][Me_3SiT]^2}$
Br	Cl	5.5 ± 0.6	10.3 ± 1.4	2.5 ± 0.2
OCH_3	Cl	$(1.0 \pm 0.5) \times 10^{-8}$	$(7.1 \pm 2.7) \times 10^{-10}$	$(5.3 \pm 1.7) \times 10^{-4}$
SCH_3	Cl	$(5.0 \pm 0.9) \times 10^{-6}$	$(6.7 \pm 2.4) \times 10^{-7}$	$(9.8 \pm 1.8) \times 10^{-3}$
SCH_3	Br	$(1.5 \pm 0.2) \times 10^{-6}$	$(3.5 \pm 2.6) \times 10^{-6}$	$(3.5 \pm 0.3) \times 10^{-3}$
$N(CH_3)_2$	Cl[a]	$(2.1 \pm 1.3) \times 10^{-8}$	$(1.2 \pm 0.2) \times 10^{-10}$	$(8.0 \pm 3.3) \times 10^{-4}$
$N(CH_3)_2$	Br[a]	$(1 \pm 0.2) \times 10^{-12}$	$(6.4 \pm 1.4) \times 10^{-12}$	$(4.2 \pm 0.2) \times 10^{-4}$
H	Cl[b]	$(1 \pm 0.6) \times 10^{-7}$	$(1 \pm 0.9) \times 10^{-8}$	$(5.6 \pm 3.4) \times 10^{-3}$
Ideal randomness		1.00	1.00	1.00

[a] Constants correspond to 25° C.

[b] Constants correspond to 100° C.

TABLE IX

INTERSYSTEM EQUILIBRIUM CONSTANTS[a] FOR THE EXCHANGE OF PAIRS OF MONOFUNCTIONAL SUBSTITUENTS BETWEEN MOIETIES OF SILICON AND GERMANIUM AT 120° C

Z	T	$K_I' = \frac{[Me_2SiT_2][Me_2GeZ_2]}{[Me_2SiZ_2][Me_2GeT_2]}$	$K_I' = \frac{[MeSiT_3][MeGeZ_3]}{[MeSiZ_3][MeGeT_3]}$
Cl	Br	$(2.9 \pm 1.2) \times 10^{-4}$	$(9.7 \pm 4.0) \times 10^{-6}$
I	Cl	$(8.3 \pm 1.9) \times 10^{+5}$	$(6.7 \pm 3.1) \times 10^{+11}$
I	Br	$(5.0 \pm 0.9) \times 10^{+3}$	$(2.4 \pm 0.5) \times 10^{+4}$
Cl	NC	$(6.7 \pm 1.0) \times 10^{-2}$	—
Br	NC	$(2.6 \pm 1.0) \times 10^{+2}$	—
Cl	OCH_3	$(4.5 \pm 1.6) \times 10^{+14}$	$(1 \pm 10) \times 10^{+14}$
Br	OCH_3	$(9.2 \pm 5.4) \times 10^{+12}$	$(1 \pm 10) \times 10^{+20}$
I	OCH_3	$(1.1 \pm 0.2) \times 10^{+10}$	—
Cl	SCH_3	$(1.0 \pm 0.3) \times 10^{-3}$	$(1.4 \pm 0.5) \times 10^{-7}$
Br	SCH_3	4.5 ± 0.5	6.3 ± 1.5
I	SCH_3	$(3.5 \pm 0.5) \times 10^{+4}$	$(9.1 \pm 4.1) \times 10^{+3}$
OCH_3	SCH_3	$(2.6 \pm 0.4) \times 10^{-4}$	—
Cl	$N(CH_3)_2$	—	$(3.5 \pm 3.0) \times 10^{+12}$
Br	$N(CH_3)_2$	—	$(4.0 \pm 3.4) \times 10^{+20}$
I	$N(CH_3)_2$	—	$(4.2 \pm 8.6) \times 10^{+28}$

[a] From refs. (*182*, *195*, *199*, *291*).

equilibrium in the cases of exchange of halogens with methoxyl groups is such that the halogen strongly gravitates toward the germanium moiety, there is continuous change in the value of K_I when going from Cl to Br to I for the redistribution of these substituents with methylthio groups. Extreme nonrandom distribution was also observed for the exchanges involving dimethylamino groups with halogens, with the halogens preferring the germanium moiety. Again, the nonrandom values of the intersystem constants are ascribed to π effects.

The kinetics of such redistributions as exemplified in Fig. 11 for the reactions of $CH_3SiBr_3 + CH_3GeCl_3$ and $CH_3SiCl_3 + CH_3GeBr_3$ indicate that a sequence of reactions occurs. The first reaction of the left-hand graph is that of Eq. (104).

$$CH_3SiBr_3 + CH_3GeCl_3 \rightarrow CH_3SiClBr_2 + CH_3GeCl_2Br \qquad (104)$$

Once a small amount of the halogen from the methylsilicon moiety has been transferred to the methylgermanium moiety, the methylgermanium halides come to equilibrium with each other rapidly and remain in a state of dynamic

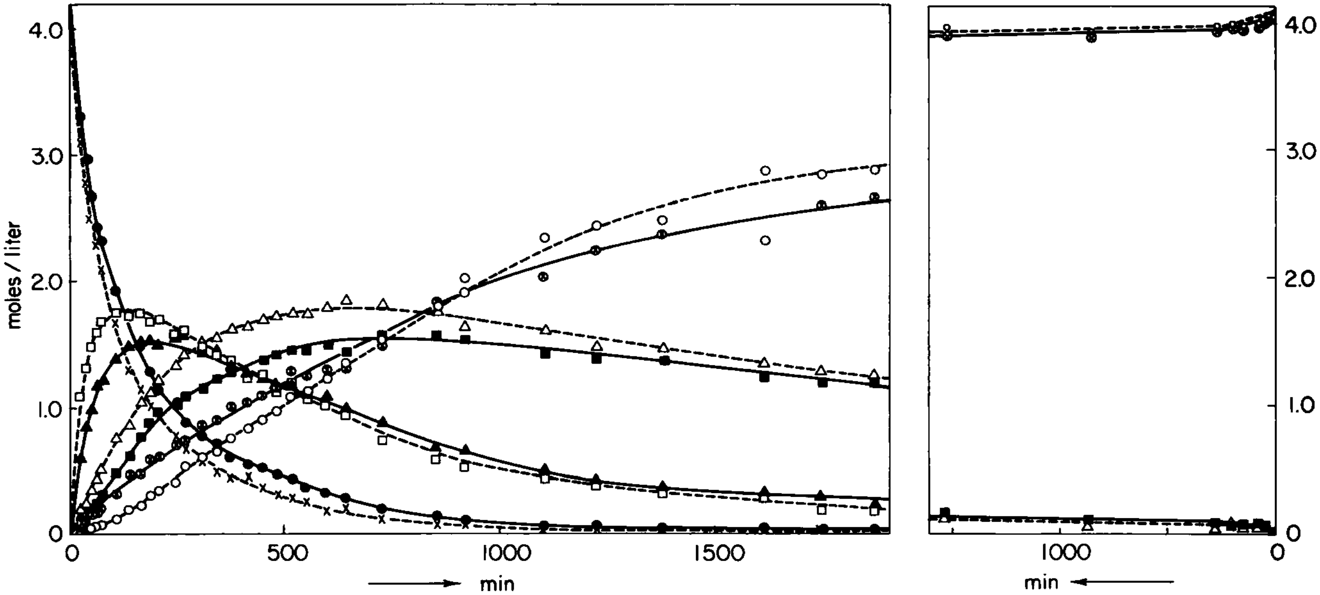


FIG. 11. Kinetics of the reaction of equimolar amounts of CH_3SiBr_3 and CH_3GeCl_3 (left-hand graph) and CH_3SiCl_3 and CH_3GeBr_3 (right-hand graph) in the neat liquid state at 35°C. The solid lines represent the silicon compounds and the broken lines the germanium compounds: ●, CH_3SiBr_3; ▲, CH_3SiBr_2Cl; ■, $CH_3SiBrCl_2$; ⊗, CH_3SiCl_3; ○, CH_3GeBr_3; △, CH_3GeBr_2Cl; □, $CH_3GeBrCl_2$; ×, CH_3GeCl_3.

equilibrium throughout the entire course of the reaction. On the other hand, exchange on the methylsilicon moiety is far slower.

The second major reaction appears to be Eq. (105) since the maxima in the amounts of $CH_3SiClBr_2$ and CH_3GeCl_2Br appear at about the same time

$$\mathrm{CH_3SiClBr_2 + CH_3GeCl_2Br \rightarrow CH_3SiCl_2Br + CH_3GeClBr_2} \tag{105}$$

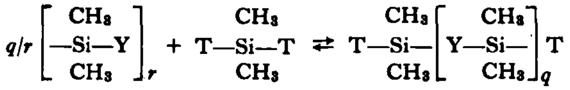
Likewise, the third major reaction of the left-hand graph seems to be Eq. (106).

$$\mathrm{CH_3SiCl_2Br + CH_3GeClBr_2 \rightarrow CH_3SiCl_3 + CH_3GeBr_3} \tag{106}$$

The right-hand graph of Fig. 11 is considerably less complicated since the equilibrium is close to the starting composition. The rate of the reaction is slow.

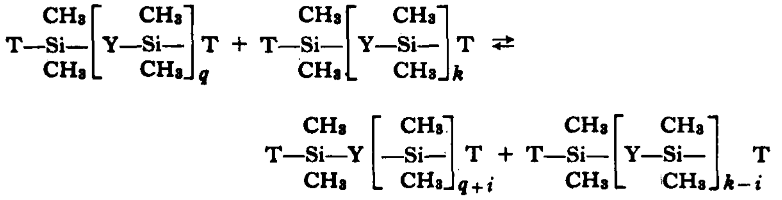
Redistribution of alkyl groups between pairs of Group IV atoms occurred only when the central atoms were adjacent members of the group, i.e., Si vs Ge, Ge vs Sn, Sn vs Pb, while the remaining combinations did not undergo reaction (*232*). However, the possibility exists that the intersystem constant in the latter case is either very large or very small.

n. *Redistribution Equilibria in Families of Silicon Compounds.* Redistribution of bridging groups Y with monofunctional substituents T on the dimethylsilicon moiety, which under the reaction conditions studied remains intact, is achieved by reacting a cyclic dimethylsilicon compound, $[(CH_3)_2SiY]_n$, where $Y = O$, S, NCH_3 (*191*, *203*, *289*) with the appropriate "*neso*" compound, $(CH_3)_2SiT_2$, according to Eq. (107),



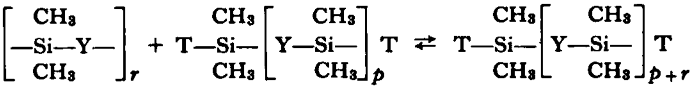
$$q/r\left[\begin{array}{c}\mathrm{CH_3}\\ -\mathrm{Si}-\mathrm{Y}\\ \mathrm{CH_3}\end{array}\right]_r + \mathrm{T}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{T} \rightleftarrows \mathrm{T}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\left[\mathrm{Y}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\right]_q\mathrm{T} \tag{107}$$

The equilibrium state is characterized by chain–chain equilibria symbolized by the overall process of Eq. (108) according to which two chain molecules exchange one or more middle groups



$$\mathrm{T}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\left[\mathrm{Y}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\right]_q\mathrm{T} + \mathrm{T}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\left[\mathrm{Y}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\right]_k\mathrm{T} \rightleftarrows \mathrm{T}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{Y}\left[-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\right]_{q+i}\mathrm{T} + \mathrm{T}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\left[\mathrm{Y}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\right]_{k-i}\mathrm{T} \tag{108}$$

and ring–chain equilibria of the type of Eq. (109) of which Eq. (107) is a special case.



$$\left[\begin{array}{c}\mathrm{CH_3}\\ -\mathrm{Si}-\mathrm{Y}-\\ \mathrm{CH_3}\end{array}\right]_r + \mathrm{T}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\left[\mathrm{Y}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\right]_p\mathrm{T} \rightleftarrows \mathrm{T}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\left[\mathrm{Y}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\right]_{p+r}\mathrm{T} \tag{109}$$

It is seen that the molecules present at equilibrium in such a system are composed of the three types of building units, the *neso* molecule, $(CH_3)_2SiT_2$, end groups, $T(CH_3)_2Si—Y_{1/2}$, and middle groups, $Y_{1/2}—Si(CH_3)_2—Y_{1/2}$. Depending on the nature of T and Y, several families of compounds may be visualized, the equilibrium constants of which are summarized in Table X.

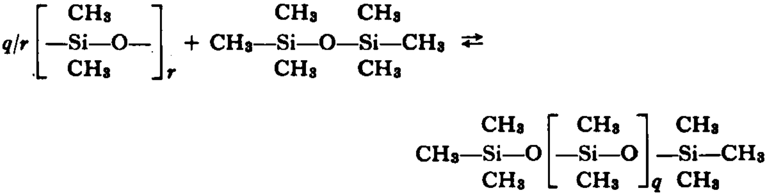
o. *Ring–Ring Equilibria in Dimethylsilthianes.* Exchange reactions involving bridging sulfur in dimethylsilthianes have to include the interconversion of the cyclic dimer into the trimer and vice versa, as shown by Eq. (110),

$$3\,[(CH_3)_2SiS]_2 \rightleftarrows 2\,[(CH_3)_2SiS]_3 \tag{110}$$

The reversibility of this process has been observed earlier (*304*). From the two well-resolved NMR signals (at −0.67 ppm for the trimer and at −0.72 ppm for the dimer) the constant of Eq. (111) corresponding to the equilibrium at 200° C has been calculated (*203*)

$$K^{\circ\circ}_{3,2} = \{[(CH_3)_2SiS]_3\}^2/\{[(CH_3)_2SiS]_2\}^3 = (3.5 \pm 0.4)\ \text{liters/mole} \tag{111}$$

p. *Equilibria in Silicones.* Redistribution equilibria in the systems $(CH_3)_3SiOSi(CH_3)_3$ vs $[(CH_3)_2SiO]$ are important for the production of silicones. Making and breaking of siloxane linkages in this system is brought about thermally as well as catalytically by acids and bases.



$$q/r\left[\begin{array}{c}\mathrm{CH_3}\\ -\mathrm{Si}-\mathrm{O}-\\ \mathrm{CH_3}\end{array}\right]_r + \mathrm{CH_3}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{CH_3} \rightleftarrows \mathrm{CH_3}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}\left[-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}\right]_q-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{CH_3} \tag{112}$$

Equilibration is often carried out in the presence of concentrated sulfuric acid (*263*) at room temperature or at elevated temperatures. Using fractional distillation, linear and cyclic species were separated from equilibrated mixtures. A sample having a number-average molecular weight 438 ± 20

TABLE X

EQUILIBRIUM CONSTANTS IN FAMILIES OF SILICON AT 200°C[a]

T	Y	Family of compounds	K_1	K_2°	K_3°	References
Cl	O	α,ω-Dichloropolydimethylsiloxanes	0.11	—[b]	—[b]	*191*
CH_3O	O	α,ω-Dimethoxypolydimethylsiloxanes	0.24	—	—	*191*
$N(CH_3)_2$	O	α,ω-Bis(dimethylamino)polydimethylsiloxanes	0.50	—	—	*191*
Cl	S	α,ω-Dichloropolydimethylsilthianes	0.13	30	307	*203*
OCH_3	S	α,ω-Dimethoxypolydimethylsilthianes	0.40	30	307	*203*
SCH_3	S	α,ω-Bis(methylthio)polydimethylsilthianes	0.20	30	307	*203*
Cl[c]	NCH_3	α,ω-Dichloropolydimethyl(*N*-methyl)silazanes	2.7×10^{-3}	—	300	*289*

[a] $K_1 = [(CH_3)_2SiT_2]$[middle groups in chains]/[end groups]^2; K_2° and K_3° are ring-chain constants for ring sizes 2 or 3 [defined by Eq. (29)].

[b] The total amount of rings at equilibrium of the compositions studied was < 5%. The ring–chain constants of Table XI apply here also.

[c] At 120°C.

upon distillation gave linear siloxanes $(CH_3)_3SiO[Si(CH_3)_2O]_nSi(CH_3)_3$ where $n=0$, 1, 2, 3, 4, 5, and 6 and, cyclic siloxanes $[(CH_3)_2SiO]_r$, where $r=4$ and 5. Recently, however, gas chromatography (*53*, *114*) has been employed and molecules with chain lengths up to $n=13$ have been separated quantitatively. The average molecular weight of the siloxane polymer can be varied over several orders of magnitude by controlling the amount of end groups added. The composition at equilibrium of high-molecular-weight (number-average molecular weight = 10,000) dimethylsiloxane polymers (*55*) has been found to be ~15 wt % of cyclic molecules and ~85 wt % of linear molecules. The average distribution, in weight percent, in the portion of cyclic molecules, $[(CH_3)_2SiO]_r$ at 150° C is 0.21% for $r=3$, 6.6% for $r=4$, 4.8% for $r=5$; 1.7% for $r=6$; 0.44% for $r=7$; 0.19% for $r=8$; 0.11% for $r=9$; and 0.07% for $r=10$.

The data obtained in these equilibrium studies have been treated quantitatively by Carmichael and Heffel (*53*) and by Brown and Slusarczuk (*33*), who evaluated the equilibrium data in terms of cyclization constants. The latter are identical with ring–chain constants of the type of Eq. (29) where the concentrations are expressed in mole fractions of building units. Table XI

TABLE XI

RING–CHAIN EQUILIBRIUM CONSTANTS IN METHYL-TERMINATED POLYDIMETHYLSILOXANES (SILICONES) FROM SEVERAL SOURCES

	K_r°			
r	Scott[a]	Hartung[b, c]	Carmichael and Winger[d]	Carmichael and Heffel[e]
3	—	0.0194	0.0179	0.0481
4	0.386	1.293	0.749	1.462
5	1.245	0.986	0.686	1.352
6	—	0.359	0.292	0.638
7	—	0.0873	0.102	0.224
8	—	0.0647	0.0407	0.124
9	—	0.0485	0.0271	—

[a] Scott (*263*).

[b] Data were extrapolated to zero solvent.

[c] Hartung and Camiolo (*114*).

[d] Carmichael and Winger (*55*).

[e] Carmichael and Heffel. (*53*).

shows that the ring–chain constants obtained by several authors maximize at $r=4$ or 5, and drop off to increasingly smaller values for r larger than 5.

The ratio of linear to cyclic molecules is shifted heavily in favor of cyclic compounds in equilibrated 3,3,3-trifluoropropylmethylsiloxane polymers (*31*) which consist of 86 wt % of rings and 14% of chains.

A kinetic study (*52*) of the redistribution of bridging oxygen occurring in mixtures of hexamethyldisiloxane and octamethylcyclotetrasiloxane by gas chromatography has been reported recently. At 80° C with acid-clay catalysis, equilibrium is reached within 3 to 17 hours. Early and prominent maxima for $n=4$ and 8 in $(CH_3)_3SiO[Si(CH_3)_2O]_nSi(CH_3)_3$, indicate that the following net reactions are initially important:

$$(CH_3)_3SiOSi(CH_3)_3+[(CH_3)_2SiO]_4 \rightarrow (CH_3)_3SiO[Si(CH_3)_2O]_4Si(CH_3)_3 \tag{113}$$

$$(CH_3)_3SiO[Si(CH_3)_2O]_4Si(CH_3)_3+[(CH_3)_2SiO]_4 \rightarrow (CH_3)_3SiO[Si(CH_3)_2O]_8Si(CH_3)_3 \tag{114}$$

$$(CH_3)_3SiOSi(CH_3)_3+2[(CH_3)_2SiO]_4 \rightarrow (CH_3)_3SiO[Si(CH_3)_2O]_8Si(CH_3)_3 \tag{115}$$

These reactions indicate that during the early stages of the reaction, tetrameric siloxane rings enter the linear molecules as a unit. Reorganization, however, occurs rapidly so that, after ~0.5 hour, the distribution of the chains from the 11-mer to the 15-mer is approximately random. The distribution of shorter chains becomes increasingly more random as the reaction proceeds until, at equilibrium, the distribution of all linear species is in agreement with the random-reorganization model.

A theoretical study of ring closure as applied to the cyclic linear distribution in polydimethylsiloxanes assuming a three-rotational-state model resulted in good correlations between experimental and theoretical equilibrium constants (*54*).

In the case of methylphenylsiloxanes, stereoisomer ring molecules are possible; e.g., for the cyclic trimer, there exist a cis and a trans form and for the cyclic tetramer, there are four stereoisomer forms. Based on gas chromatography data, it has been suggested that these are in statistical equilibrium with each other at elevated temperature (*117*, *210*).

2. *Germanium*

A characteristic feature of the exchange reactions on germanium as compared to silicon is the much faster rate of equilibration observed for analogous germanium compounds. But again, in view of the stability of germanium–carbon bonds with respect to redistribution and the ease with which other substituents on germanium undergo redistribution, studies of exchange equilibria on an alkylgermanium moiety may be performed in a temperature range below ~250° to 300° C without affecting this moiety. Equilibrations involving non-carbon-bonded substituents usually are quite rapid and proceed at room temperature or moderately elevated temperature.

a. *Exchange of Germanium–Carbon with Germanium–Carbon Bonds.* Redistribution of tetraethylgermane with tetrapropylgermane and of tetramethylgermane with tetrabutylgermane, both in the presence of catalytic amounts of aluminum halides, have been studied by gas chromatographic separation (*264*) of the resulting mixed compounds. The reaction proceeded upon refluxing of the mixture and the reported data show that the distribution of the two kinds of alkyl groups is random.

Recently, aluminum-chloride-catalyzed redistributions in systems GeR_4 vs GeR'_4, where R and R′ were pairs of the groups CH_3, C_2H_5, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$, $n\text{-}C_5H_{11}$, and $n\text{-}C_6H_{13}$, were carried out. Random distribution was observed with the components being separated by gas chromatography (232). A random mixture of tetraalkylgermanes is also obtained by the addition of mixed Grignard reagents ($C_2H_5MgBr + n\text{-}C_3H_7MgBr$) to germanium tetrachloride.

With excess of aluminum chloride, the exchange reaction (*264*) of two kinds of tetraalkylgermanes results in cleavage of single alkyl groups to give mixed trialkylchloro derivatives according to Eq. (116)

$$Ge(CH_3)_4 + Ge(C_3H_7)_4 \xrightleftharpoons{\text{excess AlCl}_3} Ge(CH_3)_i(C_3H_7)_{3-i}Cl \qquad (116)$$

The redistribution and cleavage reaction of mixtures of tetramethylgermane and tetrabutylgermane with excess of aluminum chloride give di- as well as trichlorogermanes having mixed alkyl groups.

b. *Exchange of Germanium–Carbon with Germanium–Hydrogen Bonds.* Very little information is available on the redistribution of alkyl or aryl groups with hydrogen atoms on germanium. One communication (*135*) mentions the fact that triphenylgermane, $(C_6H_5)_3GeH$, when heated briefly at 300° C disproportionates into tetraphenylgermane, diphenylgermane, $(C_6H_5)_2GeH_2$, and possibly other products.

c. *Exchange of Germanium–Carbon with Germanium–Halogen Bonds.* Redistributions involving germanium–carbon bonds require the presence of a Lewis-type catalyst, as shown (*148, 161*) by the preparation of diethyl-, dibutyl-, and diphenyldibromogermane and of triethylbromogermane from the corresponding tetraorganogermanes with germanium tetrabromide, in the presence of aluminum bromide as catalyst. Surprisingly, the failure to effect redistribution between tetra-*n*-propylgermane and germanium tetrachloride in the absence as well as in the presence of aluminum chloride is also mentioned.

A broad study of the catalyzed alkyl–halogen redistribution reaction on germanium has been reported recently (*244*, *284*). In these studies, germanium tetrachloride was equilibrated mainly with tetrabutylgermane and also other tetraalkylgermanes, such as the methyl, ethyl, *n*-propyl, *n*-pentyl, *n*-hexyl, and phenyl derivative. The composition of the mixtures after reaction (generally several hours between 120° and 200° C) was established by isolating the compounds by a combined distillative and conversion method. The results were estimated to be reliable within 5% to 10% and indicate that the presence of aluminum chloride is required for the transfer of butyl groups, with this transfer probably proceeding via butylaluminum halides. Furthermore, in almost all of the experiments, there is some loss of butyl groups, probably thermally split off as butene, which actually has been detected in the reaction products. Calculation of equilibrium constants was possible in only part of the cases since in many experiments an insufficient number of compounds was determined quantitatively. In the cases where information was available, it turned out that the constant $K_1 = [GeCl_4][Bu_2GeCl_2]/[BuGeCl_3]^2$ ranged from about 70 to 2 and the constant $K_2 = [BuGeCl_3][Bu_3GeCl]/[Bu_2GeCl_2]^2$ varied in order of magnitude from 0.05 to 1. In the second paper (*244*) by these authors, K_1 for various alkyl groups other than butyl varied between 0.01 and 3. Based on these calculations, it appears that equilibrium was not reached in all of the experiments.

In a kinetic study of the exchange of methyl groups for chlorine atoms on germanium at 300° C in the presence of 0.1% of aluminum chloride, it is shown (*38*) that the reaction of Eq. (117)

$$Ge(CH_3)_4 + GeCl_4 \rightleftarrows (CH_3)_3GeCl + CH_3GeCl_3 \qquad (117)$$

involving the first exchange process is faster than the succeeding ones. The next reaction, which is about 100-fold slower, is shown in Eq. (118)

$$(CH_3)_3GeCl + CH_3GeCl_3 \rightleftarrows 2(CH_3)_2GeCl_2 \qquad (118)$$

Additional reactions of the form of Eq. (119) were found to be considerably slower than those of the preceding equations except for the case where $j = 4$ and $k = 1$, which is about as fast as the reaction of Eq. (118).

$$(CH_3)_jGeCl_{4-j} + (CH_3)_kGeCl_{4-k} \rightarrow (CH_3)_{j-1}GeCl_{5-j} + (CH_3)_{k+1}GeCl_{3-k} \qquad (119)$$

Equilibrium in this system is reached in about 30 days at 300° C, resulting in the following constants:

$$K_1 = [(CH_3)_2GeCl_2][GeCl_4]/[CH_3GeCl_3]^2 \leqslant 10^{-8} \tag{120}$$

$$K_2 = [(CH_3)_3GeCl][CH_3GeCl_3]/[(CH_3)_2GeCl_2]^2 = (5 \pm 0.4) \times 10^{-3} \tag{121}$$

$$K_3 = [(CH_3)_4Ge][(CH_3)_2GeCl_2]/[(CH_3)_3GeCl]^2 = (2 \pm 9) \times 10^{-4} \tag{122}$$

d. *Other Exchange Equilibria on Germanium.* The equilibrium data presented in Table XII and XIII demonstrate that halogen–halogen exchanges on methylgermanium moieties are close to the case calculated for random distribution. Nonrandom behavior was found for halogen–methylthio and halogen–methoxyl exchanges.

TABLE XII

EQUILIBRIUM CONSTANTS FOR SUBSTITUENT INTERCHANGE ON THE METHYLGERMANIUM MOIETY

Z	T	K_1[a]	s_1[b]	K_2[c]	s_2[b]	Temperature (°C)	Equilibrium reached (hours)	References
Cl	Br	0.412	0.034	0.415	0.033	35°	<1	*195*
Br	I	0.444	0.034	0.421	0.030	35°	<1	*195*
Cl	I	0.719	0.061	0.793	0.066	35°	<1	*195*
Cl	OCH_3	0.013	0.002	0.021	0.002	35°	<20	*182*
Br	OCH_3	0.040	0.014	0.021	0.007	35°	<3	*182*
I	OCH_3	0.152	0.014	0.106	0.012	35°	<4	*182*
Cl	SCH_3	0.040	0.006	0.048	0.006	120°	<197	*182*
Br	SCH_3	0.032	0.008	0.031	0.007	120°	<42.5	*182*
I	SCH_3	0.033	0.005	0.043	0.006	120°	<17.5	*182*
Ideal randomness		0.333		0.333				

[a] $K_1 = [CH_3GeZ_2T][CH_3GeT_3]/[CH_3GeZT_2]^2$.

[b] Standard error.

[c] $K_2 = [CH_3GeZ_3][CH_3GeZT_2]/[CH_3GeZ_2T]^2$.

An equilibrium constant which is larger than the random value is observed for the exchange of methoxyl with methylthio groups. Similar values also have been found for the exchange of these substituents on the dimethylsilicon moiety.

TABLE XIII

EQUILIBRIUM CONSTANTS FOR SUBSTITUENT INTERCHANGE ON THE DIMETHYLGERMANIUM MOIETY

Z	T	K_1[a]	s[b]	Temperature (°C)	Equilibrium reached (hours)	References
Cl	Br	0.302	0.018	120°	<27	*199*
Cl	I	0.674	0.068	25°	<2.5	*199*
Br	I	0.344	0.008	25°	<18	*199*
Cl	OCH_3	0.011	0.005	25°	<24	*193*
Br	OCH_3	0.011	0.002	25°	<24	*193*
I	OCH_3	0.054	0.017	25°	<24	*193*
Cl	SCH_3	0.055	0.005	25°	<100	*194*
Br	SCH_3	0.025	0.008	25°	<30	*194*
I	SCH_3	0.012	0.001	25°	<3	*194*
OCH_3	SCH_3	2.60	0.11	120°	<46	*291*
Ideal randomness		0.250				

[a] $K_1 = [(CH_3)_2GeZ_2][(CH_3)_2GeT_2]/[(CH_3)_2GeZT]^2$.

[b] Standard error.

The rates of equilibration are fastest for halogen–halogen and halogen–methoxyl interchange, with equilibrium being reached in the order of magnitude of hours or maybe even minutes at room temperature. Exchanges involving the methylthio group require somewhat longer, with the rate being faster for iodine than for bromine and the latter being faster than for chlorine. A temperature of 120° C is required for the interchange of methoxyl with methylthio groups on the dimethylgermanium moiety.

e. *Exchanges on Digermanium Compounds.* Mixed hexaalkyldigermanes of the general formula $Ge_2(CH_3)_iR_{6-i}$, where $R = C_2H_5$, n-C_3H_7, or iso-C_3H_7, were obtained in 7–35% yield by a modified reaction (*265*) of the $GeCl_4$ reaction with mixed Grignard reagents or mixed alkyllithium compounds. Diethyltetramethyldigermane and tetramethyldi-*n*-propyldigermane were isolated from the products of the alkyllithium reactions, and their isomer ratios were found to be close to the values calculated on the assumption of a random distribution of alkyl groups. There is some evidence that this reaction also results in mixed octaalkyltrigermanes. Unfortunately, exchange reactions using Ge_2R_6 and Ge_2R_6' as starting materials have not been run.

f. *Ring–Ring Equilibria.* It has been reported (*34*) that dimethylgermanium oxide exists in three oligomeric forms. Recently (*185*), however, it was found by proton NMR that any of the three forms of dimethylgermanium oxide or mixtures thereof, when dissolved in an inert solvent tended to approach an equilibrium state. This equilibrium state is characterized by the coexistence of the trimeric (−0.495 ppm) and tetrameric (−0.472 ppm) species, with the proportions of the two depending on the overall concentration and temperature. Quantitative evaluation of a series of NMR spectra of equilibrated dimethylgermanium oxide at various dilutions gave the following average value for the ring–ring equilibrium constant at 35° C:

$$K^{\circ\circ}_{4,3} = \{[(CH_3)_2GeO]_4\}^3/\{[(CH_3)_2GeO]_3\}^4 = 6.0 \pm 0.3 \text{ liters/mole} \qquad (123)$$

The equilibrium is concentration- and dilution-dependent, i.e., the trimeric species will be preferred in dilute solution and high temperatures, and the tetramer in the concentrated ones and at low temperatures. Rate studies of the interconversion of the tetramer into the trimer indicate that the half-life of the reaction is ~30 minutes when diluted with 58 parts of carbon tetrachloride.

g. *Redistribution Equilibria in Families of Germanium Compounds.* Interest in macromolecular species of germanium declined after it had become apparent that suitable germanium compounds could not be condensed to materials of silicone like properties. This area of research, however, was revived very recently when it turned out that exchange reactions on germanium proceed quite rapidly. Extrapolating from the results obtained on simple exchange equilibria on germanium, it was anticipated that "labile polymers" could be obtained which would be ideally suited for study by NMR.

Equilibria resulting from mixing various proportions of dimethyldihalogermanes, $(CH_3)_2GeT_2$ (T = Cl, Br, or I) with dimethylgermanium oxide (*193*) or dimethylgermanium sulfide (*194*), respectively, are interpreted in terms of ring–ring, ring–chain, and chain–chain equilibria based on quantitative proton NMR data. Representative reactions describing the dynamic equilibrium state are given in Eqs. (107)–(109) by substituting Ge for Si, halogen for T, and O or S for Y. Equilibrium constants for these systems are listed in Table XIV.

These data were obtained on the a priori stipulation that the ring–ring equilibrium of Eq. (123) (due to thermodynamic reasons) must also apply to these systems and the ring–chain constants—regardless of the terminating

TABLE XIV

EQUILIBRIUM CONSTANTS IN FAMILIES OF GERMANIUM COMPOUNDS[a]

T	Y	Family of compounds	K_1	K_3°	K_4°	References
Cl[b]	O	α,ω-Dichloropolydimethylgermoxanes	0.021	0.87	1.4	*193*
Br[b]	O	α,ω-Dibromopolydimethylgermoxanes	0.043	0.87	1.4	*193*
I[b]	O	α,ω-Diiodopolydimethylgermoxanes	0.27	0.87	1.4	*193*
Cl[c]	S	α,ω-Dichloropolydimethylgermthianes	0.09	50	—	*194*
Br[c]	S	α,ω-Dibromopolydimethylgermthianes	0.06	50	—	*194*
I[c]	S	α,ω-Diiodopolydimethylgermthianes	0.09	50	—	*194*

[a] $K_1 = [(CH_3)_2GeT_2]$[middle groups in chains]/[end groups]^2; K_3° and K_4° are ring–chain constants for ring sizes 3 or 4 [defined by Eq. (29)].

[b] At 35°C.

[c] At 120°C.

group T—must each have a fixed value for Y = O or S, respectively, although the value of the constant K_1 may differ greatly, as seen in Table XIV.

h. *Exchange Rates in Families of Germanium Compounds.* The NMR line shapes of spectra of equilibrated samples of dihalopolydimethylgermoxanes (see Fig. 8) permit an estimate of the preexchange lifetimes (*193*, *236*) of the species in these mixtures. In the neat liquids, lifetimes were found to be of the order of 0.1 second for exchange processes in the chain part of the systems. Exchanges involving rings, i.e., chain–ring as well as ring–ring interchanges, are much slower, as evidenced by the fact that the NMR signals for the ring molecules consistently exhibit the narrow natural line width. These observations indicate that the chain species present in equilibrated mixtures of this type are quite labile. Therefore, it appears to be an almost hopeless task to attempt to isolate even the shorter chain molecules by ordinary separation methods under the usual conditions. If, however, some low-temperature method should give a separation, the resulting isolated species—when brought to room temperature—will undoubtedly rearrange rapidly to the equilibrium distribution of molecules characteristic of that particular overall composition.

In a kinetic study (*194*) of the scrambling of sulfur with chlorine on the dimethylgermanium moiety in a mixture of 1 mole of $[(CH_3)_2GeS]_3$ and 3 moles of $(CH_3)_2GeCl_2$ at 35° C, it is shown that the rate is quite fast but not fast enough to cause line-broadening. Equilibrium is reached in several hours at this temperature and the mechanism appears to be quite complex.

3. *Tin*

a. *Exchange of Tin–Carbon with Tin–Carbon Bonds.* Extending the studies on mixed tetraalkyllead compounds, Calingaert (*44*) also investigated the redistribution of alkyl groups on tin. The data given for redistribution of tetramethyltin with tetraethyltin in the presence of 2.5 mole % of aluminum chloride are of somewhat lower order of accuracy than those obtained for the lead compounds due to difficulties in the distillative assay of the equilibrated mixture. It was concluded, however, that these redistribution equilibria are also random. Tetrabutyltin and tetraphenyltin (*133*) were found to undergo redistribution in the presence of $AlCl_3$ at 190° C to give the mixed butylphenyltin compounds. Similar observations (*134*) were made in the systems tetraethyltin vs tetraisobutyltin; tetrabutyltin vs tetraisobutyltin; and tetrabutyltin vs tetraphenyltin. Using gas chromatography as the separation method, the systems $Sn(CH_3)_4$ vs $Sn(C_2H_5)_4$; $Sn(CH_3)_4$ vs $Sn(n\text{-}C_3H_7)_4$; $Sn(CH_3)_4$ vs $Sn(n\text{-}C_4H_9)_4$; and $Sn(n\text{-}C_3H_7)_4$ vs $Sn(n\text{-}C_4H_9)_4$ were found to undergo random redistribution (*232*).

b. *Exchange of Tin–Carbon with Tin–Halogen Bonds.* Perhaps one of the most thoroughly investigated exchange reactions in tin chemistry is the redistribution of tin tetraalkyls or tetraaryls with tin tetrahalides (*186*). However, most of these investigations were aimed toward preparative uses of these reactions rather than toward elucidation of the general aspect of equilibrium control or the kinetics of the exchange processes.

Proton NMR (*104*, *187*) and gas chromatography (*220*) studies of the kinetics of the system $Sn(CH_3)_4$ vs $SnCl_4$ or $SnBr_4$ and $Sn(C_2H_5)_4$ vs $SnCl_4$ show that in the temperature range from 0° to 50° C, there is one predominant fast reaction, Eq. (123), which proceeds spontaneously, even in dilute solution (R = alkyl)

$$SnR_4 + SnCl_4 \rightarrow R_3SnCl + RSnCl_3 \tag{123}$$

This reaction goes to completion before any further reactions are seen and has been observed over a wide range of concentrations, temperatures, and mole ratios of reactants.

The reactions proceeding after the reaction of Eq. (123) has been completed are much slower. For equimolar amounts of initial reactants, the major process is described by Eq. (124).

$$R_3SnCl + RSnCl_3 \rightarrow 2\ R_2SnCl_2 \tag{124}$$

For mole ratios $SnR_4 : SnCl_4 > 1$, there is an excess of tetraalkyltin over that required for the reaction of Eq. (123). Thus, after completion of reaction

(123), the resulting mixture of SnR_4, R_3SnCl, and $RSnCl_3$ was seen to undergo further reaction according to Eqs. (125 and 126)

$$SnR_4 + RSnCl_3 \rightarrow R_3SnCl + R_2SnCl_2 \quad (125)$$

$$SnR_4 + R_2SnCl_2 \rightarrow 2\ R_3SnCl \quad (126)$$

For mole ratios $SnR_4 : SnCl_4 < 1$, there is an excess of tin tetrachloride and after completion of the reaction of Eq. (123), the reaction of Eq. (127) becomes significant. As the amount of R_2SnCl_2 builds up, the reaction of Eq. (128) contributes to the formation of $RSnCl_3$, which is the observed main product for such mole ratios.

$$R_3SnCl + SnCl_4 \rightarrow R_2SnCl_2 + RSnCl_3 \quad (127)$$

$$R_2SnCl_2 + SnCl_4 \rightarrow 2\ RSnCl_3 \quad (128)$$

At equilibrium, the distribution of alkyltin halides may be described by three equilibrium constants, the values (*104*) of which are given below for the system $Sn(CH_3)_4$ vs $SnCl_4$.

$$K_1 = [(CH_3)_4Sn][(CH_3)_2SnCl_2]/[(CH_3)_3SnCl]^2 = 3 \times 10^{-3} \quad (129)$$

$$K_2 = [(CH_3)_3SnCl][CH_3SnCl_3]/[(CH_3)_2SnCl_2]^2 = 1 \times 10^{-4} \quad (130)$$

$$K_3 = [(CH_3)_2SnCl_2][SnCl_4]/[CH_3SnCl_3]^2 = 7 \times 10^{-2} \quad (131)$$

Data for the analogous ethyl (*220*) compounds indicate that the equilibrium constants of the type of Eqs. (129)–(131) are very small for this system also. Consequently, it may be concluded that, in redistribution equilibria involving alkyl groups and halogens on tin, the mixed alkyltin halides are preferred. Mixtures having an overall composition corresponding to one of the mixed alkyltin halides contain this species in major amounts.

Similar reactions, although much slower, take place when SnR_4 is equilibrated with $GeCl_4$ or $SiCl_4$, respectively (*104*, *152*, *179*).

c. ***Exchange of Tin–Carbon Bonds with Tin–Oxygen Bonds.*** Such an exchange has been observed to occur when trimethyltin methoxide was distilled at atmospheric pressure (5)

$$2\ (CH_3)_3SnOCH_3 \rightleftarrows (CH_3)_4Sn + (CH_3)_2Sn(OCH_3)_2 \quad (132)$$

The resulting dimethyltin dimethoxide appeared to be stable with respect to disproportionation.

d. ***Exchange of Tin–Carbon with Tin–Hydrogen Bonds.*** Evidence for redistribution of alkyl or aryl groups with hydrogen atoms on tin is seen in the fact that samples of alkyl- or aryltin hydrides (*218*, *221*) containing traces of impurities redistribute into tetraalkyltin and tin hydride which spontaneously decomposes into tin and hydrogen, with the overall process given by Eq. (*133*).

$$4\ \mathrm{R}_i\mathrm{SnH}_{4-i} \rightarrow i\ \mathrm{SnR}_4 + (4-i)\mathrm{Sn} + (8-2i)\mathrm{H}_2 \qquad (133)$$

The impurities such as grease, acids, or metals act as catalysts and the driving force of the overall reaction of Eq. (133), once it is initiated, is the formation of a gaseous and solid phase. With careful exclusion of such catalysts, alkyl or aryltin hydrides appear to be stable indefinitely at room temperature.

e. *Exchange of Tin–Hydrogen Bonds with Tin–Halogen Bonds.* Redistribution equilibria involving the exchange of hydrogen with chlorine atoms on dialkyltin moieties (*219*, *254*) according to Eq. (134)

$$\mathrm{R_2SnH_2} + \mathrm{R_2SnT_2} \rightleftarrows 2\ \mathrm{R_2SnTH} \qquad (134)$$

have been observed for R = ethyl, butyl, or phenyl and T = F, Cl, Br or I. It appears that the equilibrium of Eq. (134) is quite labile, since upon distillation the dialkyltin hydride may be removed from the reaction mixture. However, upon reaction of the equilibrated mixtures with olefinic double bonds, products of the general type $\mathrm{R_2ClSnCR'_2{-}CR'_2H}$ are obtained in almost quantitative yield. This fact has been interpreted to mean that the equilibrium mixture of Eq. (134) consists preferentially of the mixed halogen hydride. Very recently (*252*), a proton NMR study of the equilibrium of Eq. (134) for R = butyl and T = F, Cl, Br, or I, showed that it lies almost completely to the side of the halide hydride. Upon mixing of the reactants in equimolar quantities at room temperature, a new single resonance peak appeared, shifted downfield from the main peak shown by the protons directly bonded to tin in di-*n*-butyltin dihydride. Simultaneously, the peak representing the dihydride disappeared.

Exchange reactions of this type but involving tributyltin and butyltin moieties have also been studied (*251*) and are summarized in Eqs. (135) and (136).

$$\mathrm{(C_4H_9)_2SnHX} + \mathrm{(C_4H_9)_3SnH} \rightleftarrows \mathrm{(C_4H_9)_2SnH_2} + \mathrm{(C_4H_9)_3SnX} \qquad (135)$$

$$n\mathrm{(C_4H_9)_3SnH} + \mathrm{C_4H_9SnX_3} \rightleftarrows \mathrm{(C_4H_9)SnH}_n\mathrm{X}_{3-n} + n\ \mathrm{(C_4H_9)_3SnX} \qquad (136)$$

Since the above reactions proceed almost completely from left to right, it appears that similar to the redistribution of chlorine and hydrogen atoms between various moieties of alkylsilicon, the halogens prefer to be bonded to the tin moiety bearing the larger number of alkyl groups.

f. *Exchange of Tin–Hydrogen Bonds with Other Bonds.* As evidenced by infrared spectroscopy, exchange of hydrogen with oxygen atoms occurs upon mixing di-*n*-butyltin dihydride with bis(tri-*n*-butyltin) oxide at room temperature, with Eq. (137) going to completion.

$$(C_4H_9)_2SnH_2 + [(C_4H_9)_3Sn]_2O \rightarrow 2(C_4H_9)_3SnH + (C_4H_9)_2SnO \qquad (137)$$

However, when performed at ~100° C, the two reactants eliminate water and form species containing tin–tin bonds (*222*, *250*). Rapid exchange has also been observed for hydrogen atoms with methoxyl groups bonded to tin in organotin compounds, although at elevated temperatures, methanol is generated, which is an indication of condensations resulting in tin–tin bonds.

For $T = OOCCH_3$ in Eq. (134), the resulting equilibrium mixture after exchange of hydrogen with acetate groups was found to contain both kinds of hydride species (*253*). However, no information is given about the relative concentrations of the three species at equilibrium.

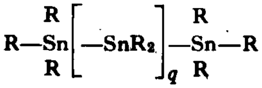
Recently, exchange of hydrogen atoms bonded to tin with a series of other groups bonded to tin has been observed, e.g., $OSnR_3$, OR, $SSnR_3$, CN, and PR_2. In each of these equilibria, condensation reactions compete with the exchange reactions (*223*).

g. *Redistribution Equilibria in Families of Tin Compounds.* Substituting tin for silicon in Eqs. (106)–(108), families of α,ω-disubstituted polydimethyltin compounds are obtained. For $Y = S$ and $T =$ halogen in these equations, equilibria in α,ω-dihalopolydimethyltin sulfides are described (*190*). These result from the exchange of bridging sulfur in trimeric dimethyltin sulfide with halogens in dimethyltin dihalides. Proton NMR spectra of the supercooled liquids or their concentrated solutions in an inert solvent showed one single, rather sharp resonance peak for any composition based on $T = Cl$, Br, or I. The chemical shift of these single resonances varied approximately linearly with the relative amounts of the two reagents. Dilution of the equilibrated mixtures with carbon tetrachloride caused broadening of the observed single peaks for the systems for which $T = Cl$ or Br. For $T = I$, the single NMR signal could be resolved into three separate resonances at 10-fold or greater dilution, representing the *neso* molecule, $(CH_3)_2SnI_2$; end groups, $I(CH_3)_2SiS_{1/2}$; and middle groups, $S_{1/2}(CH_3)_2SnS_{1/2}$. The equilibrium constant is $K_1 = [neso][\text{middles}]/[\text{ends}]^2 = 0.223 \pm 0.013$, which is close to the ideal random case. Due to poor resolution of the NMR signals, the question whether rings or chains are preferred at equilibrium cannot be answered at the present time.

From the variation in line width upon dilution with solvent, the average preexchange lifetimes at room temperature for a given species in the systems $[(CH_3)_2SnS]$ vs $(CH_3)_2SnT_2$ have been estimated. In one molar solution for $T = Cl$ or Br, the pre-exchange lifetime is of the order of 10^{-4} second, with this value increasing to $\sim 10^{-2}$ second for $T = I$.

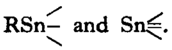
Corresponding oxygen compounds, Sn for Si and $Y = O$ in Eqs. (107) and (109), have not been realized, probably due to complications resulting from formation of superstructures using *d* orbitals of the tin atoms and electron-pair donors such as oxygen.

Formally one may consider equilibria involving catenated tin compounds of the type

 (138)

$$\mathrm{R{-}\overset{R}{\underset{R}{Sn}}\left[{-}SnR_2\right]_q{-}\overset{R}{\underset{R}{Sn}}{-}R} \qquad (138)$$

as resulting from scrambling of alkyl groups R with tin–tin bonds. Thus, the *neso* molecule would be SnR_4; an end group, R_3Sn—; a middle group, —SnR_2—; and branches,



However, such catenated molecules are metastable and, upon thermal equilibration form elemental tin (*25*, *142*), as shown in the reactions of Eqs. (139 and (140).

$$3\,(R_2Sn)_n \rightarrow n\,R_3Sn{-}SnR_3 + n/k(Sn)_k \qquad (139)$$

$$2\,(R_2Sn)_n \rightarrow n\,SnR_4 + n/k(Sn)_k \qquad (140)$$

Apparently, the equilibrium lies completely to the side of the *neso* molecule, SnR_4, and the most-branched building units,

so that K_1, K_2, and K_3 are all large ($> \sim 10^4$). Also hexachlorodistannane, $Cl_3SnSnCl_3$, disproportionates easily into $SnCl_4$ and $SnCl_2$ above $-65°$ C (*303*).

4. *Lead*

a. *Exchange of Lead–Carbon Bonds with Lead–Carbon Bonds.* Alkyl–alkyl group exchange equilibria on lead were studied by refluxing mixtures of two tetraalkyl leads in a solvent at 60° to 80° C for ~5–7 hours in the presence of a catalyst (*41*, *44*, *45*). Catalysts were metal salts, such as alkyllead salts, metal halides, such as $AlCl_3$, $AlBr_3$, $SnCl_2$, $FeCl_3$, and many others. In the absence of a catalyst, no interchange of alkyl groups takes place, and neither decomposition nor other side reactions were observed. The redistribution products were isolated by quantitative fractional distillation after the catalyst had been removed to avoid reequilibration during the distillation process. The following systems were investigated: $Pb(CH_3)_4$ vs $Pb(C_2H_5)_4$; $Pb(CH_3)_4$ vs $Pb(n\text{-}C_3H_7)_4$; $Pb(CH_3)_4$ vs $Pb(\text{iso-}C_3H_7)_4$; $Pb(CH_3)_4$ vs $Pb(\text{iso-}C_4H_9)_4$; $Pb(CH_3)_4$ vs $Pb(\text{tert-}C_4H_9)_4$; $Pb(CH_3)_4$ vs $Pb(C_6H_5)_4$; $Pb(C_6H_5)_4$ vs $Pb(p\text{-}CH_3C_6H_4)_4$. By comparing the experimentally determined amounts of each species at equilibrium with the values calculated on the basis of ideal random distribution, it was concluded that these redistribution equilibria follow random statistics.

For the system most thoroughly investigated, $Pb(CH_3)_4$ vs $Pb(C_2H_5)_4$, the data reported in Table II of Calingaert *et al.* (*44*) have been evaluated in terms of weighted-average equilibrium constants with the aid of one of the computer programs developed in this laboratory.

$$K_1 = [Pb(CH_3)_4][Pb(CH_3)_2(C_2H_5)_2]/[Pb(CH_3)_3(C_2H_5)]^2 = 0.356 \pm 0.020 \qquad (141)$$

$$K_2 = [Pb(CH_3)_3(C_2H_5)][Pb(CH_3)(C_2H_5)_3]/[Pb(CH_3)_2(C_2H_5)_2]^2 = 0.426 \pm 0.023 \qquad (142)$$

$$K_3 = [Pb(CH_3)_2(C_2H_5)_2][Pb(C_2H_5)_4]/[Pb(CH_3)(C_2H_5)_3]^2 = 0.317 \pm 0.012 \qquad (143)$$

The good agreement of the equilibrium constants with the values for ideal randomness (Table II) confirms Calingaert's conclusions. Analyses of tetramethyl- and tetraethyllead redistribution mixtures today may be performed conveniently by gas chromatography (*20*, *67*, *232*).

The redistribution of alkyl groups in trialkyllead halides may be considered as occurring on the "halogen–lead moiety" which is presumed to remain intact during the exchange processes (*49*). In these studies, trimethyllead chloride was equilibrated with triethyllead chloride by refluxing in acetone. A catalyst was not required since the trialkyllead halides act as catalysts themselves. After 5 hours at 60° C, the mixture of trialkyllead halides was analyzed by adding methylmagnesium bromide to the solution, thus converting the alleged trialkyllead halides to tetraalkyllead compounds, according to Eq. (144). The latter were analyzed in the usual manner by fractional distillation.

$$(CH_3)_i(C_2H_5)_{3-i}PbCl + CH_3MgBr \rightarrow (CH_3)_{i+1}(C_2H_5)_{3-i}Pb + MgClBr \qquad (144)$$

Using the set of data as reported by Calingaert, equilibrium constants were calculated and are as follows:

$$K_1 = [(CH_3)_3PbCl][(CH_3)(C_2H_5)_2PbCl]/[(CH_3)_2(C_2H_5)PbCl]^2 = 0.293 \tag{145}$$

$$K_2 = [(CH_3)_2(C_2H_5)PbCl][(C_2H_5)_3PbCl]/[(CH_3)(C_2H_5)_2PbCl]^2 = 0.304 \tag{146}$$

The values of K_1 and K_2 are quite close to the random values for $\nu = 3$ in Table II.

Considering the reported *(11)* tendency of trialkyllead compounds to disproportionate according to Eq. (147)

$$2\ R_3PbX \rightleftarrows R_2PBX_2 + R_4Pb \tag{147}$$

under conditions which are similar to the ones reported by Calingaert for the exchange of alkyl groups on the "lead monochloride moiety," it has to be assumed that the equilibria in the system $(CH_3)_3PbCl$ vs $(C_2H_5)_3PbCl$ probably are more complex than reported. It is very likely that in addition to alkyl–alkyl exchanges, a considerable part of the trialkyllead chlorides will equilibrate also according to Eq. (147). The conversion of the reaction mixture to tetraalkylleads for analytical purposes probably masks disproportionations of the type of Eq. (147). Therefore it is doubtful whether the constants of Eqs. (145) and (146) are meaningful.

b. *Exchange of Lead–Carbon Bonds with Lead–Halogen Bonds.* Alkyl– or aryl–halogen redistribution on lead *(11)* was observed when triethyllead chloride or triphenyllead chloride was refluxed in a solvent. Redistribution products were formed according to the reaction of Eq. (147) (X = halogen). For $R = C_6H_5$, about 10% of the triphenyllead chloride had disproportionated. Similar results were obtained for $R = C_2H_5$. The existence of an equilibrium is demonstrated by the fact that tetraphenyllead when refluxed with equimolar amounts of diphenyllead dichloride yielded 86% triphenyllead chloride. The analogous reaction for $R = C_2H_5$ gave 39% triethyllead chloride.

c. *Exchange of Lead–Carbon Bonds with Lead–Oxygen Bonds.* The results of a study of the thermal decomposition at 130° C of $(C_6H_5)_3Pb(OOCCH_3)$ and $(C_2H_5)_3Pb(OOCCH_3)_2$ in *n*-nonane in the absence of air were interpreted on the basis of redistribution of alkyl with acetate groups on lead *(4)*. The following equilibria were observed:

$$2\ (C_2H_5)_3Pb(OOCCH_3) \rightleftarrows (C_2H_5)_2Pb(OOCCH_3)_2 + (C_2H_5)_4Pb \tag{148}$$

$$2\ (C_2H_5)_2Pb(OOCCH_3)_2 \rightleftarrows (C_2H_5)_3Pb(OOCCH_3) + (C_2H_5)Pb(OOCCH_3)_3 \tag{149}$$

$$(C_2H_5)Pb(OOCCH_3)_3 \rightleftarrows Pb(OOCCH_3)_2 + C_2H_5OOCCH_3 \tag{150}$$

Rate studies showed that under otherwise identical conditions, reaction (149) is more rapid than reaction (148). Due to the decomposition reaction of Eq. (150), which also proceeds quite fast, quantitative data describing the redistribution equilibria could not be obtained.

d. *Redistribution Equilibria in Families of Lead Compounds.* No polymeric systems similar to the ones discussed for silicon, germanium, or tin have been reported. However, catenated species, such as hexaalkyl- and hexaaryllead were found to disproportionate upon heating—with redistribution of alkyl groups and Pb—Pb bonds—according to Eq. (151)

$$2\ R_3PbPbR_3 \rightarrow 3\ R_4Pb + 1/k\ (Pb)_k \tag{151}$$

The reaction of Eq. (151) indicates that the equilibrium in the system PbR_4 vs Pb is shifted completely towards the side of the *neso* molecule, PbR_4, and the most-branched building unit, tetrafunctional elemental lead. The existence of equilibria of the type of Eq. (151) is supported by the finding that hexaphenyldilead which has been tagged with radium D (a radioactive lead isotope) exchanges rapidly with tetraphenyllead (*239*).

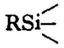
The ease of disproportionation according to Eq. (151) depends on the nature of R. Hexaphenyldilead, when refluxed in toluene for a few hours, gives 90% of the expected tetraphenyllead. The following R groups are arranged in the order of decreasing ease of disproportionation (*96*):

Ethyl, methyl > *m*-tolyl, phenyl > *p*-tolyl, *p*-ethoxyphenyl, *p*-methoxyphenyl, *o*-tolyl, *o*-ethoxyphenyl, *o*-methoxyphenyl > cyclohexyl, mesityl, 1-naphthyl. The reaction is catalyzed by metal salts such as aluminum chloride.

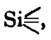
5. *Discussion*

Since redistribution equilibria have been studied most extensively involving compounds of Group IV elements, it appears appropriate to discuss the general trends seen in the redistribution equilibria and the redistribution rates as well as the nature of the ring–chain distribution in the families of compounds of these elements. When comparing the equilibrium distribution of a given pair of substituents—as represented by the equilibrium constant—on a central atom of Group IV or a moiety thereof, it appears that deviations from randomness are independent of the central atom or moiety. Thus, exchange equilibria involving similar or closely related substituents for all practical purposes, may be considered as random, e.g., halogen or pseudohalogen vs halogen or pseudohalogen groups, alkyl vs alkyl groups, or alkoxyl vs alkoxyl groups. Nonrandom distribution is generally observed for pairs of dissimilar or unrelated substituents, such as halogen vs alkyl, halogen vs alkoxyl, halogen vs alkylthio, or halogen vs dialkylamino groups, with the latter pair exhibiting extreme nonrandom behavior. Enthalpies of nonrandom redistribution reactions are larger or smaller than zero and therefore these equilibria are temperature-dependent. Ideal random equilibria, for which the enthalpy is zero, must, of course, be temperature-independent.

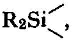
The rates of redistribution reactions for given pairs of substituents on a central atom or moiety of Group IV, under comparable conditions, increases in the order Si < Ge < Sn < Pb. Furthermore, for a given element, the exchange rates increase upon reducing the sites available for exchange. Exchange reactions proceed faster on the alkylsilicon moiety,



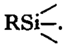
than on tetrafunctional silicon,



and the same substituent-exchange process is faster on the dialkylsilicon moiety,



than on



Also, the equilibria in the families of compounds of Group IV elements reveal interesting trends. The α,ω-dihalopolydimethylsiloxanes equilibrate quite slowly (with half-lives of ~3 hours at 200° C in the presence of $AlCl_3$ as catalyst) to form essentially all chain molecules. The amounts of rings in this system become significant only at $R \equiv Cl/Si$ values close to zero (in accord with the mathematical requirement that the ring population increase rapidly as R diminishes close to zero). At the composition $R = 0$, the rings represent only about 15 wt % of the total silicon (as measured for the α,ω-dimethylpolydimethylsiloxanes). In contrast, the α,ω-dihalopolydimethylgermoxanes equilibrate extremely rapidly, as evidenced by the line-broadening of the NMR signals. The average preexchange lifetime in this system is of the order of 0.1 second at 35° C. Molecules in this system, therefore, are quite labile and—unlike the analogous silicon compounds—the lower-molecular-weight chain molecules cannot be isolated by fractional distillation nor by any other ordinary separations method. Furthermore, at the high dilutions where the germoxanes were investigated, cyclic compounds predominate and chain molecules are present in only small amounts. This apparent difference relative to the analogous siloxanes, however, is not real since the data for the germoxanes were obtained at very high dilutions. Due to the fact that ring–chain equilibria are dilution-dependent, it is necessary to first extrapolate to zero dilution before a comparison can be made. At dilution zero, the ring–chain constants of the halogen-terminated dimethylgermoxanes show that the amounts of cyclic species must be small, being of the same order of magnitude as for the analogous siloxanes.

The silthiane systems equilibrate more slowly than the analogous siloxane systems but, in contrast to the latter, dimeric and trimeric ring molecules predominate at equilibrium. For the α,ω-dihalopolydimethylgermanium sulfides, the rates of equilibration were found to be quite rapid at room temperature but not fast enough to cause NMR line-broadening as in the dimethylgermoxane systems. In the dimethylgermanium sulfide systems as well as in the dimethylsilicon sulfide systems, the amount of rings at equilibrium was large compared to the chains. Information concerning ring–chain equilibria in the dimethyltin sulfides could not be obtained due to the very fast exchange rates. As indicated by line-broadening, exchange rates in the dimethyltin sulfide systems are about 10^4 times faster than the rates observed for the dimethylgermanium sulfide systems, and the latter systems equilibrate about 10^6 times faster than the dimethylsilicon sulfur systems. These findings stress that the great differences in behavior between analogous systems of silicon, germanium, and tin lie in the reaction rates rather than in the equilibrium constants describing the systems.

Considering the equilibrium constant for exchange of "monofunctional" oxygen (i.e., alkoxyl groups) with other substituents on the dimethylsilicon moiety, e.g., the systems $(CH_3)_2Si(OCH_3)_2$ vs $(CH_3)_2SiT_2$, and the corresponding systems involving "difunctional" oxygen, e.g., the systems $[(CH_3)_2SiO]$ vs $(CH_3)_2SiT_2$, the value of K_1 is always smaller for the first type of system than for the second. This indicates that a greater degree of nonrandomness is observed for the "monofunctional" oxygen system than for the chain portion of the "difunctional" oxygen system. The same is true for the corresponding data on the dimethylgermanium moiety and for "monofunctional" sulfur—e.g., the system $(CH_3)_2Si(SCH_3)_2$ vs $(CH_3)_2SiT_2$—and "difunctional" sulfur—e.g., the system $[(CH_3)_2SiS]$ vs $(CH_3)_2SiT_2$ on either the dimethylsilicon or dimethylgermanium moieties.

E. Group V

1. *Arsenic*

Of the equilibria in organoarsenic chemistry, only one system has been investigated quite thoroughly. Based on earlier reports that triphenylarsenic reacts with arsenic trichloride with exchange of phenyl and chloro groups (*173*, *235*), a quantitative study (*82*) of the resulting equilibria has been undertaken, yielding the equilibrium constants given in Eqs. (152) and (153) for a temperature of 252° C,

$$K_1 = [\mathrm{AsCl_3}][(\mathrm{C_6H_5})_2\mathrm{AsCl}]/[\mathrm{C_6H_5AsCl_2}]^2 = 5.7\times10^{-2} \tag{152}$$

$$K_2 = [\mathrm{C_6H_5AsCl_2}][(\mathrm{C_6H_5})_3\mathrm{As}]/[(\mathrm{C_6H_5})_2\mathrm{AsCl}]^2 = 5.9\times10^{-2} \tag{153}$$

and $K_1 = 7.0\times10^{-2}$ and $K_2 = 8.2\times10^{-2}$ for 304° C.

From these data, the enthalpies have been determined ($\Delta H_1 = 2.6$ and $\Delta H_2 = 3.8$ kcal). Studying these equilibria over a wider temperature range, a very satisfactory correlation of all data (*86*) was obtained from the constants $\ln K_1 = 1.784 - 4800/RT$ and $\ln K_2 = 6.639 - 10{,}500/RT$, giving somewhat differing values for the enthalpies, $\Delta H_1 = 4.8$ kcal and $\Delta H_2 = 10.5$ kcal. The disproportionation of phenylarsenic dichloride and diphenylarsenic chloride, respectively, as well as the comproportionation of arsenic trichloride with triphenylarsenic have been studied kinetically. At ~300° C, equilibrium is generally reached within several hours.

Also alkyl groups reorganize with halogen atoms on arsenic; however, only qualitative statements to this effect have been made in the literature e.g., in the systems $(\mathrm{CF_3})_3\mathrm{As}$ vs $\mathrm{AsI_3}$ (*79*, *295*); $(\mathrm{CF_3})_3\mathrm{As}$ vs $\mathrm{AsCl_3}$ (*66*); $(\mathrm{CH_2{=\!=}CH})_3\mathrm{As}$ vs $\mathrm{AsBr_3}$ (*155*); $(\mathrm{C_2H_5})_3\mathrm{As}$ vs $\mathrm{AsBr_3}$; and $(\mathrm{C_6H_5CH_2})_3\mathrm{As}$ vs $\mathrm{AsCl_3}$ (*174*)].

Evidence for exchange of arsenic–carbon with arsenic–oxygen and arsenic–sulfur bonds, respectively, is obtained from the thermal disproportionation of methylarsenous oxide (*143*) according to Eq. (154), of phenylarsenous oxide according to Eq. (155), and of alkyl or arylarsenous sulfides according to Eq. (156).

$$4\,\mathrm{CH_3AsO} \rightarrow [(\mathrm{CH_3})_2\mathrm{As}]_2\mathrm{O} + \mathrm{As_2O_3} \tag{154}$$

$$3\,\mathrm{C_6H_5AsO} \rightarrow (\mathrm{C_6H_5})_3\mathrm{As} + \mathrm{As_2O_3} \tag{155}$$

$$3\,\mathrm{RAsS} \rightarrow \mathrm{R_3As} + \mathrm{As_2S_3} \tag{156}$$

Owing to the insolubility of $\mathrm{As_2O_3}$ and $\mathrm{As_2S_3}$ in the common solvents and probably also in the alkyl and arylarsenous oxides and sulfides, respectively, the equilibria of Eqs. (154)–(156) are shifted completely to the right as a result of phase separation.

2. *Antimony*

Exchange of antimony–carbon bonds with antimony–halogen bonds in triphenylantimony and antimony trichloride upon heating at ~250° C for ~75 hours has been utilized for the preparation of phenylantimony chlorides (*108*, *109*). Also exchange of vinyl groups with chlorine atoms on antimony has been observed (*155*). Recently, however, a quantitative study of the kinetics of the reaction between trimethylantimony and antimony trichloride has been reported (*298*), details of which have been discussed in Section IV, A,1.

Exchange of antimony–carbon bonds with antimony–oxygen bonds is reported in a thorough study of the disproportionation of arylantimony oxides, RSbO (*126*, *127*). At moderately elevated temperatures (~100° C) in the solid state, the reaction of Eq. (157)

$$4\ RSbO \rightarrow (R_2Sb)_2O + Sb_2O_3 \qquad (157)$$

is bimolecular autocatalytic. The rates at which substituted arylantimony oxides disproportionate to bis(diarylantimony) oxides are greatly influenced by the character of the substituents on the benzene ring. The order of stability for some para substituents is $NO_2 > CH_3CO > Br > Cl > H > CH_3$. The disproportionation probably involves a free-radical mechanism.

At ~200° C, arylantimony oxides disproportionate (*144*) according to the reaction of Eq. (158)

$$3\ RSbO \rightarrow SbR_3 + Sb_2O_3 \qquad (158)$$

3. *Bismuth*

Similar to the other elements in this group, the exchange reactions studied first and most extensively involve the redistribution of bismuth–carbon bonds with bismuth–halogen bonds. Reactions of the type of Eqs. (159) and (160)

$$2\ BiR_3 + BiX_3 \rightarrow 3\ R_2BiX \qquad (159)$$

$$BiR_3 + 2\ BiX_3 \rightarrow 3\ BiRX_2 \qquad (160)$$

have been utilized for the preparation of aliphatic as well as aromatic bismuth halides; e.g., CH_3BiCl_2, CH_3BiBr_2, $C_2H_5BiCl_2$, $C_2H_5BiBr_2$ (*157*), iso-$C_4H_9BiBr_2$, iso-$C_5H_{11}BiBr_2$ (*158*), $(C_6H_5)_2BiBr$, $(C_6H_5)_2BiCl$ (*156*, *172*, *314*), $(ClC_6H_4)_2BiBr$, $ClC_6H_4BiBr_2$, (*56*). Mixed alkylbismuth compounds of the type $R_2R'Bi$ were found to be quite stable with respect to disproportionation when pure (*100*).

F. Group VI

Since sulfur chemistry lies beyond the scope of this review and organotellurium chemistry so far has not been of any impact on organometallic chemistry in general, this section will be restricted to the discussion of redistribution equilibria on selenium.

Scrambling equilibria in mixtures of dimethyl selenide and dichlorodiselenide as well as dimethyl diselenide and dichloro diselenide have been investigated recently (*103*). The reactions observed at room temperature to occur in such mixtures are scrambling of methyl groups and chlorine atoms on selenium as well as condensation polymerization resulting from the elimination of methyl chloride.

In the interaction of dimethyl diselenide and dichloro diselenide, it was shown by proton NMR that the first more-condensed species than the diselenide to appear in the spectra is the mixed tetraselenide, $CH_3SeSeSeSeCl$, Eq. (161).

$$CH_3SeSeCl + CH_3SeSeCl \rightarrow CH_3SeSeSeSeSeCl + CH_3Cl \tag{161}$$

Then follows continuing condensation and scrambling until the larger chains reorganize to give elemental selenium, leaving the monofunctional terminal substituents (with a selenium atom still attached to the methyl group) in shorter chain molecules. In the range of equimolar proportions of the reagents, the precipitate finally formed is metallic selenium which has been shown to consist of long spiralled chains (*105*, *280*). For ratios of the starting materials quite far from the equimolar mixture, the onset of the precipitation is slow, about 3–7 days at room temperature, and the precipitate has been shown to be composed of red selenium, Se_8. Thus, prior to precipitation of metallic selenium, it appears that complex equilibria are established involving ring and chain molecules with the latter being terminated by either two chlorine atoms, one chlorine atom and one methyl group, or two methyl groups, respectively. Similar quantitative studies in the analog sulfur systems where no precipitate is formed upon equilibration and where final equilibrium data could be obtained perhaps may be extrapolated to the selenium systems (*103*).

VI

REDISTRIBUTIONS IN COMPOUNDS OF TRANSITION METALS

A. Transition Metal Alkyls and Aryls

1. *Zinc and Cadmium*

Investigations of mixtures of dimethylzinc and dimethylcadmium in benzene by proton NMR resulted in a single rather broad signal, the chemical shift of which varied linearly with the relative composition (*163*). Moderately dilute solutions of the two components ($\sim 0.1\ M$) exhibited two proton signals, thus establishing rapid exchange of methyl groups in this system. The mean lifetime before exchange in these systems is of the order of 0.1 second.

An equimolar solution of dimethylzinc and dimethylmercury exhibited two sharp resonances indicating no or slow exchange. A similar observation was made with the dimethylcadmium–dimethylmercury system. The mean lifetime of a methyl group before exchange, therefore, has been estimated to be greater than 0.08 second for the first system and greater than 0.14 second for the latter system.

Rapid exchange was also observed between dimethylmagnesium and dimethylzinc or dimethylcadmium, respectively, with the average lifetime being of the order of < 0.009 second (*70*).

Earlier, attempts have been made to equilibrate dimethylzinc with diethylzinc in the presence of aluminum chloride. However, the distillative separation of the reaction mixture yielded only the two starting materials. In view of the above NMR evidence regarding rapid exchange which probably also takes place intramolecularly in zinc alkyls, it is quite understandable that mixed zinc alkyls were not separated (*47*).

Exchange of zinc–carbon bonds with zinc–halogen bonds has been observed to yield alkylzinc halides, RZnX (*274*).

2. *Mercury*

a. *Exchange of Mercury–Carbon Bonds with Mercury–Carbon Bonds.* Various methods, such as distillation, proton, or ^{19}F NMR and gas chromatography have been utilized to study exchange equilibria in mercury dialkyls and diaryls (*44*, *47*, *238*, *243*). The reported equilibrium constants for such exchanges are summarized in Table XV. These data indicate that alkyl–

TABLE XV

EQUILIBRIUM CONSTANTS FOR EXCHANGE REACTIONS ON MERCURY

Z	T	$K = \frac{[HgZ_2][HgT_2]}{[HgZT]^2}$	Temperature (°C)	References
CH_3	C_2H_5	0.33	25°	*44, 47*
CH_3	C_6H_5	0.23 ± 0.04	150°	*238*
CH_3	C_6F_5	$<10^{-3}$	150°	*238*
C_2H_5	n-C_3H_7	0.23	100°	*243*
C_2H_5	iso-C_3H_7	0.19	100°	*243*
C_2H_5	cyclo-C_3H_5	0.01	100°	*243*
C_2H_5	$CH_2{=}CH$	0.01	100°	*243*
C_2H_5	C_6H_5	0.2	100°	*243*
iso-C_3H_7	iso-C_3F_7	$<10^{-3}$	100°	*243*
$C_6H_5CH_2$	C_6H_5	0.31	120°	*238*
Ideal randomness		0.25		

alkyl, alkyl–aryl, and aralkyl–aryl exchanges essentially follow random statistics. The greatest degree of nonrandomness is found to occur in the redistributions involving alkylperfluoroalkyl or alkylperfluoroaryl groups. Because of the high electronegativity of perfluoroalkyl and perfluoroaryl groups and the suggestion that they are "pseudohalogens," it is not surprising that the equilibrium constants are very small, similar to the ones obtained for halogen–alkyl exchanges, thus favoring the formation of the mixed species. The abnormal values obtained for the constants for the exchange of ethyl groups with vinyl and cyclopropyl groups, respectively, has been interpreted to be the result of electronic delocalization in the strained three-member cyclopropane ring and different hybridization in the vinyl carbon atoms next to mercury.

In addition to these quantitative results, there are a few purely qualitative statements regarding exchange reactions on mercury in the literature, e.g., bis(pentachlorophenyl)mercury with diphenylmercury or dimethylmercury has been found to yield the respective mixed compounds (*228*).

b. *Exchange of Mercury–Carbon Bonds with Mercury–Halogen Bonds.* The reaction between dialkyl- or diarylmercury compounds with mercuric halides has long been used as a convenient synthetic route to alkyl- or arylmercuric halides. An attempt to obtain equilibrium constants for these reactions by conductance measurements was not successful (*132*). Proton

NMR studies in dilute organic solutions indicate that the methylmercuric halides exist in preponderant amounts in equilibrium mixtures with dimethylmercury and mercuric halides (*238*). The equilibrium constant,

$$K = [HgR_2][HgX_2]/[RHgX]^2 \tag{162}$$

must be very small, $< 10^{-4}$. These findings are in agreement with the small K values calculated from thermochemical data (*113*). Thus for Eq. (162) in ethanol with $R = CH_3$ and $X = Cl$, $K = 2.9 \times 10^{-12}$, for $R = CH_3$ and $X = Br$, $K = 4 \times 10^{-10}$, and for $R = CH_3$ and $X = I$, $K = 3 \times 10^{-6}$. Also in the benzylmercuric halide system, the equilibrium constants are very small.

Considerable effort has been expended on the elucidation of the mechanism (*57*, *58*, *123*, *131*, *238*, *309*, *310*) of the electrophilic substitution that occurs in the reaction of Eq. (163)

$$R_2Hg + HgX_2 \rightarrow 2\,RHgX \tag{163}$$

The reported data indicate that the substitution occurs with retention of configuration at the attached carbon, and there seems to be little doubt that the reaction involves front-side attack. Possible mechanisms for this reaction are S_{E1}, S_{E2}, and S_{Ei}. It has also been suggested that the reaction involves a four-center transition state arising from molecular or ion-pair attack (*72*).

Rate data obtained by spectrophotometric methods as well as by proton NMR indicate that the relative rates (*72*, *73*, *238*) of reaction of dimethylmercury with mercuric dihalides in methanol proceed in the decreasing order $HgCl_2 > HgBr_2 > HgI_2$ whereas in dioxane as solvent, the relative reaction rates exhibit the sequence $HgBr_2 > HgCl_2 > HgI_2$. For the corresponding phenyl compounds, this order is $HgCl_2 > HgBr_2 > HgI_2$, which is the sequence of decreasing order of ionic character of the mercury–halogen bond.

c. *Other Exchange Reactions Involving Mercury*. Redistribution of methyl and ethyl groups between mercury and lead has been studied by distillative separation of the components in the equilibrated mixture (*50*, *51*). The equilibrium distribution has been expressed in terms of a "relative affinity" constant defined by Eq. (164)

$$K = [CH_3{-}Hg][C_2H_5{-}Pb]/[C_2H_5{-}Hg][CH_3{-}Pb] \tag{164}$$

where the bracketed concentrations denote the proportion of the four different metal–alkyl bonds in the total product. The value of the constant of Eq. (164) was found to be 4.5, indicating a greater affinity at equilibrium of the methyl groups for mercury than for lead.

In contrast to the preceding studies, equilibria in the systems dimethylmercury vs diethylmagnesium (*248*) are shifted completely to one side, favoring methyl–magnesium bonding. This appears to indicate that ionic binding contributions—more important in magnesium than in lead compounds—are significant in these exchanges. Several other examples for nonrandom alkyl-group exchange in mercury–magnesium systems are summarized in Table XVI. These studies have resulted in an order of relative carbanion stability of the organic groups studied. The order of decreasing carbanion stability is phenylethynyl, phenyl, methyl, ethyl, isopropyl. In these systems, the more electronegative group, or the more stable carbanion, should, at equilibrium, be linked to magnesium—the more electronegative metal—because the ionic character in R—Mg bonds is higher than in R—Hg bonds.

TABLE XVI

EXCHANGE REACTIONS[a] IN THE SYSTEM R_2Hg VS R'_2Mg IN TETRAHYDROFURAN AT 25°C

R_2Hg	Conc. (moles/liter)	R'_2Mg	Conc. (moles/liter)	Result of reaction[b]	Half-life
$(C_6H_5)_2Hg$	0.45	$(C_6H_5C{\equiv}C)_2Mg$	0.45	$K = \sim 0.3$	Fast[c, d, e]
$(C_6H_5C{\equiv}C)_2Hg$	0.3	$(CH_3)_2Mg$	0.3	Complete reaction	Fast[e]
$(C_6H_5)_2Hg$	0.3	$(CH_3)_2Mg$	0.3	$K = \sim 40$	0.4 hours[c]
$(C_6H_5)_2Hg$	0.5	$(C_2H_5)_2Mg$	0.5	Complete reaction	0.1 hours
$(C_6H_5)_2Hg$	0.5	$[(CH_3)_2CH]_2Mg$	0.5	Complete reaction	0.05 hours
$(C_6H_5)_2Hg$	0.2	$[(CH_3)_3C]_2Mg$	0.2	No reaction	—
$(C_2H_5)_2Hg$	0.6	$[(CH_3)_2CH]_2Mg$	0.6	Complete reaction	Slow[d]
$[(CH_3)_2CH]_2Hg$	0.2	$[(CH_3)_3C]_2Mg$	0.2	No reaction	—
$[(CH_3)_2CH]_2Hg$	0.55	$(C_2H_5)_2Mg$	0.55	No reaction	—
$(CH_3)_2Hg$	0.9	$(C_2H_5)_2Mg$	0.9	Complete reaction	3.5 hours
$(CD_3)_2Hg$	0.9	$(CH_3)_2Mg$	0.6	Statistical exchange[f]	7 hours[f]

[a] From ref. (*248*).

[b] Values for K are approximate; $K = [\mathrm{Rmg}][\mathrm{R'hg}]/[\mathrm{R'mg}][\mathrm{Rhg}]$.

[c] These reactions reach an equilibrium; half-life taken as time required for 50% approach to equilibrium concentrations.

[d] Complexity of NMR spectrum precludes more accurate calculation.

[e] Too fast to measure.

[f] From mass spectral studies (*241*, *242*).

Equilibrium constants in the system R_2Mg vs $(C_6H_5)_2Hg$ have been found to correlate well with similar values for the equilibria in the systems

RLi vs C_6H_5I (*9*). These K values represent a first-order sequence of carbanion stabilities and relate directly to the parent weak acid RH (M-SAD Series) (*71*).

B. Transition Metal Acetylacetonates

Rapid exchange of β-diketonate ligands has been observed by proton as well as ^{19}F NMR upon mixing of solutions of eight-coordinated metal acetylacetonates $M(acac)_4$ and metal trifluoroacetylacetonates $M(tfac)_4$, where M = Zr, Hf, Ce, and Th (*1, 2, 231*). As a result of the exchange of the bidentate ligands, solutions of $M(acac)_4$ and $M(tfac)_4$ contain, in addition to the two starting materials, the following components: $M(acac)_3(tfac)$, $M(acac)_2(tfac)_2$, $M(acac)(tfac)_3$. The equilibria may be described by the three following independent equilibrium constants:

$$K_1 = [M(acac)_4][M(acac)_2(tfac)_2]/[M(acac)_3(tfac)]^2 \tag{165}$$

$$K_2 = [M(acac)_3(tfac)][M(acac)(tfac)_3]/[M(acac)_2(tfac)_2]^2 \tag{166}$$

$$K_3 = [M(acac)_2(tfac)_2][M(tfac)_4]/[M(acac)(tfac)_3]^2 \tag{167}$$

For M = Zr in benzene solution at 31° C, the above equilibrium constants were $K_1 = 0.17$, $K_2 = 0.17$, and $K_3 = 0.14$, which are smaller than the random values given in Table II for $\nu = 4$. Similar results were obtained for M = Zr and M = Hf. The proton as well as ^{19}F NMR spectra of solutions of equilibrated metal acetylacetonates on increasing temperature show exchange-broadening and finally coalescence to a single peak indicating rapid exchange. Average preexchange lifetimes have not been calculated.

Also, the rates of exchange of zirconium and hafnium trifluoroacetylacetonate or acetylacetonate, respectively, with the free ligand have been studied (*3*). Rates for acetylacetone exchange in benzene and chlorobenzene are faster for zirconium than for hafnium; however, for the trifluoroacetylacetone ligand, the exchange rates are essentially the same for both metals. The exchange for thorium is faster than for zirconium or hafnium regardless of solvent.

C. Transition Metal Carbonyls

Although it is well known that coordinated carbon monoxide in metal carbonyls may be replaced quite easily by other coordinating ligands, only a few studies have been made of the exchange equilibria resulting from the exchange of one coordinated ligand by another. One such study deals with the exchange of phosphorus trifluoride with carbon monoxide, both coordinatively bonded to nickel (*8*, *60*) in the system $Ni(CO)_4$ vs $Ni(PF_3)_4$.

On heating $Ni(CO)_4$ and $Ni(PF_3)_4$ or any of the intermediates having mixed ligands at 75° C, a mixture of all five redistribution compounds $Ni(CO)_{4-n}(PF_3)_n$ ($n = 0$, 1, 2, 3, and 4) is obtained. Quantitative separation has been accomplished by gas chromatography and a nearly random distribution has been observed. However, the authors claim that the study was not performed with sufficient accuracy to determine equilibrium constants or to judge how closely this system comes to being truly random.

The rate of exchange is relatively fast, but only approximate times are given that are required for 20% disproportionation of the mixed compounds. For $Ni(CO_3)(PF)$, this time is about 10 minutes, for $Ni(CO)_2(PF_3)_2$ about 100 minutes, and for $Ni(CO)(PF_3)_3$ about 480 minutes, indicating that the rate of disproportionation decreases significantly as the degree of phosphine substitution increases. The rate is also affected by the presence of free carbon monoxide. The observed facile disproportionation creates some problems in purifying the compounds and keeping them pure on storage.

Similarly, the reaction of phosphorus trifluoride and iron pentacarbonyl (*59*) at elevated temperatures and pressures results in a mixture of compounds of the general formula $Fe(CO)_{5-n}(PF_3)_n$, where $n = 0$–5. All of these compounds were isolated from the reaction mixture by gas chromatography. However, it is stated that equilibrium was most probably not reached and thus no efforts were made to calculate equilibrium constants. Similar studies have been mentioned to be in progress with molybdenum carbonyls (*8*).

D. π-Complexes and Coordination Compounds

In the last decade, an immense amount of experimental material has been generated describing the preparation and the chemical and physical properties of transition metal π complexes and coordination compounds. Recently great emphasis has been placed on the study of the kinetics and the reaction mechanisms involving such compounds. Although redistribution reactions as defined earlier in this review and as exemplified specifically by the reaction of Eq. (168) (M = transition metal, L = coordinated ligand)

$$(\nu - i)\, ML_\nu + i\, ML'_\nu \rightleftarrows \nu\, ML_{\nu-i}L'_i \tag{168}$$

have been explored in only a very few instances for preparative purposes, a great body of literature exists on "substitution reactions" of the type described by Eq. (169)

$$ML_n + L' \rightarrow ML_{n-1}L' + L \qquad (169)$$

These, to some extent, are related to redistribution reactions but, of course, do not lie within the scope of this review. Probably one of the first redistribution reactions of π-bonded compounds is the exchange of carbonyl groups with π-bonded benzene (*85*) on chromium leading to the mixed compound, benzenechromium tricarbonyl.

$$Cr(C_6H_6)_2 + Cr(CO)_6 \rightarrow 2\ C_6H_6Cr(CO)_3 \qquad (170)$$

Another redistribution involving a metallocene is the synthesis of cyclopentadienyltitanium trichloride according to Eq. (171)

$$(C_5H_5)_2TiCl_2 + TiCl_4 \rightleftarrows 2\ C_5H_5TiCl_3 \qquad (171)$$

which involves exchange of chlorine atoms with cyclopentadienyl groups on titanium (*101*, *102*).

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Mass Spectra of Organometallic Compounds

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I

INTRODUCTION

In recent years, the widespread introduction of high-resolution instruments has made mass spectrometry a routine tool of the same utility in organic chemistry as IR or NMR spectroscopy. However, it is only within the last year or two that systematic investigations into the behavior of organometallic compounds in the mass spectrometer have started to be reported. This review is an attempt to summarize many of the results obtained.

The practical aspects of mass spectrometry have been adequately described (*31*, *37*, *156*, *200*) and will not be mentioned further here. However, it is pertinent to note the main uses of the mass spectrometer, together with certain observations of particular relevance to organometallic chemistry. The most obvious use of the mass spectrometer is for the accurate determination of molecular weights. The peak appearing at highest *m/e* value is assumed to be the *parent* or molecular ion, P^+.[1] Use of high-resolution mass matching techniques then enables the exact empirical formula to be determined. Some care must be exercised, however, since the compound may not exhibit a parent ion, or may decompose in the spectrometer. Decomposition is often the result of high temperatures (~150°–250°C) in the inlet or source, and may be catalyzed by the metal surfaces. Some cases where parent ions are not seen are $CpMo(CO)_3Ti(O\text{-iso-}Pr)_3$ (*62*), $PtCl(PPh_3)_2SnMe_3$ (*62*), $[Mn(CO)_4SR]_3$ (*1*), $[Re(CO)_4SPh]_2$ (*1*), and $(CF_3)_4C_5ORu(CO)_3$ (*53*); others are mentioned below.

The mass spectra of organic compounds seldom show peaks above *m/e* 600, and the spectrum of perfluorotributylamine, with its highest peak at *m/e* 614, is used for calibration purposes. Many organometallic compounds exceed this value, so other mass markers have to be found. In this connection, the mass spectra of the perfluoroalkylphosphonitriles seem to be of potential use. The spectrum of $\{N{=}P[OCH_2(CF_2)_7CF_2H]_2\}_4$ has been reported (*97*), and shows many peaks in the region *m/e* 1500–3628 (P^+). These compounds are reasonably volatile, and one example of this class of compounds, $\{N{=}P[OCCl_2(CF_2)_9CF_2Cl]_2\}_4$, with a molecular weight of ~5200, has been described as distilling at 0.1 mm (*198*).

When fragmentation patterns are studied, determination of metal-containing ions is often facilitated by considering isotope patterns. Among elements likely to be encountered by organometallic chemists, only 20 are monoisotopic,[2] and only a further eight[3] have less than 2% of other isotopes present. The expected isotope patterns can easily be calculated (*37*, p. 223), even when two or more polyisotopic elements are present. Sometimes, however, the presence of many isotopes is a disadvantage, giving complicated patterns which may be difficult to interpret,[4] especially when the presence or absence of hydrogen atoms is suspected. Some combinations of polyisotopic elements have been illustrated, for example, Zr—Cl (*202*), Ru—C (*122*), Mo—Ge (*64*), and Ge—C (*63*). Tables of isotopes and relative

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[1] Although the molecular ion is commonly designated M^+, we choose to use the symbol P^+, in order to minimize confusion with metal ions (M^+).

[2] Be, F, Na, Al, P, Mn, Co, As, Y, Nb, Rh, I, Cs, Pr, Tb, Ho, Tm, Au, Bi, Th.

[3] H, C, N, O, V, La, Ta, U.

[4] Notorious in this respect are tin, tellurium, ruthenium, and molybdenum with 10, 8, 7, and 7 isotopes, respectively.

abundances are available (*34*, *59*, *157*) and a computer program for the calculation of relative abundances in multi-isotope ions is given (*64*).

The relative abundance of peaks arising by rearrangement processes can be used as a rough indication of their stability. It is not always possible to write specific structures for ions, and in general some sort of valency change has been invoked. In the spectrum of $[Cp_2ZrCl]_2O$, for example, ions such as Cp_2Zr^+, $CpZrCl^+$, and $CpZr_2Cl_2O^+$ are found (*202*). The first two may be said to contain zirconium(III), and the latter may be written as a resonance species $[CpClZr^{IV}OZr^{II}Cl \leftrightarrow CpClZr^{III}OZr^{III}Cl]^+$. The mode of dissociation of a metal complex may be dependent on the valency states normally assumed by the metal (*213*).

A point of practical interest is that the presence of metals in the compounds examined may result in the necessity for more frequent cleaning and/or replacement of sources than is necessary for conventional organic compounds. This has been reported to be the case with many metal carbonyls (*244*), and also for some tin and mercury compounds.

Few correlations can be drawn from the data at present available, especially concerning the effect of the metal on the fragmentation of the organic part of the molecule. However, this situation can be expected to be remedied in the next few years.

Many reported mass spectra give only the molecular weight of the complex with few or no details of the fragmentation patterns. Table I (see Section VI) summarizes these cases, together with other complexes discussed below. Here we shall confine our attention to organometallic complexes of transition metals, although a few salient features of main group compounds are presented (Section VIII). Section VII and Table II summarize the work reported on metallocene and related complexes, but these are not discussed in detail. The spectra of many other metal-organic complexes have been reported, such as acetylacetonates (*165*, *170*, *171*), phthalocyanines (*33*, *124*), porphyrins (*129*), and dithiolate complexes (*39*), but they do not come within the scope of this present summary.

II

METAL CARBONYLS AND NITROSYLS

A. Mononuclear Carbonyls

The most characteristic feature in the mass spectra of the metal carbonyls and their derivatives is the successive loss of CO groups to give a series of peaks corresponding to $M(CO)_n^+$. There is little further fragmentation, although as the number of carbonyl groups decreases, there is an increasing tendency for the carbon–oxygen bond to be cleaved to form metal carbide species. This is presumably a reflection of the increased metal–carbon bond strength in ions with fewer carbonyl groups.

Mononuclear carbonyls have been studied since the early days of mass spectroscopy as readily volatile sources of the elements for isotopic studies. Nickel carbonyl was rapidly decomposed by the electric discharge and Thomson (*6*) could not maintain the discharge long enough to obtain satisfactory parabolas. Later, Aston found four isotopes (*8*, *19*); other investigations were made by de Gier and Zeeman (*110*) and by Dempster (*81*). Other similar early studies used $Fe(CO)_5$ (*111*), $Cr(CO)_6$ (*13*, *16*), $Mo(CO)_6$ (*16*, *112*), and $W(CO)_6$ (*14*, *17*, *82*). After World War II, iron, nickel, and tungsten carbonyls were examined to determine their suitability for use in electromagnetic separation of isotopes (*26*, *27*).

Winters and Kiser have reported appearance potentials and cracking patterns for $Ni(CO)_4$ (*243*), $Fe(CO)_5$ (*243*), and the Group VI hexacarbonyls (*244*). These carbonyls fragment by a series of consecutive unimolecular reactions with loss of neutral CO groups. Support for this scheme came from an investigation of the metastable transitions in the spectrum of $Fe(CO)_5$ (*242*), which were observed for the following processes:

$$Fe(CO)_n^+ \rightarrow Fe(CO)_{n-1}^+ + CO \qquad (n = 1\text{–}5)$$

$$Fe(CO)_n^{2+} \rightarrow Fe(CO)_{n-1}^{2+} + CO \qquad (n = 2\text{–}4)$$

$$FeC(CO)^+ \rightarrow FeC^+ + CO$$

Also reported was the ion FeO^+, but no evidence was found for any transitions of the type

$$Fe(CO)_2^{2+} \rightarrow Fe(CO)^+ + CO^+$$

The hexacarbonyls $M(CO)_6$ (M = Cr, Mo, W) have also been studied (*102*). The low abundance of $M(CO)_5^+$ is noteworthy, and with these compounds, ions of the type $M(CO)_nC^+$ are more abundant than for $Ni(CO)_4$ and $Fe(CO)_5$, the abundance of these ions increasing with increasing atomic number.

In the fragmentation of $W(CO)_6$, competition can occur between different ionization and fragmentation processes, as shown by analysis of the electron-impact ionization efficiency curves (*61*). The ion $W(CO)_3^+$ can be formed by successive loss of three CO groups from $W(CO)_6^+$, and also by loss of three CO groups at once from an electronically excited $W(CO)_6^{+*}$ ion. Other ions, $W(CO)_n^+$ ($n = 0$–2), all originate from $W(CO)_3^+$. A definite relationship was found between the relative abundances of singly and doubly charged ions. With the other carbonyls, only the most intense singly charged species were found as doubly charged ions. The decomposition of these ions was also interpreted in terms of unimolecular loss of neutral CO groups (*249*), and observation of corresponding metastable peaks supports this view (*242*).

Vilesov and Kurbatov (*229*) suggested that the initial ionization process consists of loss of one of the valence electrons associated with the metal–carbon bond, or of one of the *p* electrons of the oxygen atom. Foffani *et al.* (*102*) found that the evidence pointed to removal of an electron from a partially bonding molecular orbital with prevailing metal character. Cracking patterns depend on the geometry of molecules and fragments, on the relative positions of the electronic levels, and of the potential curves and on appearance potentials. Formation of doubly charged ions similarly requires considerable charge to be associated with the metal atom, and, as might be expected, they occur much more readily with di- and polynuclear metal species.

The appearance potential of CO^+ in the spectra of mononuclear carbonyls is similar to the ionization potential of carbon monoxide. This excludes a process

$$M(CO)_n + e \rightarrow M(CO)_{n-1} + CO^+ + 2e$$

since in this case, the dissociation energy $D[M(CO)_n—CO]$ would have to approach zero. The high abundance of this ion suggests some decomposition of the carbonyl, followed by ionization of the carbon monoxide.

Quasi-equilibrium theory of positive-ion mass spectra (*206*, *207*, *228*) has been applied to the negative-ion spectra of mononuclear carbonyls (*245*). The theory explains the spectra of systems of positive ions and metastable transitions in terms of competing and consecutive unimolecular reactions of excited molecular ions. Negative ions were found to arise by dissociative electron capture and by ion-pair production. Parent molecule ions were not observed, but $(M - CO)^-$ were the most abundant species. Comparison of the relative abundances of $(M - CO)^+$ and $(M - CO)^-$ indicates the greater stability obtained by adding an electron to the $Ni(CO)_3$, $Fe(CO)_4$, and $M(CO)_5$ ($M = Cr, Mo, W$) radicals. Further fragmentation gives $(M - nCO)^-$, but no cleavage of the C—O bonds is observed. Energies of the electron capture maxima increase with decreasing number of CO groups, and suggest successive removal of these groups. Application of the quasi-equilibrium theory gave excellent agreement with all experimentally observed negative-ion abundances, except $Ni(CO)_2^-$, for the following scheme:

$$\begin{array}{lcl} M(CO)_n + e & \rightarrow & M(CO)_{n-1}^- + CO^+ + e \\ & & \quad\downarrow \\ & & M(CO)_{n-2}^- + CO \\ & & \quad\downarrow \\ & & M^- + CO \end{array}$$

Further work (*193*) has confirmed the absence of parent negative ions in the spectra of the iron and Group VI carbonyls but other ions, $Fe(CO)_n^-$ ($n=1$–4), $Cr(CO)_n^-$ ($n=0$–5) and $M(CO)_n^-$ (M = Mo or W, $n=2$–5) were found. These authors (*193*) suggest that the $(M–CO)^-$ ions are produced in a repulsive state markedly flattened in form. Low values for the appearance potentials suggest that the dissociative limits for the states of the parent anions involved in the capture process are higher than the zero vibrational levels for the ground states of the neutral molecules by this small amount. Double peaks were found for most negative ions, possibly due to the production of the fragment anions and/or CO in vibrationally excited states.

B. Binuclear Carbonyls

An early report (*131*) of the spectrum of $Mn_2(CO)_{10}$ mentioned no parent ion, but only strong peaks due to $Mn_2(CO)_n^+$ ($n=5$, 6, and 7) together with other weaker carbonyl-containing ions. More recently, appearance potentials and cracking patterns for $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ were reported (*247*) and the spectra of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ have been compared (*49, 164*).

For $Mn_2(CO)_{10}$, the ions corresponding to $Mn_2(CO)_n^+$ ($n=8$ or 9) were either not seen (*247*) or were of very low abundance (*49, 164*), and $Mn_2(CO)_7^+$ was only apparent with less than the normal 70-V ionizing potential. All other $Mn(CO)_n^+$ ($n=0$–5) and $Mn_2(CO)_n^+$ ($n=0$–10) ions were observed, but no doubly charged ions were seen. The carbide ions $MnC(CO)_n^+$ ($n=0$–2) were observed in low abundance. Similar ions were found in the spectrum of $Re_2(CO)_{10}$, as also was the series $Re_2(CO)_nC^+$ ($n=0$–5), and the doubly charged ions $Re_2(CO)_n^{2+}$ and $Re_2(CO)_nC^{2+}$ ($n=0$–6). Major differences in intensities in the two spectra can be attributed to the greater strength of the rhenium–rhenium bond. About 60% of the ions produced from $Mn_2(CO)_{10}$ contain two manganese atoms, whereas the figure for $Re_2(CO)_{10}$ is 96%. Metastable peaks occur for the transitions

$$Mn_2(CO)_n^+ \rightarrow Mn_2(CO)_{n-1}^+ + CO \qquad (n = 4, 6)$$
$$Re_2(CO)_n^+ \rightarrow Re_2(CO)_{n-1}^+ + CO \qquad (n = 3\text{–}8, 10)$$
$$Re(CO)_5^+ \rightarrow Re(CO)_4^+ + CO$$

The spectrum of $Co_2(CO)_8$ shows no $Co_2(CO)_5^+$ ion, suggesting that the bridge unit is symmetrically homolytically cleaved (*247*). No doubly charged ions were found. The negative-ion spectra of both $Co_2(CO)_8$ and $Mn_2(CO)_{10}$ have been recorded (*247*), the predominant ions being tetrahedral $Co(CO)_4^-$, and trigonal bipyramidal $Mn(CO)_5^-$.

The mass spectrum of $Fe_2(CO)_9$, long assumed to be completely involatile, shows a parent ion, but the base peak is $Fe_2(CO)_3^+$, with a structure retaining the three bridging carbonyl groups $[Fe(CO)_3Fe]^+$ (*70*). Similar bridged ions containing iron have been postulated in the spectra of some phosphine and sulfide complexes (Section VI).

C. Polynuclear Carbonyls

Triiron dodecacarbonyl was used (*8*) in determining the isotopic composition of iron, and the spectra of $M_3(CO)_{12}$ (M = Fe and Ru) have recently been described (*151*, *164*). Stepwise loss of CO from the iron compound only occurs as far as $Fe_3(CO)_3^+$, after which the metal–metal bonds rupture to give species such as $Fe_2(CO)_4^+$ and $Fe(CO)_4^+$. With $Ru_3(CO)_{12}$, loss of 12 CO groups occurs, and a bare metal cluster ion (Ru_3^+), probably triangular, is formed. The increased stability of the metal–metal bonds in $Ru_3(CO)_{12}$ is also shown by recent chemical work, which has demonstrated that the Ru_3 cluster is retained in reactions of the carbonyl with triphenylphosphine (*53*, *60*) and 1,3-cyclooctadiene (*60*), whereas the corresponding reactions of $Fe_3(CO)_{12}$ give mainly the mononuclear complexes (*5*, *73*). Ions present in the spectrum of $Fe_3(CO)_{12}$ include $Fe_3(CO)_n^+$ ($n = 0$–12), $Fe_2(CO)_n^+$ ($n = 3, 4, 6, 7$), $Fe(CO)_n^+$ ($n = 0$–5), and FeC^+. No ions $Ru_2(CO)_n^+$ ($n = 4$–7) or $Ru(CO)_n^+$ ($n = 4$ or 5) were found in the spectrum of $Ru_3(CO)_{12}$. Carbide ions include $Ru_3(CO)_nC^+$ ($n = 0$–2), Ru_2C^+, and RuC^+, and other ions seen were Ru_2^+, Ru^+, Ru_3C^{2+}, and Ru^{2+} (*164*). For $Fe_3(CO)_{12}$ the base peak was $Fe(CO)^+$, but for the ruthenium carbonyl it was Ru_3^+. The increased strength of the metal–metal bonds is finally demonstrated by the fact that 92% of all ions contain the Ru_3 cluster, compared with 35% of ions from $Fe_3(CO)_{12}$ which contain Fe_3 (*164*). The absence of $Ru(CO)_5^+$, and presence of $Fe(CO)_5^+$

can be related to the structures of the carbonyls; rearrangement of the carbonyl-bridged iron complex could give $Fe(CO)_5^+$, whereas formation of $Ru(CO)_5^+$ requires migration of a terminal carbonyl group.

The spectrum of $Os_3(CO)_{12}$ has been briefly described (*138*) and confirms that the predominant fragmentation involves successive loss of CO groups; the corresponding doubly charged series $Os_3(CO)_n^{2+}$ ($n = 0$–12) was also observed. Loss of all 12 CO groups occurs similarly with the tetranuclear $Co_4(CO)_{12}$, to give the presumably tetrahedral Co_4^+ ion (*151*). Further fragmentation of the cluster to give Co_n^+ ($n = 1$–3) is also observed.

D. Heteronuclear Polymetallic Compounds

Lewis and co-workers (*164*) have investigated some complexes containing bonds between two or more different metal atoms. The complex $Ph_3SnMn(CO)_5$ did not give any ions $Ph_3SnMn(CO)_n^+$ ($n = 1$–5), and the major ions were Ph_3Sn^+ (base peak), $PhSn^+$, and Ph_3SnMn^+. The latter ion lost the three phenyl groups stepwise and some transfer of the phenyl groups to manganese may occur to give, e.g., $PhMn^+$. The corresponding iron complex, $Ph_3SnFe(CO)_2Cp$ ($Cp = \pi\text{-}C_5H_5$), shows similar transfer of phenyl and cyclopentadienyl groups, and metastable transitions indicated that $PhSnFeCp^+$ was a common precursor of $CpSn^+$ and $FePh^+$. The major ions were Ph_3Sn^+ (base peak), $PhSn^+$, $SnCp^+$, $Ph_2SnFeCp^+$, and $Ph_3SnFe(CO)Cp^+$.

Complexes containing three metal atoms, e.g., $Cl_2Sn[Fe(CO)_2Cp]_2$, give ions which retain the three metal atoms, e.g., $Cl_2SnFe_2(CO)_3Cp_2^+$, and ions where transfer of groups has occurred, e.g., $SnCp^+$ (base peak). Preferential loss of CO groups was found, as with $Hg[Fe(CO)_2Cp]_2$; in this compound some formation of $Cp_2Fe_2(CO)_4^+$, $FeCp_2^+$, and derived ions is observed. No migration of chlorine from tin to iron was found, nor of any similar groups in the mercury compound.

E. Other Polynuclear Carbonyl Derivatives

Mass spectroscopy has recently demonstrated the existence of several novel polynuclear metal carbonyl derivatives. Hydrogen is never easy to detect, and in the mass spectrum of $H_4Ru_4(CO)_{12}$, the highest ion observed has *m/e* 754, corresponding to $H_2{}^{104}Ru_4(CO)_{12}^+$ (*134*). As expected, peaks corresponding to loss of 12 CO groups were seen, and a group of peaks at *m/e* 393–414 was assigned to Ru_4^+. Later work (*137*) has confirmed that the parent ions are not always observed in these hydrides, and for $H_3Mn_3(CO)_{12}$, the presence of hydrogen atoms was only confirmed by detailed examination of all the ions $H_3Mn_3(CO)_n^+$ ($n < 12$). With $H_3Re_3(CO)_{12}$ or $H_2Ru_4(CO)_{13}$, the parent ions are observed. Similarly, the mass spectra of two new osmium cluster compounds indicated a composition $H_nOs_4(CO)_{12}$ (n at least 4 and 5).

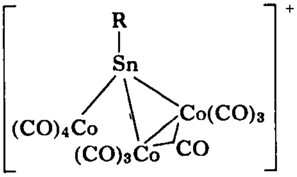
Fragmentation patterns for these complex hydrides involve loss of H and CO. A more detailed report on $HMn(CO)_5$ (*91*) shows that pairs of peaks, separated by one mass unit, are seen, corresponding to $HMn(CO)_n^+$ and $Mn(CO)_n^+$ ($n = 0$–5), as well as the doubly charged ions $HMn(CO)_n^{2+}$ and $Mn(CO)_n^{2+}$ ($n = 1$–3). The appearance of the peak at m/e 56 (MnH^+) is evidence for the existence of a Mn–H bond in the carbonyl hydride. From infrared data, the Mn–H and metal–CO stretching force constants are 1.9 and 2.0–2.7 mdynes/Å, respectively, and the relative abundances of ions formed by loss of H and CO from the parent ion are in agreement with these values.

The first metal carbonyl oxide, $Os_4O_4(CO)_{12}$, was recently characterized (*138*). The ions $Os_4O_4(CO)_n^+$ ($n = 0$–12) occur in high abundance, and the Os_4 cluster does not break up until all CO groups are lost. An interesting feature is the presence of the doubly-charged series $Os_3(CO)_{12}^{2+}$, although the singly charged ions are absent; the following scheme was suggested:

$$Os_4O_4(CO)_{12}^+ \rightarrow OsO_4^- + Os_3(CO)_{12}^{2+}$$

The complexes $RCCo_3(CO)_9$ [R = Cl, CH_3 (*151*), CF_3CH_2 (*51*)] have been examined and stepwise loss of the nine CO groups is seen. Where $R = CF_3CH_2$, loss of one fluorine from the parent ion gives the series $CF_2CH_2CCo_3(CO)_n^+$ ($n = 0$–9). Further fragmentation of $CH_3CCo_3^+$ gives ions such as $HCCCo_3^+$, HCo_3^+, Co_3^+, $HCCCo_2^+$, HCo_2^+, and Co_2^+, but in the compound where R = Cl similar fragments are much weaker relative to the carbonyl-containing fragments. In the fluorocarbon complex, fragmentation is more extensive, and ions corresponding to $Co(CO)_n^+$ ($n = 0$–3), $CF_3CH_2CCo(CO)_n^+$ ($n = 0$–2), CoF_2^+, and $Co_2F_3^+$ are found, along with $CF_3CH_2C^+$ and $CF_3CH_2^+$.

The spectra of the compounds $RSn[Co(CO)_4]_3$ (R = Me, CH:CH_2, Ph, Cl, Br, or I) have been reported (*190*, *191*), confirming that the complexes had this formulation rather than $RSn[Co(CO)_3]_3$ (*132*). Only when R = Me or Ph was the parent ion observed, although $(M - CO)^+$ was always present in medium to high abundance. The high stability was explained by a structure (I) involving a bridging CO group and cobalt–cobalt bond. Some support for this is given by the mass spectrum of $Cl_2Sn[Co(CO)_4]_2$, which also shows no parent ion but has a strong peak due to $Cl_2SnCo_2(CO)_7^+$,



(I)

and by that of $Me_3SnCo(CO)_4$, which shows peaks formed by loss of CO which have like intensities to other fragments formed similarly. Another series of abundant fragments in the spectra of the $RSn[Co(CO)_4]_3$ complexes was that formed by loss of $Co(CO)_4$ groups. Successive loss of CO groups from all the fragments was observed, giving Co^+, $SnCo(CO)_n^+$, $RSnCo(CO)_n^+$, $Co(CO)_n^+$ and Co_2^+. Comparison with $RCCo_3(CO)_9$ shows a greater tendency for fission of the Sn–Co bonds. Noteworthy in this respect are the relative abundances of $MeCCo_3(CO)_n^+$ ($n = 0$–9) and $RSnCo_3(CO)_n^+$ ($n = 0$–12) (75% and 30–50% respectively), and the fact that the ions $RSnCo_3(CO)_9^+$ do not appear to be especially stable.

F. *Metal Nitrosyl Complexes*

The base peak in the spectrum of $CpMo(CO)_2NO$ is the parent ion, and fragmentation occurs by loss of CO rather than of NO or Cp groups (*248*). The presence of $CpMo^+$ and absence of $MoNO^+$ suggests that the ring–metal bond is stronger than the Mo–NO bond. The characteristic formation of $C_3H_3Mo^+$ is also found. The doubly charged $MoCp^{2+}$ was present in significant amount. As in similar cases, the ionization process probably involves removal of an electron from a hybrid molecular or orbital with considerable contribution from the metal atom.

Consideration of the relative donor abilities of nitrosyl, carbonyl, and phosphine groups as measured by their ionization potentials, provides an explanation for variations in the molecular ionization potentials of these complexes (*103*, *194*). As shown in Table III (Section IX) the ionization potentials decrease on introduction of the phosphine ligand, and parallel the corresponding decrease in ionization potentials of the phosphine ligands. Similar correlations were made for ν_{CO} and ν_{NO} in the infrared spectra.

For a variety of phosphine complexes, the ionization potential of the complex is linearly related to that of the phosphine, if the latter involves the lone pair used in the formation of the complex (*89a*). As for the metal carbonyls, the electron appears to come from an orbital with a high metallic character, probably a π electron involved in back-bonding. The fragmentation patterns indicate that NO and PR_3 groups are lost much less readily than CO, and the relative abundances of these ions decrease in order of decreasing ionization potential of the ligand detached. Where two ligands are lost, the relative abundances are comparable, whichever ligands are detached; however, for loss of three groups, the relative abundances are in the order $M(PR_3)^+ > M(CO)^+ > M(NO)^+$. Some explanation of this seemingly anomalous situation may lie in the number of routes by which a particular group may be lost. The complex $Co(CO)_2(NO)PCl_3$ tends to lose one chlorine atom, followed by CO or NO groups, giving finally $CoPCl_2^+$. The fragmentation pattern for CpNiNO indicates, as for the carbonyl derivatives, that NO is lost more readily than Cp; in this case, $NiCp^+$ forms the base peak.

III

METAL CARBONYL HALIDES

In $Mn(CO)_5Br$, loss of CO groups and halogen seems to occur with equal ease, and ions $Mn(CO)_nBr^+$ ($n = 0$–3,5) and $Mn(CO)_n^+$ ($n = 0$–5) are found with similar intensities (*164*). The base peak is Mn^+ and the doubly charged series $Mn(CO)_n^{2+}$ ($n = 1$–3) is also seen. The dimeric $[Mn(CO)_4X]_2$ ($X = Cl$ and Br) on the other hand, retain the Mn_2X_2 unit, losing the CO groups to give $Mn_2(CO)_nCl_2^+$ ($n = 0$–5) and $Mn_2(CO)_nBr_2^+$ ($n = 0$–8). Both compounds also showed the series $Mn(CO)_n^+$ ($n = 0$–5) and $Mn_2(CO)_n^+$ ($n = 0$–10), presumably originating from $Mn_2(CO)_{10}$ formed by decomposition (*164*).

The mass spectra of both isomers of $[Ru(CO)_3Cl_2]_2$, described recently (*55*), are virtually identical, and show a weak parent ion, and successive loss of six CO groups. The Ru_2Cl_4 group appears as both singly and doubly charged ions. Further fragmentation gives $Ru_2Cl_n^+$ ($n = 0$–3) and $RuCl_n^+$ ($n = 0$–2). The iodide shows a similar spectrum (*54*). The tetracarbonyl iodide shows all peaks $Ru(CO)_nI_2$ ($n = 0$–4) and also loses iodine to give $Ru(CO)_nI^+$ ($n = 0$–4). Other ions seen are Ru^+, I^+, and a strong peak due to HI^+, perhaps due to decomposition in the spectrometer (*54*).

The spectra of the cyclopentadienyl metal halides of iron and molybdenum have been reported *(212)*. The halide atoms are lost less readily than the CO groups, but about as readily as the Cp group. Thus for $CpFe(CO)_2Br$, the most abundant ions are $CpFeBr^+$, $FeCp^+$, P^+, $FeBr^+$, and $CpFe(CO)Br^+$. Most of the other expected ions are also found, such as $FeCp_2^+$, $CpFe(CO)_2^+$, $C_3H_3FeBr^+$, $C_3H_3Fe^+$, C_2HFe^+, $FeBr^+$, and Fe^+. Similar results were observed for $CpFe(CO)_2Cl$ *(49)*. The molybdenum compound shows a similar pattern.

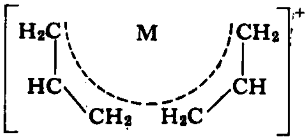
IV

COMPLEXES CONTAINING π-BONDED LIGANDS

A. *π-Allyl Complexes*

Bis(π-allyl)nickel shows a parent ion with the expected isomer distribution *(238)*. A more extensive investigation of metal–π-allyl complexes, using field-ionization and electron-impact methods, has recently been reported *(28)*. Little fragmentation occurs in the field-ionization mass spectra, no electronic excitation being induced by this technique and parent ions only being observed for $M(C_3H_5)_2$ (M = Ni or Pt). The palladium compound loses a C_3H_5 radical, and compounds with more than two allyl groups, e.g., $Zr(C_3H_5)_4$, $Hf(C_3H_5)_4$, while still having the parent ion in greatest abundance, lose an allyl radical even more readily.

The electron impact spectra are dominated by peaks derived from hydrocarbon decomposition products; the parent ion is sometimes very weak, and a variety of metal-containing ions occur in low abundance. For $M(C_3H_5)_2$, the parent ion is strong and peaks due to loss of C_3H_5 and H occur. For M = Ni, loss of C_2H_4 (confirmed by the appropriate metastable peak) is thought to proceed via an intermediate (II), which eliminates ethylene to form a divinylmetal complex. With M = Pt, the predominant fragmentation was loss of C_3H_6; this complex is more stable than the corresponding palladium compound.



(II)

With compounds having more than two allyl groups, the parent ions are very much weaker and the dominant species is always $(P-C_3H_5)^+$. For $Zr(C_3H_5)_4$, there are no peaks $Zr(C_3H_5)_n^+$ ($n=0$–2), further fragmentation of $Zr(C_3H_5)_3^+$ involving elimination of C_2H_4, as discussed above. The chromium complex $Cr(C_3H_5)_3$ showed the ions Cr^+ and $Cr(C_3H_5)^+$, and the rhodium compound was briefly reported (*29*) to lose all three allyl groups successively.

The spectrum of $[\pi\text{-}C_3H_5PdCl]_2$ shows a parent ion, which can lose Cl or C_3H_5 successively; no ion $C_3H_5PdCl^+$ was seen. The base peak corresponds to $C_3H_5Pd^+$, which can be formed from many of the other ions. Some metal–metal interaction is suggested to account for the persistence of two Pd atoms in most of the ions, even in Pd_2Cl^+ (*167*). The corresponding rhodium complex, $[(\pi\text{-}C_3H_5)_2RhCl]_2$, has $(C_3H_5)_2Rh^+$ as the base peak, and allyl-rhodium moieties readily lose hydrogen to form, e.g., $C_3H_3Rh^+$, which is probably a cyclopropenium ion. Ions such as $(MeC_3H_4)_3Rh^+$ in the spectrum of the 2-methallyl complex indicate that migration of the allylic groups occurs (*56a*).

The σ-allyl complex, $(Ph_3P)_2Pt(C_3H_5)_2$, showed a cracking pattern due to triphenylphosphine, presumably formed by thermal decomposition in the inlet ($\sim 200°C$). The main ions were $Pt(C_3H_5)_2^+$, $Pt(C_3H_5)^+$, and $C_3H_5^+$; $PtC_3H_4^+$ and Pt^+ appear with lower abundances (*28*).

B. π-Cyclobutadiene Complexes

Pyrolysis of $[Ph_4C_4PdCl_2]_2$ gives diphenylindenoindene and 1,4-dichlorotetraphenylbutadiene (*74*, *75*). Ions such as $Ph_4C_4^+$, $Ph_4C_4Cl^+$, and $Ph_4C_4Cl_2^+$ in the mass spectrum of this complex probably arise by thermal decomposition (*32*). In the presence of water or oxygen, molecular ions of tetraphenylfuran and *cis*-dibenzylstilbene are prominent; these compounds are formed from the complex and triphenylphosphine in solution. Cyclobutadieneiron tricarbonyl (*96*) shows no loss of C_2H_2 fragments, confirming the presence of a C_4 moiety in the complex.

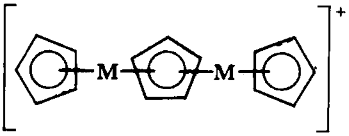
C. π-Cyclopentadienyl Complexes

1. *Derivatives Containing No Carbonyl Groups*

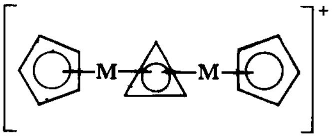
The mass spectra of the dicyclopentadienyl complexes, MCp_2 ($M = V$, Cr, Fe, Ni, Co, Ru, Mn, or Mg), and the hydride Cp_2ReH, show little evidence of loss of anything other than Cp groups or metal atoms in the cases where the ring may be considered to be predominantly π-bonded to the metal atom (*104*, *239*). With the magnesium and manganese compounds, the M^+ and MCp^+ ions predominate. In terms of total ion yield, the parent ions of the π- and σ-bonded species contribute more than 50% and $\sim$20%, respectively. This difference offers yet another criterion of the ring–metal bond character in these compounds. The spectrum of the titanium compound could not be obtained, which perhaps is not surprising in view of the work of Watt *et al.* (*233*) which casts some doubt on the nature of titanium-cyclopentadienyl complexes previously reported.

Low intensities for MCp_2^+ ($M = Cr$, Ni, or V) over these cases where $M = Fe$ or Co is reflected in the larger yields of MCp^+ and M^+ for these compounds. In the spectra of the vanadium and nickel compounds, the ion MCp^+ is much stronger than in the Cr, Fe, Co, and Ru derivatives, with corresponding decreases in M^+. The ruthenium complex shows a strong parent ion, indicating a more stable structure than the iron compound. Appearance potentials for the ions M^+, MCp^+, and MCp_2^+ are summarized in Table I (Section IV), the relative metal–ring bond energies indicated by these being in agreement with those obtained from thermochemical determinations. The higher ionization potentials indicated removal of an electron either from the ring, or from ring–metal bonds rather than from non-bonding metal orbitals, and the low value for $CoCp_2^+$ agrees with the closed-shell configuration for the positive ion.

The mass spectrum of ferrocene (*172*) has been discussed briefly in terms of its well-known stability. The iron (*83*, *211*) and nickel (*211*) compounds were also reported to show the ions $MC_3H_3^+$, $MC_3H_2^+$, and MC_2H^+, and the appearance of MCp^+ and $MC_3H_3^+$. The latter, presumably a cyclopropenium–metal ion, seems to be characteristic of many compounds containing the MCp group (*49*). Peaks at higher *m/e* values than the parent ion were found in low abundance in the spectra of ferrocene and nickelocene (*211*). In a mixture of the two complexes, peaks due to $^{56}Fe_2Cp_3^+$, $^{56}Fe^{58}NiCp_3^+$, and $^{58}Ni_2Cp_3^+$ were identified. "Triple-decker" sandwich structures [(III) and (IV)] have been postulated for these ions.



(III)



(IV)

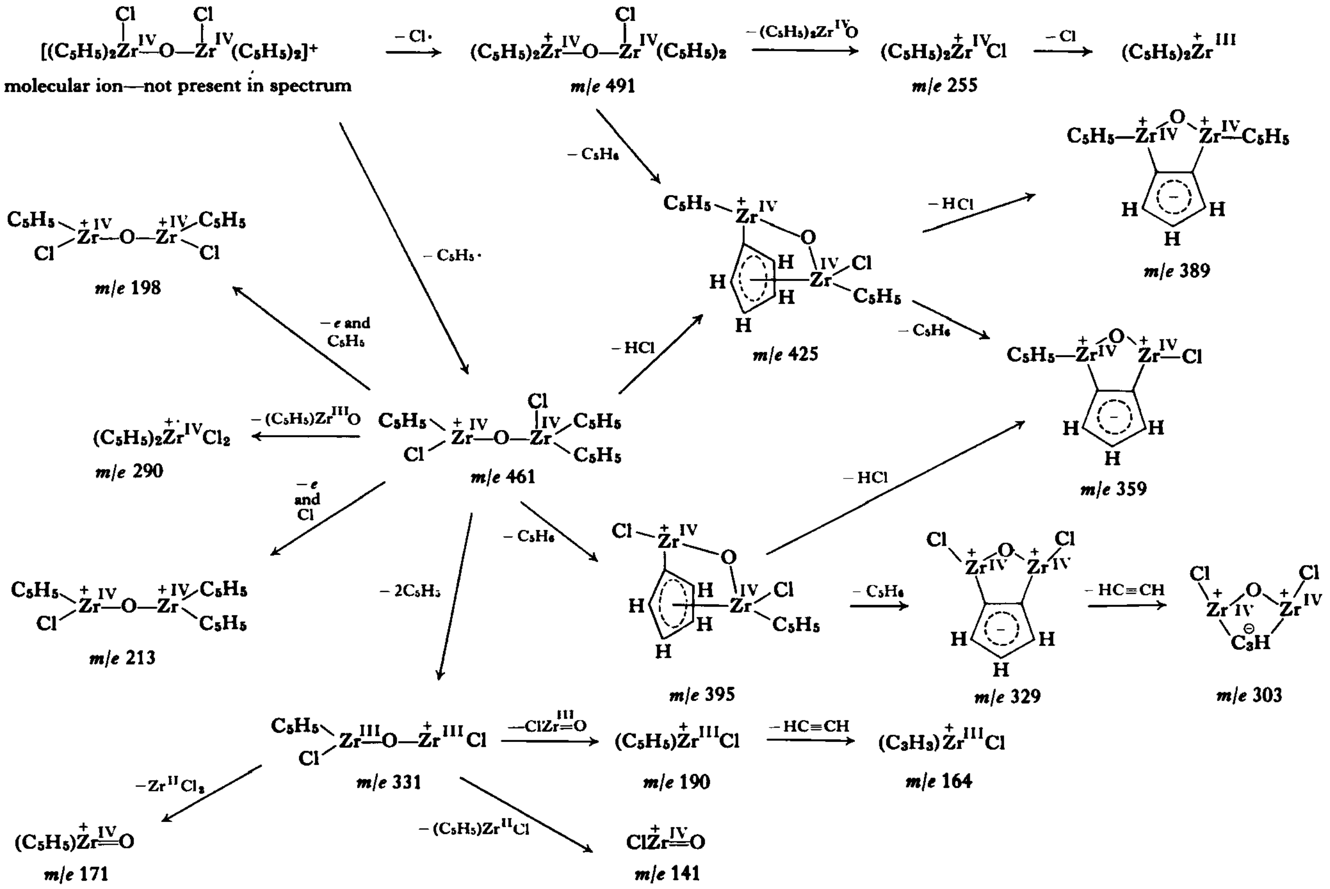


FIG. 1. Suggested mechanisms for ionic fragmentation of $[Cp_2ZrCl]_2O$ in the mass spectrometer. (Reproduced, with permission, from Reid *et al.*, *202*).

Similar ions were recently observed in the spectrum of Cp_2TiNCO (*78*). Ion association was assumed but probably some thermal polymerization process is responsible (cf. $[CpFe(CO)_2]_2$, Section C, 2).

The hydride Cp_2ReH behaves differently. Loss of a hydrogen atom, and also of C_2H_4 groups, replaces loss of Cp groups (*104*). No peak corresponding to $ReCp^+$ is observed, the three strongest peaks being $C_{10}H_{11}Re^+$ (P^+), $C_{10}H_{10}Re^+$ [$(P-H)^+$], and $C_8H_7Re^+$, followed by $C_8H_8Re^+$, $C_8H_6Re^+$, $C_6H_4Re^+$, and Re^+. The relative intensities of P^+ and $(P-H)^+$ in Cp_2TcH are equal, whereas $(P-H)^+$ is only 65% of the parent ion in Cp_2ReH, indicating a weaker M—H bond in the former case (*98a*).

The main features of the spectra of $CpTi(OEt)_{3-n}Cl_n$ ($n = 0$–3) are the parent ions, and peaks due to $(P-A)^+$ and $(P-2A)^+$ ($A = Cl$ or OEt), and $C_5H_5^+$ (*184*). The ion $(P-HCl)^+$ was observed where $n = 1$ or 2, and $CpTiO^+$ was present with $n = 0$–2. The intensity ratios I_{MCp}/I_M and I_{MCp}/I_{Cp} increase along the series $CpTiCl_3 < CpTi(OEt)Cl_2 < CpTi(OEt)_2Cl < CpTi(OEt)_3$, which is also the direction of increase in ionic character of the metal–ring bond, as shown by other studies. Reid *et al.* (*202*) have discussed the mass spectra of Cp_2ZrCl_2 and $[Cp_2ZrCl]_2O$. All major ions in both spectra can be explained by successive loss of C_5H_5 radicals or chlorine atoms from the parent ion, with some fragmentation of one Cp ring to give groups such as C_3H_3, C_3H and C_2H attached to the metal. The relative abundances indicate that loss of Cp occurs more readily than Cl. In the chloride, a strong doubly charged peak is assigned to $CpC_5H_4ZrCl^{2+}$ but no singly charged ion appears. A suggested fragmentation scheme for the oxide is presented in Fig. 1. No parent ion was found in this case, but many ions containing the Zr—O—Zr unit were observed.

2. *Cyclopentadienyl Metal Carbonyls*

The fragmentation patterns of $CpCo(CO)_2$, $CpMn(CO)_3$, and $CpV(CO)_4$ have been related to those found for the corresponding metal carbonyls and dicyclopentadienyls (*246*). In general, there are significant differences in the bond energies of the M—CO and M—Cp bonds and the processes involve only simple bond rupture. The high abundance of peaks due to $CpM(CO)_n^+$ ($n = 0$–2, 3 or 4 for $M = Co$, Mn, and V, respectively) indicates that the CO groups are more readily lost than is the ring. The only carbonyl-containing fragment which does not also contain the ring is $M(CO)^+$. No fragmentation of the C—O bond occurs. In the cobalt and vanadium compounds, ions $MC_3H_3^+$ are abundant, and an ion at m/e 39 is assigned to

$C_3H_3^+$. Values for the bond strengths $D[R—M^+]$ were obtained for the C_5H_5– and C_3H_3–metal bonds; the low value found for $D[Cp—Mn^+]$ and by analogy for $D[C_3H_3—Mn^+]$ (probably negative), was substantiated by the very low abundance (~0.4%) observed for $MnC_3H_3^+$.

Negative-ion spectra were also recorded, and showed ions $C_5H_xM(CO)_n^-$ ($M = Co$, $n = 1, 2$; $M = Mn$, $n = 0–3$; $M = V$, $n = 2, 3$) but no ions $M(CO)_n^-$ were observed. The errors in measurements (± 3 m/e units) precluded an accurate determination of the value of x. These ions were probably formed by an ion-pair production process

$$C_5H_5M(CO)_n + e \rightarrow C_5H_xM(CO)_n^- + H_{5-x}^+ + e$$

At a lower ionizing energy, $CoCp^-$ was observed, probably from the reaction

$$CpCo(CO)_2 + e \rightarrow CpCo^- + 2\,CO$$

The spectra of $[CpFe(CO)_2]_2$ and $[CpMo(CO)_3]_2$ show a similar ready loss of CO (*164*, *212*). In the iron compound, the most abundant ions are $FeCp_2^+$, $Fe_2Cp_2^+$, $FeCp^+$, $CpFe(CO)^+$, and Fe^+. Other ions were the expected $Cp_2Fe_2(CO)_n^+$ ($n = 0–4$) and $CpFe(CO)_n^+$ ($n = 0–4$), and $FeC_3H_3^+$. Metastable peaks indicate initial fragmentation to give $CpFe(CO)_2^+$ or $Cp_2Fe_2(CO)_3^+$; the latter may lose either one or two CO groups (*164*). Ions formed by loss of hydrogen were very weak. The molybdenum compound showed the expected $Cp_2Mo_2(CO)_n^+$ ($n = 0–6$) and $CpMo(CO)_n^+$ ($n = 0–3$). Most abundant were $Mo_2Cp_2^+$ and $Cp_2Mo_2(CO)_n^+$ ($n = 2$, 3, or 4), and the spectrum contained a high proportion of dimetallic ions. Comparison of these two spectra again indicates that in the metal–metal bonded molybdenum complex, migration of a CO group to give ions $CpMo(CO)_n^+$ ($n > 3$) does not occur, whereas with the iron complex, containing bridging CO groups, ions $CpFe(CO)_n^+$ ($n = 0–4$) can form by simple cleavage reactions (*164*).

In contrast to the molybdenum complex, $[CpCr(CO)_3]_2$ gives ions only up to m/e 202 and 201, corresponding to $[CpCr(CO)_3H]^+$ and $[CpCr(CO)_3]^+$, respectively (*151*). The ions $CpCr(CO)_n^+$ ($n = 0–2$) were also produced, but no bimetallic ions have been observed, suggesting that the compound may be monomeric in the vapor phase and implying a very weak metal–metal bond.

The complex $[CpNi(CO)]_2$ shows similar types of ions to the iron complex, the most abundant being $NiCp_2^+$, $Ni_2Cp_2^+$, $NiCp^+$, $Ni(C_5H_4)_2^+$, and $Ni_2(C_5H_4)_2^+$ (*212*). The expected ions $Cp_2Ni_2(CO)_n^+$ ($n = 1, 2$), $CpNiCO^+$, and $NiC_3H_3^+$ were relatively weak.

Ions of greater complexity than the parent compound have been reported for the iron and nickel compounds (*212*), but explanations involving ion association should be treated with caution. Controlled pyrolysis of $[CpFe(CO)_2]_2$ has given moderate yields of a polynuclear complex $[CpFe(CO)]_4$, and its mass spectrum has been briefly reported (*147*). This shows a strong $FeCp_2^+$ peak, probably due to pyrolysis in the inlet. It is relevant to note here that the tetramer does not melt, but decomposes to ferrocene at ~220°C. Other ions result from loss of CO or FeCp groups: no bare cluster ion Fe_4^+ was reported. Similarly, the complex $[Cp_3Ni_3(CO)_2]$ may be prepared by thermal decomposition of $[CpNi(CO)]_2$ (*98*) and ions formed from this complex may account for the peaks seen above that due to the parent ion in the spectrum of $[CpNi(CO)]_2$ (*212*). In the spectrum of the trinuclear complex, the most abundant ions contain no CO groups, and are characteristic of a NiCp group; the ions $(CpNi)_3(CO)_n^+$ ($n = 0$–2) were relatively weak, and the only other Ni_3 fragments were $Ni_3Cp_3^+$, $Ni_3Cp(C_5H_4)_2^+$, and $Ni_3Cp_2^+$ (*212*).

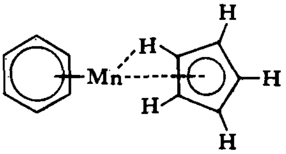
D. π-Arene Complexes

The fragmentation pattern of $Cr(C_6H_6)_2$ is relatively simple (*192*). The base peak is Cr^+, and other ions are $C_3H_3^+$, $C_6H_5^+$, $C_6H_6^+$, $C_6H_6Cr^+$, and possibly $C_6H_6CrC_3H_3^+$, as well as P^+ and P^{2+}. Another investigation (*83*) showed $C_6H_6^+$ as the base peak, but these authors suggested that this was inflated by thermal decomposition, the true base peak being Cr^+. They also observed $CrC_3H_3^+$ and $CrC_4H_4^+$ in small amounts. The mass spectra of some substituted complexes of this type are described in Section VII.

Benzenechromium tricarbonyl also gives Cr^+ as the base peak (*192*). Successive loss of three CO groups occurs, together with loss of C_6H_6 to give $Cr(CO)_n^+$ ($n = 0$–2). Again the spectrum is relatively simple and the only other important ions are the expected $C_3H_3^+$, $C_6H_5^+$, and $C_6H_6^+$. The hexamethylborazole complex similarly shows $B_3N_3Me_6^+$, as well as $B_3N_3Me_6Cr(CO)_n^+$ ($n = 0$, 1, and 3) (*196b*).

The mass spectrum of the mixed complex $CpMnC_6H_6$ has been compared with those of ferrocene and $Cr(C_6H_6)_2$ (*83*). The base peak is $MnCp^+$ (cf. ferrocene, $FeCp_2^+$; dibenzenechromium, $C_6H_6^+$ or Cr^+), followed by Mn^+ and P^+. The principal reaction is thus loss of the C_6H_6 group. Of the remaining metal-containing ions, these corresponding to MnC_2H^+, MnH^+, and $C_6H_6MnH^+$ are prominent, but $C_6H_6Mn^+$ is only about a quarter as abundant as the corresponding hydride ion. At 20-eV ionizing energy,

$C_6H_6Mn^+$ was not seen but $C_6H_6MnH^+$ was as common as Mn^+. The formation of this hydride probably occurs by a concerted mechanism during the loss of the Cp group.



The low intensity of $MnC_6H_6^+$ is probably due to its very rapid decomposition into Mn^+ and C_6H_6. This idea is supported by the molecular ion ionization curve, which shows two apparent breaks at the energies corresponding to the breaking of the Mn—C_6H_6 and Mn—C_5H_5 bonds. The stability of the other metal-containing ions in this and similar compounds can be associated with combinations of Mn^{2+} with a relatively stable anion, such as acetylide or cyclopentadienide.

E. Olefin and Acetylene Complexes

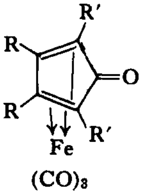
A comparison of the mass spectra of $C_6H_8Fe(CO)_3$ and its fluorocarbon analog has been made (*248*). Wilkinson *et al.* (*128*) reported the partial mass spectrum of the latter complex, observing successive loss of three CO groups from the parent ion, with $C_6F_6^+$ as the major fluorocarbon ion. Similar loss of CO groups was observed with the hydrocarbon derivative, but no ion $C_6H_8Fe^+$ was observed. The ions $C_6H_6Fe(CO)_n^+$ ($n = 0$, 1) were present in high abundance, although the corresponding fluorocarbon ions do not appear, and this may reflect the greater ionic strength of C—F bonds compared to C—H bonds. No ion $Fe(CO)_3^+$, and only weak ions $Fe(CO)_n^+$ ($n = 1, 2$) were found, indicating that the C_6H_8—Fe bond is stronger than the C_6F_8—Fe bond. These differences are accounted for by the relative contributions of π and σ bonding in the ring-to-metal bonding in these complexes and ions.

Norbornadienechromium tetracarbonyl fragments by different routes (*41*). The expected loss of CO groups occurs to give $C_7H_8Cr^+$, which then loses C_2H_2 to give $C_5H_6Cr^+$. Loss of CH_2 from the parent ion gives $C_6H_6Cr(CO)_4^+$, possibly a derivative of Dewar benzene. An interesting series of ions is $CpCr(CO)_n^{2+}$ ($n = 0$–3), which are not seen as their singly charged counterparts.

A number of hitherto incompletely characterized olefin complexes of iron carbonyl have been examined by King (*151*), who has reformulated some of them. The product originally thought to be butatriene-$Fe_2(CO)_5$ (*182*) shows a parent ion corresponding to the presence of six carbonyl groups at *m/e* 332, and peaks due to the successive loss of these groups are found (*151*, *183*). Conversely, the product from acenaphthylene and $Fe_3(CO)_{12}$, formulated as $C_{12}H_8Fe_2(CO)_6$ (*155*), gives as its highest peak $C_{12}H_8Fe_2(CO)_5^+$. King suggests this compound may be similar to the corresponding azulene complex, originally prepared by Wilkinson *et al.* (*56*), and confirmed as $C_{10}H_8Fe_2(CO)_5$ by mass spectrometry (*151*) and a crystal structure determination (*71*). Slightly different reaction conditions, however, afford a new complex, formulated as $[C_{10}H_8Fe(CO)_2]_2$ from mass spectral data. The fragmentation of all these complexes apparently involves loss of all CO groups before any more fundamental disruption of the molecule occurs.

The cyclooctatetraene complex, $C_8H_8Ru(CO)_3$, fragments by loss of CO groups, followed by loss of four C_2H_2 groups (*50*). The series $RuC(C_2H_2)_n^+$ ($n = 0$–3) is also observed, being presumably carbide species formed by fission of the last carbonyl group. The related $C_8H_8Ru_2(CO)_6$ shows all ions $C_8H_8Ru_2(CO)_n^+$ ($n = 0$–5) and then loses C_2H_2 to form $C_6H_6Ru_2^+$.

The spectrum of (V) ($R = H$, $R' = CF_3$) shows a parent ion and loss of three CO groups, as expected (*51*). Further fragmentation involves loss of the metal, and then of CO from the ligand ion to give a cyclobutadiene



(V)

species. The C_4 skeleton persists during loss of F, CF, or CF_3 groups, to give $C_4H_2^+$. A similar ruthenium complex with $R = R' = CF_3$, behaves analogously (*53*).

V

FLUOROCARBON COMPLEXES

Wilkinson *et al.* (*128*) have reported the partial mass spectrum of the heterocyclic complex $C_4F_8Fe(CO)_4$. Fragmentation occurs by loss of CO, and also with formation of $C_4F_6^+$, the high abundance of which is probably related to the case with which the complex forms perfluorocyclobutene when heated.

The mass spectrum of the product from hexafluoro-2-butyne and nickel carbonyl was used to establish its formula as $(C_4F_6)_3Ni_4(CO)_3$ (*152*). The principal peaks above *m/e* 300 were due to loss of fluorine and the CO groups; stepwise loss of C_4 units suggested that the acetylene had not polymerized during complex formation. The tetrahedral Ni_4 cluster persisted to give ions such as $C_4F_6Ni_4^+$, but further fragmentation then occurs to give tri- and binuclear species.

Comparison of the breakdown patterns of 1,2-dichlorohexafluorocyclopentene with those of the derived complexes, $C_5H_6ClM(CO)_5$ (M = Mn or Re) showed that the presence of the metal results in an extra fragmentation route (*48*). Loss of the CO groups occurs readily, as does that of one fluorine atom, to give $C_5F_6ClM^+$ and $C_5F_5ClM^+$. Further cleavage occurs with loss of F, Cl, M (if present) or CF_3, the latter route being of minor importance in the case of the metal complexes. Rupture of the metal–carbon σ bond gives $C_5F_6Cl^+$ and $M(CO)_5$ rather than a charged metal ion. This cleavage occurs to a far greater extent with manganese, which is in keeping with the known relative thermal stabilities of organomanganese and organorhenium complexes.

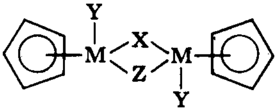
With $CpFe(CO)_2CH_2C_6H_5$, the base peak corresponds to $C_5H_5FeCH_2C_6H_5^+$; peaks due to the parent and $(P—CO)^+$ are relatively weak, and other ions observed are characteristic of CpFe groups. The pentafluorobenzyl complex, on the other hand, shows a base peak at *m/e* 181, corresponding to $C_7H_2F_5^+$ and the only other significant ions are the parent and $C_5H_5Fe^+$ (*49*).

By analogy with the well-known rearrangement of most C_7H_8 compounds in the mass spectrometer to form the very stable tropylium cation (*179*), the base peak in the spectrum of the benzyl complex is probably the π-cyclopentadienyl-π-tropyliumiron cation, and that in the pentafluorobenzyl complex is the pentafluorotropylium cation. The differences in the spectra are rationalized in terms of the apparent reluctance of highly fluorinated ring systems to form π-bonded metal complexes analogous to those formed by the corresponding hydrocarbons.

VI

SULFUR, NITROGEN, AND PHOSPHORUS COMPLEXES

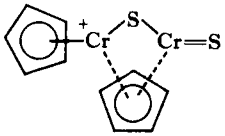
Preston and Reed (*196, 196a*) have studied some binuclear complexes of chromium, iron, and nickel (VI). With chromium complexes, formation of $CrCp_2^+$ was observed from many ions, e.g., where X = Z = SMe,



(VI)

X, Z = SMe, SPh, OMe, or NMe_2
M = Cr, Fe, Ni
Y = NO or CO

by elimination of CrS_2 from an intermediate $[Cp_2Cr_2S_2]^+$ (VII).



(VII)

Labeling experiments showed that loss of C_5H_6 and C_6H_6 (from phenyl derivatives) occurred, hydrogen being transferred between cyclopentadienyl and phenyl groups in the chromium complex, but only between cyclopentadienyl groups with iron. Other fragmentations are largely as expected, e.g., loss of CO or NO groups, and of the bridging groups.

Both series[5] of compounds $[ReER(CO)_4]_2$ and $[ReER(CO)_3]_n$ (E = S, R = Me, Et, *n*-Bu, or Ph; E = Se, R = Ph) apparently decompose in the spectrometer to give ions derived from a tetrameric species, $[ReER(CO)_3]_4$ (*1*). The ions observed from the phenylthio and phenylseleno complexes were similar. The major features are strong peaks corresponding to successive loss of the 12 CO groups and 4 R groups, which are also observed as doubly charged series of ions. The $Re_4E_4^+$ ion appears to withstand further fragmentation, and no significant amounts of Re_n^+ ($n = 1$–4) were observed.

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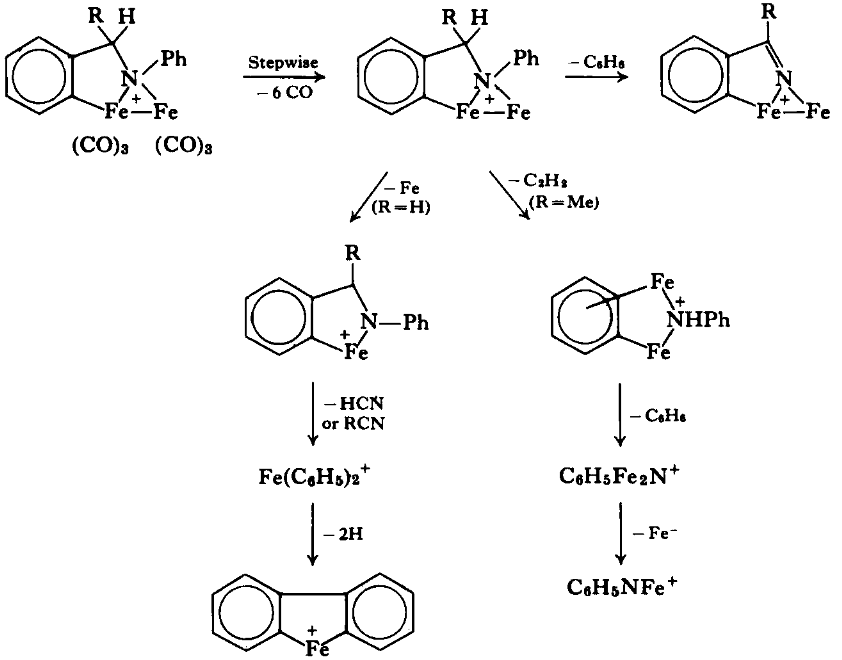
[5] The complexes $[ReER(CO)_3]_n$, and the manganese analogs, originally formulated as trimers on the basis of osmometric molecular weight measurements (*1a, 187a*), have been reinvestigated (*1b, 138a*). The results, together with the mass spectrometric data, indicate that these complexes should be regarded as tetramers.

The mass spectrum of $[(CF_3)_2C_2S_2Co(CO)]_3$ shows a parent ion (*m/e* 758) and ions due to loss of three CO groups (*154*). Loss of neutral CoF_2, confirmed by the appropriate metastable ion, is then a preferred route for the decomposition of the carbonyl-free ion.

$$C_{12}F_{18}S_6Co_3^{+} \rightarrow C_{12}F_{16}S_6Co_2^{+} + CoF_2$$

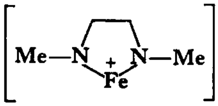
A similar product from a reaction of the dithietene with $Hg[Fe(CO)_3NO]_2$ was shown to be a mixture of $[(CF_3)_2C_2S_2Fe(NO)]_3$, from which loss of three NO groups and a fluorine atom was observed, and $[(CF_2)_2C_2S_2]_2Fe_3S(NO)_4$, which gave a series of ions corresponding to $(C_4F_6S_2)_2Fe_3S(NO)_n^{+}$ ($n = 0$–4).

Schiff-base complexes fragment according to the scheme below (*25*, *196a*); labeling experiments were used to determine which phenyl group was lost. The localization of charge on the iron atoms explains loss of benzene by fission of an N—C bond, which is contrary to the usual β-fission of amines.



The fragmentation patterns of a number of phosphine–metal carbonyl complexes have been reported (*164*). Complexes of bis(diphenylphosphino)ethane (diphos) appear to lose ethylene to give ions of the type $(Ph_2P)_2Mo^{+}$. In contrast to thermal decomposition by loss of phosphine, breakdown in the mass spectrometer occurs by loss of CO groups. With diphos$[W(CO)_5]_2$, no ions containing only one tungsten atom were recorded, all being of the type $LW_2(CO)_n^+$ ($n = 0$–10) or $(Ph_2P)_2W_2^+$. In a series of complexes $[R_3PMn(CO)_4]_2$ ($R = Et$ or Ph, for example), ions containing two metal atoms are very much less abundant, and the abundance is lower with the aryl phosphines than with alkyl phosphines. In general, the molecules lose CO, to give R_3PMn^+ as the most abundant metal ion, also observed as a doubly charged peak. Breakdown of the phosphine while attached to the metal gives species such as R_2PMn^+ and R_2PHMn^+, and with some analogous phosphite complexes, loss of an alkoxy group occurs. A process such as $L_2Mn_2(CO)_8^+ \rightarrow L_2Mn_2(CO)_4^+ \rightarrow L_2Mn^+$ seems to occur to give these ions as the most abundant ones in the spectra.

Studies (*41*, *42*) have demonstrated that cleavage patterns of phosphines coordinated to metals are significantly different from the free ligands. For example P—R bond cleavage occurs in $Bu_3PCr(CO)_5^+$, but not to any marked extent in Bu_3P itself (*43*). In $L_2Cr(CO)_4$ $[L = P(OMe)_3]$ competing processes are loss of CO and of OMe, to give $CrL_2(CO)_n^+$ and $MeO_2PCrL(CO)_n^+$ ($n = 0$–4). Further breakdown gives $LCrPO(OMe)_2^+$, $(MeO)_2PCrP(OH)(OMe)_2^+$, $HCrP(OMe)_2^+$, and $CrP(OH)(OMe)^+$. In complexes of $P(NMe_2)_3$, hydride transfer occurs between ligand and metal, and between ligands (*41*). From $[P(NMe_2)_3]_2Fe(CO)_3$, CO and NMe_2 groups are lost competitively, further fragmentation occurring in an analogous manner to the $P(OMe)_3$ complex described above, with formation of ions such as $Fe(CO)\cdot P(NMe_2)_2\cdot HP(NMe_2)_2^+$, $(NMe_2)_2PH\cdot Fe\cdot HPNMe_2^+$, and $FeN_2C_4H_{10}^+$. The latter ion has been tentatively formulated as

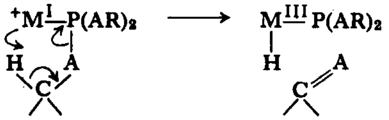


and is formed by loss of PH_3 from $HFeP(NMe_2)_2^+$.

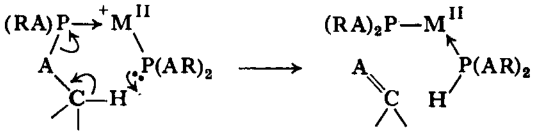
The main fragmentations of coordinated phosphines seem to be the following:

(1) $$^{+}M^{I}\text{—}P(AR)_3 \longrightarrow {}^{+}M^{II}\text{—}P(AR)_2 + AR$$

(2)

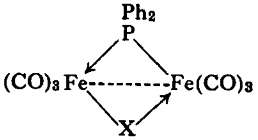


(3)



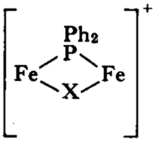
where A may be CR_2, NR or O.

The complexes (VIII) and (IX)

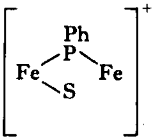


(VIII) X = SPh
(IX) $X = PPh_2$

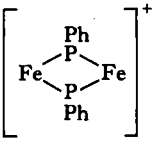
show prominent peaks corresponding to the parent ion and successive loss of six CO groups, resulting in (X) (*136*). Further fragmentation of this ion occurs by loss of a single phenyl group to a limited extent, but strong peaks corresponding to (XI) and (XII) indicate that elimination of two phenyl groups is favored. Ions are also observed indicating thermal degradation to PPh_3 and PPh_2H, and Ph_2PSPh and Ph_2PPPh_2, respectively, in the spectrometer.



(X)

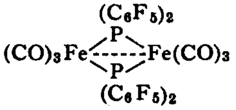


(XI)

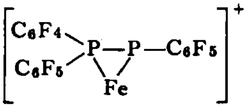


(XII)

Complex (XIII) shows a weak molecular ion and peaks due to $(P - nCO)^+$ ($n = 1$–3, 5, 6), the latter being the base peak, which also occurs as a doubly charged ion (*3*, *180*). There is no evidence for loss of $P(C_6F_5)_2$ or $P_2(C_6F_5)_4$. Loss of neutral FeF_2 occurs from the base peak to give $[(C_6F_4)_2PP(C_6F_4)_2]^+$; similarly, elimination of C_6F_5FeF from the base peak gives (XIV). This loss of FeF_2 species is similar to the loss of CoF_2 from $[(CF_3)_2C_2S_2Co(CO)]_3$ and may be a general phenomenon.



(XIII)



(XIV)

TABLE I

TRANSITION METAL COMPOUNDS FOR WHICH MASS SPECTRAL DATA HAVE BEEN REPORTED

Compound	Principal ions[a]	References
(*a*) *Metal carbonyls*		
$V(CO)_6$	$P^+,(P-nCO)^+$	*36a*
$Cr(CO)_6$	See Section II,A	*13, 16, 36a, 102, 140a, 193, 229, 244, 245*
$Mo(CO)_6$	See Section II,A	*16, 36a, 102, 112, 140a, 193, 229, 244, 245*
$W(CO)_6$	See Section II,A	*14, 17, 26, 27, 36a, 61, 82, 102, 140a, 193, 229 244, 245, 249*
$Mn_2(CO)_{10}$	See Section II,B	*35, 49, 131, 164, 224a, 247*
$MnRe(CO)_{10}$	Loss of CO groups	*224a*
$Re_2(CO)_{10}$	See Section II,B	*49, 164, 224a*
$Fe(CO)_5$	See Section II,A	*8, 19, 26, 27, 36a, 102, 111, 140a, 193, 229, 242, 243, 245*
$Fe_2(CO)_9$	See Section II,B	*70*
$Fe_3(CO)_{12}$	See Section II,C	*8, 151, 164*
$Ru_3(CO)_{12}$	See Section II,C	*49, 122, 151, 164*
$Os_3(CO)_{12}$	See Section II,C	*138*
$Co_2(CO)_8$	See Section II,B	*36, 247*
$Co_4(CO)_{12}$	See Section II,C	*151*
$Ni(CO)_4$	See Section II,A	*6, 8, 19, 26, 27, 36a, 81, 110, 140a, 243, 245*
(*b*) *Metal carbonyl derivatives*		
$HMn(CO)_5$	See Section II,E	*91*
$H_3Mn_3(CO)_{12}$	See Section II,E	*137*
$H_3Re_3(CO)_{12}$	See Section II,E	*137*
$H_2Ru_4(CO)_{13}$	See Section II,E	*137*
$H_4Ru_4(CO)_{12}$	See Section II,E	*134, 137*
$H_nOs_4(CO)_{12}$	See Section II,E	*137*
$Os_4O_4(CO)_{12}$	See Section II,E	*138*
$Mn(CO)_5Br$	See Section III	*164*
$[Mn(CO)_4Cl]_2$	See Section III	*164*
$[Mn(CO)_4Br]_2$	See Section III	*164*

TABLE I—*continued*

Compound	Principal ions	References
(*b*) *Metal carbonyl derivatives*—(continued)		
$[Ru(CO)_3Cl_2]_2$	See Section III	*55*
$[Ru(CO)_3I_2]_2$	See Section III	*54*
$Ru(CO)_4I_2$	See Section III	*54*
$Fe(CO)_2(NO)_2$	See Section II,F	*103*
$Co(CO)_3NO$	See Section II,F	*103*
$Ph_3SnMn(CO)_5$	See Section II,D	*164*
$Me_3SnNCW(CO)_5$	P^+, $(P-nCO)^+$, $Me_3SnNCW(CO)_nC^+$	*149*
$ClCCo_3(CO)_9$	See Section II,E	*151*
$MeCCo_3(CO)_9$	See Section II,E	*151*
$MeCH_2CCo_3(CO)_9$	See Section II,E	*51*
$R_3SnCo_3(CO)_{12}$ (R = Me, CH:CH$_2$, Bu, Ph, Cl, Br, I)	See Section II,E	*190, 191*
(*c*) *Cyclopentadienyl compounds*		
$MgCp_2$	See Section IV,C,1	*104, 239*
VCp_2	See Section IV,C,1	*104, 239*
$CrCp_2$	See Section IV,C,1	*104, 239*
$MnCp_2$	See Section IV,C,1	*104, 239*
$FeCp_2$	See Section IV,C,1	*72, 83, 104, 172, 211, 221, 239*
$RuCp_2$	See Section IV,C,1	*104, 239*
$CoCp_2$	See Section IV,C,1	*104, 192, 239*
$NiCp_2$	See Section IV,C,1	*101, 135, 211, 239*
$CpTiCl_3$	See Section IV,C,1	*184*
$CpTiCl_2(OEt)$	See Section IV,C,1	*184*
$CpTiCl(OEt)_2$	See Section IV,C,1	*184*
$CpTi(OEt)_3$	See Section IV,C,1	*184*
Cp_2TiNCO	P^+, $(P-NCO)^+$, $(P-Cp)^+$, $TiNC^+$; also $(P+C_3H)^+$, $(P+C_3H_3)^+$	*78*
$[Cp_2TiCN]_3$	P^+; loses Cp, CN, or Cp_2TiCN	*78*
$[Cp_2TiNCS]_3$	None above Cp_2TiNCS; loses Cp, NCS	*78*
Cp_2ZrCl_2	See Section IV,C,1	*202*
$(Cp_2ZrCl)_2O$	See Section IV,C,1	*202*
$Cp_2Zr(H)BH_4$	P^+	*133*
$CpV(OAc)_2$	P^+, $CpV(OH)(OAc)^+$, $CpVCO_2Me^+$, $CpV(OH)_2^+$, $CpVO^+$, CpV^+	*148*
$CpV(CO)_4$	See Section IV,C,2	*246*

TABLE I—*continued*

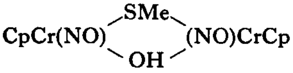
Compound	Principal ions	References
(*c*) *Cyclopentadienyl compounds*—(continued)		
$[\mathrm{CpCr(CO)_3}]_2$	See Section IV,C,2	*151*
$[\mathrm{CpCr(NO)X}]_2$ ($\mathrm{X=SMe, SPh, OMe, NMe_2}$)	See Section VI	*196*
 $\mathrm{CpCr(NO)}\genfrac{}{}{0pt}{}{\diagup\mathrm{SMe}\diagdown}{\diagdown\mathrm{OH}\diagup}\mathrm{(NO)CrCp}$	See Section VI	*196*
$[\mathrm{CpMo(NO)I_2}]_2$	$\mathrm{(P-2I)^+, (P-2I-NO)^+, P^{2+}}$; loss of NO, Cp, or I	*150*
$[\mathrm{CpMo(CO)_3}]_2$	See Section IV,C,2	*151, 164, 212*
$\mathrm{CpMo(NO)(CO)_2}$	See Section II,F	*248*
$\mathrm{CpMo(CO)_3Br}$	See Section III	*212*
$\mathrm{CpMo(CO)_3GeEt_3}$	Isotope pattern only	*64*
$\mathrm{CpW(CO)_3SnMe_2}$	$\mathrm{P^+}$	*62*
$\mathrm{CpMn(CO)_3}$	See Section IV,C,2	*246*
$[\mathrm{CpMn(NO)_2}]_n$	Decomp. products, e.g., $\mathrm{Cp_2MnH^+, C_5H_nMn^+}$ ($n=3, 4, 5$)	*150*
CpTcH	See Section IV,C,1	*98a*
$\mathrm{Cp_2ReH}$	See Section IV,C,1	*98a, 104, 239*
$[\mathrm{CpFe(CO)_2}]_2$	See Section IV,C,2	*164, 212*
$\mathrm{CpFe(CO)_2Cl}$	See Section III	*49*
$\mathrm{CpFe(CO)_2Br}$	See Section III	*212*
$\mathrm{CpFe(CO)_2SnCl_3}$	See Section II,D	*164*
$\mathrm{CpFe(CO)_2SnPh_3}$	See Section II,D	*164*
$\mathrm{Hg[CpFe(CO)_2]_2}$	See Section II,D	*164*
$\mathrm{CpFe(CO)_2CH_2C_6H_5}$	See Section V	*49*
$\mathrm{CpFe(CO)_2CH_2C_6F_5}$	See Section V	*49*
$[\mathrm{CpFe(CO)SR}]_2$ ($\mathrm{R=Me, Ph}$)	See Section VI	*196*
$[\mathrm{CpFeCO}]_4$	$\mathrm{P^+, (P-CO)^+, (P-2CO)^+}$, $\mathrm{Cp_3Fe_3(CO)_n^+, Cp_2Fe_2(CO)_n^+}$, $\mathrm{CpFe(CO)_n^+, Cp_3Fe_3^+, Cp_3Fe_2^+}$, $\mathrm{Cp_2Fe_2^+, Cp_2Fe^+, CpFe^+}$	*147*
$\mathrm{CpCo(CO)_2}$	See Section IV,C,2	*192, 246*
$[\mathrm{CpNiCO}]_2$	See Section IV,C,2	*212*
$\mathrm{CpNi(CO)C_2F_5}$	$\mathrm{P^+}$	*169*
$\mathrm{Cp_3Ni_3(CO)_2}$	See Section IV,C,2	*212*
CpNiNO	See Section II,F	*103*
$[\mathrm{CpNiSR}]_2$ ($\mathrm{R=Me, Ph}$)	See Section VI	*196*
(*d*) *Other π-bonded complexes*		
$\mathrm{Zr(\pi\text{-}C_3H_5)_4}$	See Section IV,A	*28*
$\mathrm{Hf(\pi\text{-}C_3H_5)_4}$	See Section IV,A	*28*

TABLE I—*continued*

Compound	Principal ions	References
(*d*) *Other π-bonded complexes*—(continued)		
$Cr(\pi\text{-}C_3H_5)_3$	See Section IV,A	*28*
$Rh(\pi\text{-}C_3H_5)_3$	P^+, $(P-nC_3H_5)^+$	*29*
$[(\pi\text{-}C_3H_5)_2RhCl]_2$	See Section IV,A	*56a*
$[(\pi\text{-}MeC_3H_4)_2RhCl]_2$	See Section IV,A	*56a*
$Ni(\pi\text{-}C_3H_5)_2$	See Section IV,A	*28, 135, 238*
$CpNi(\pi\text{-}1\text{-}methallyl)$ (*syn* and *anti* isomers)	P^+, $C_9H_{12}Ni^+$, $NiCpH^+$, $NiCp^+$, $NiC_4H_6^+$, Ni^+	*169*
$Pd(\pi\text{-}C_3H_5)_2$	See Section IV,A	*28*
$Pt(\pi\text{-}C_3H_5)_2$	See Section IV,A	*28*
$[\pi\text{-}C_3H_5PdCl]_2$	See Section IV,A	*167*
Trimethylenemethane-$Fe(CO)_3$	P^+, $(P-nCO)^+$	*95*
Cyclobutadiene-$Fe(CO)_3$	P^+, $(P-nCO)^+$	*96*
$[Ph_4C_4PdCl_2]_2$	See Section IV,B	*32*
$Cr(C_6H_6)_2$	See Section IV,D	*83, 192*
$C_6H_6Cr(CO)_3$	See Section IV,D	*192*
$CpCrC_6H_6$	See Section IV,D	*83*
$Me_6B_3N_3Cr(CO)_3$	P^+, $(P-2,3CO)^+$, $Me_6B_3N_3^+$	*196b*
$CpW(CO)_2C_7H_7$	P^+, $(P-2CO)^+$	*153*
(*e*) *Olefin and acetylene complexes*		
Norbornadiene-$Cr(CO)_4$	See Section IV,E	*41*
Dicyclopentadiene-$W(CO)_4$	P^+, $(P-nCO)^+$	*153*
(1,3-Cyclohexadiene)$_2W(CO)_2$	P^+, $(P-CO)^+$, $C_6H_8W(C_6H_6)CO^+$, $C_6H_6W(CO)_{2,1,0}$; $W(C_6H_6)_2^+$ and $W(C_6H_6)_2^{2+}$	*153*
$(MVK)_3W$ MVK = methylvinyl ketone	P^+, $(P-MVK)^+$, $W(MVK)(CH_2{:}CHCO)^+$, further degradation resulting in rather complex rupture of MVK groups	*153*
Cyclohexadiene-$Fe(CO)_4$	See Section IV,E	*248*
Butatriene-$Fe_2(CO)_6$	P^+, $(P-nCO)^+$	*151, 183*
Acenaphthylene-$Fe_2(CO)_5$	P^+, $(P-nCO)^+$, $C_{12}H_8Fe^+$, $C_{12}H_8^+$	*151*
Azulene-$Fe_2(CO)_5$	See Section IV,E	*151*
[Azulene-$Fe(CO)_2]_2$	P^+, $(P-nCO)^+$, $C_{10}H_8Fe^+$, $C_{10}H_8^+$	*151*
(Allene dimer)$Fe(CO)_2$	P^+, $(P-nCO)^+$	*151*
Cyclooctatetraene-$Ru(CO)_3$	See Section IV,E	*50*
Cyclooctatetraene-$Ru_2(CO)_6$	See Section IV,E	*50*
$(CF_3C{\equiv}CH)Co_2(CO)_6$	No P^+; $acCo_2(CO)_5^+$	*89*
$(CF_3C{\equiv}CH)_3Co_2(CO)_4$	Loss of 4CO, then 2Co to give ac_3^+	*89*

TABLE I—*continued*

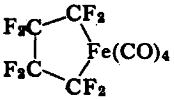
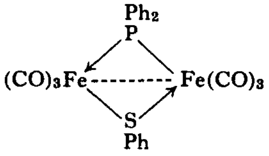
Compound	Principal ions	References
(*e*) *Olefin and acetylene complexes*—(continued)		
$[(CF_3)_2C_2]_3W(CH_3CN)$	P^+, $(P-C_4F_6)^+$, $(P-F)^+$, $(C_4F_6)_2C_4F_5W^+$, $(C_4F_6)_2W(NCMe)F^+$, $W(C_4F_6)_2^+$, $C_4F_6WC_4F_5^+$., $C_4F_6W(NCMe)F_2^+$, $(MeCN)WF_2^+$, other C_{12} and C_{11} fluorocarbon ions	*153*
$[(CF_3)_2C_2]_3Ni_4(CO)_3$	P^+, $(P-F)^+$, $(P-nCO)^+$ also loss of C_4F_6 units to give $(C_4F_6)_2Ni_4^+$, $C_4F_6Ni_4^+$; $C_8F_8Ni_4^+$, $C_4F_4Ni_3^+$	*152*
(*f*) *σ-Bonded Compounds*		
Me_3NbCl_2	No parent; $Me_2NbCl_2^+$	*141*
$(Ph_3P)_2Pt(\sigma\text{-}C_3H_5)_2$	See Section IV,A	*28*
(*g*) *Fluorocarbon complexes*		
Perfluorocyclohexadiene-$Fe(CO)_3$	See Section IV,E	*128*
	See Section V	*128*
$(CF_3)_2H_2C_5O\cdot Fe(CO)_3$	See Section IV,E	*51*
$(CF_3)_4C_5O\cdot Ru(CO)_3$	See Section IV,E	*53*
$C_5F_6ClMn(CO)_5$	See Section V	*48, 52*
$C_5F_6ClRe(CO)_5$	See Section V	*48, 52*
(*h*) *Phosphorus and sulphur complexes*		
$[CpVS_2C_2(CF_3)_2]_2$	P^+; other ions with 2 V atoms	*148*
$Et_3PCr(CO)_5$	—	*89a*
$Bu_3PCr(CO)_5$	See Section VI	*43, 89a*
$(BuO)_3PCr(CO)_5$	—	*89a*
$[(MeO)_3P]_2Cr(CO)_4$	See Section VI	*43*
$BuNCMo(CO)_5$	—	*89a*
$Et_3PMo(CO)_5$	—	*89a*
$Bu_3PMo(CO)_5$	—	*89a*
$Ph_3PMo(CO)_5$	P^+, $(P-nCO)^+$ (except $n=5$)	*164*
$PhCl_2PMo(CO)_5$	—	*89a*
$(BuO)_3PMo(CO)_5$	—	*89a*
diphos$Mo(CO)_4$	P^+, $(P-nCO)^+$, Ph_2PMo^+	*164*
py$W(CO)_5$	—	*89a*
$BuNCW(CO)_5$	—	*89a*

TABLE I—*continued*

Compound	Principal ions	References
(*h*) *Phosphorus and sulphur complexes*—(continued)		
$Et_3PW(CO)_5$	—	*89a*
$Bu_3PW(CO)_5$	—	*89a*
$Ph_3PW(CO)_5$	P^+, $(P-n\mathrm{CO})^+$ (except n = 5)	*164*
$PhCl_2PW(CO)_5$	—	*89a*
$(BuO)_3PW(CO)_5$	—	*89a*
[diphos $W(CO)_5]_2$	See Section VI	*164*
diphos$W(CO)_4$	P^+, $(P-n\mathrm{CO})^+$, Ph_2PW^+	*164*
$(PhP)_5W(CO)_5$	$(P-CO)^+$ highest ion; $(PhP)_5^+$	*4*
$[R_3PMn(CO)_4]_2$ ($R_3 = Et_3$, Pr_3, Bu_3, $PhEt_2$, Ph_2Et, Ph_3, $(OMe)_3$, $(OEt)_3$, $(OPh)_3$)	See Section VI	*164*
cis-$PEt_3Mn(CO)_4Cl$	—	*164*
$[Re(CO)_3SPh]_2$	See Section VI	*1*
$[Re(CO)_4SePh]_2$	See Section VI	*1*
$[Re(CO)_3SPh]_4$	See Section VI	*1*
$[Re(CO)_3SePh]_4$	See Section VI	*1*
$[P(NMe_2)_3]_2Fe(CO)_3$	See Section VI	*41*
$[Fe(CO)_3PPh_2]_2$	See Section VI	*136*
$[Fe(CO)_3P(C_6F_5)_2]_2$	See Section VI	*3, 180*
$Bu_3PFe(CO)_4$	—	*89a*
$(MeO)_3PFe(CO)_4$	—	*89a*
$(EtO)_3PFe(CO)_4$	—	*89a*
$Cl_3PFe(CO)_4$	—	*89a*
	See Section VI	*136*
$Fe(CO)(NO)_2P(OEt)_3$	See Section II,F	*103*
$[(CF_3)_2C_2S_2Fe(NO)]_3$	See Section VI	*154*
$[(CF_3)_2C_2S_2]_2Fe_3S(NO)_4$	See Section VI	*154*
$Co(CO)_2(NO)PCl_3$	See Section II,F	*103*
$Co(CO)_2(NO)PEt_3$	—	*89a*
$Co(CO)_2(NO)PBu_3$	—	*89a*
$Co(CO)_2(NO)P(OMe)_3$	—	*89a*
$Co(CO)_2(NO)P(OEt)_3$	—	*89a*
$[(CF_3)_2C_2S_2Co(CO)]_3$	See Section VI	*154*

[a] $(P—n\mathrm{R})^+$ indicates that the parent ion loses all the groups R in a stepwise process.

VII

ORGANIC DERIVATIVES OF METALLOCENES AND RELATED COMPOUNDS

It is well known that certain transition metal organometallic complexes, such as ferrocene, cymantrene (cyclopentadienylmanganese tricarbonyl) and butadieneiron tricarbonyl, and to a lesser extent, benzenechromium tricarbonyl, form organic derivatives and have an extensive derivative chemistry of their own. The parent complexes have already been discussed; there follows a summary of the main features observed in the mass spectra of their organic derivatives (Table II, at the end of this section).

Analysis of ferrocene derivatives at low ionizing voltages (~8V) gave intense molecular ions, but compounds containing acidic substituents, e.g., CO_2H, $B(OH)_2$, SO_3H, decomposed in the high-temperature inlet (*73*). Some polyferrocenylenes were also examined using this method, and various polynuclear derivatives obtained by coupling lithiated ferrocenes with $CoCl_2$ and alkyl halides were conclusively identified (*221*). In a series of ferrocenes, the base peak was found to be the parent ion, the electron supposedly coming from the metal to give cations analogous to the ferricinium cation (*201*). There is no evidence for stabilization of a tropylium-type ion from compounds containing a CH_2 group bonded to the ring. Fragmentation was found to be generally in accord with recognized weak bonds in the molecules.

The main fragmentation patterns of a series of metallocene carbinols have been elucidated by means of deuterium labeling (*92*). Elimination of water occurred by several mechanisms, some of which have not been observed in the purely organic counterparts, indicating involvement of the central metal atom. Stereoisomeric cyclic carbinols have been distinguished on the basis of intensity ratios of the ions P^+, $(P-H_2O)^+$, and $(P-2H_2O)^+$ (*93*) or of $FeCp^+$ and $CpFeOH^+$ (*178*).

Studies on monosubstituted ferrocenes containing a carbonyl group in the α-position to the ring have been reported briefly (*174*, *175*). Usually the molecular ion is the base peak, and cleavage occurs on both sides of the carbonyl group. In contrast to the earlier report (*201*), fragments formed by loss of iron, such as $C_5H_5C_5H_4^+$ and $C_5H_4:C_5H_4^+$, were found.

The presence or absence of the ion $FeC_5H_5^+$ (*m/e* 121) has been suggested (*176*) as a more sensitive criterion for distinguishing between homo- and heteroannularly disubstituted ferrocenes than the 9–10 μ rule commonly used (*205*), which has been known to fail in the case of some silicon derivatives (*208*). Furthermore, a recent report (*218*) giving an example of the distinction between 1,1′- and 1,2-disubstituted ferrocenes using other peaks in the mass spectra is of interest.

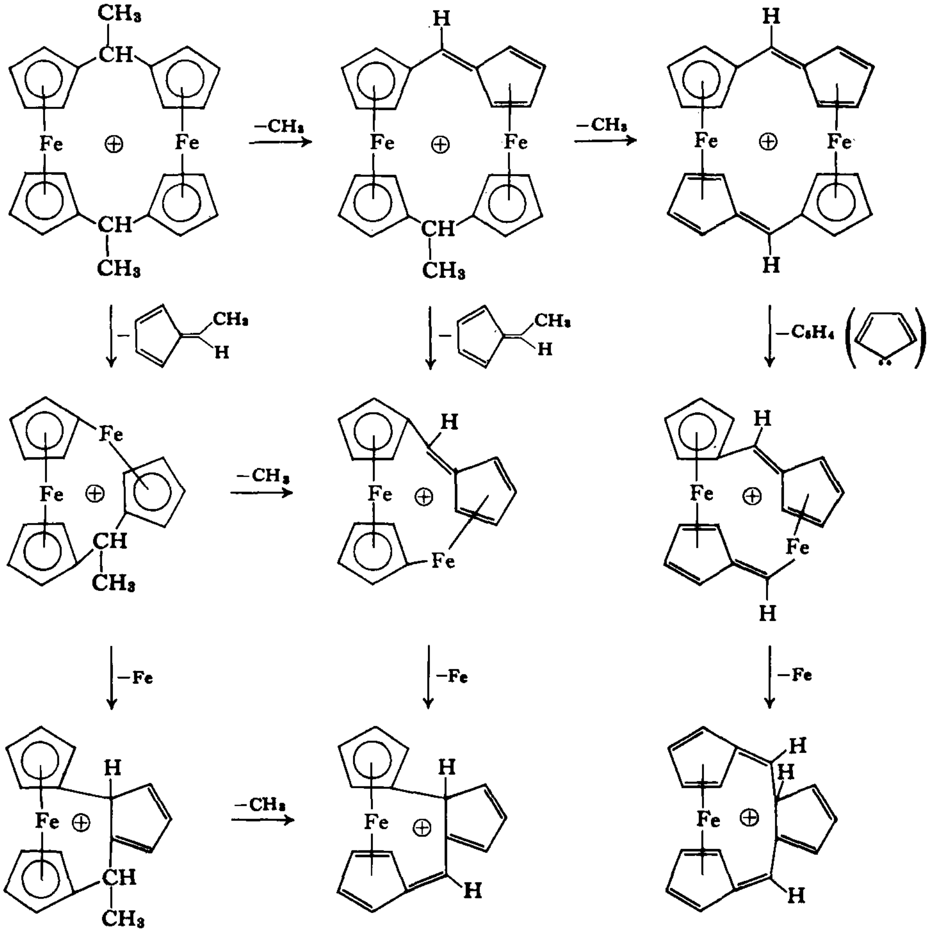
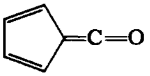


FIG. 2. Major cracking patterns for 1,2-dimethyl[1.1]ferrocenophane (*235*).

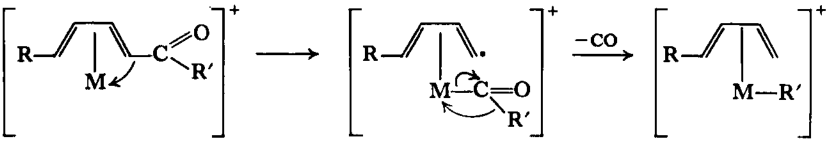
The mass spectra of 1,12-dimethyl- and 1,12-diphenyl[1.1]ferrocenophanes (*235*) are explained by the fragmentation scheme shown in Fig. 2.

The diketo derivative successively eliminates two CO groups, or a group with *m/e* 92, probably



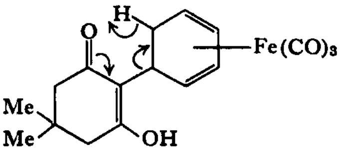
but further breakdown of these ions is extremely limited. As with some trimethylene-bridged ferrocenes (*203*), the characteristic features are extremely intense parent-ion peaks and many doubly charged ions. Alkane cleavage is more pronounced with diferrocenylalkanes, and P^+ are relatively less intense. Some unusual fragmentations were observed involving transfer of iron atoms.

Studies on various derivatives of ferrocene, cymantrene, benzenechromium tricarbonyl, and butadieneiron tricarbonyl were recently reported (*174*, *176*). Carbonyl derivatives containing the COR′ group lose CO to give an ion probably containing the R′ group attached to the metal, e.g.

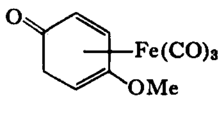


Derivatives containing metal tricarbonyl groups thus show peaks corresponding to loss of *four* carbonyl groups. This decarbonylation process is not observed in the metal-free systems, nor does it occur where the COR′ group is not directly bonded to the metal carrying π-organic moiety.

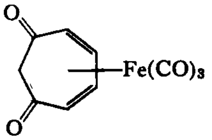
Haas and Wilson (*117*) have studied a number of substituted butadiene-iron tricarbonyl complexes, finding that in most cases loss of three CO groups precedes fragmentation of the ligand. Compared with the ligands the spectra of the complexes show a number of instances where the iron atom tends to stabilize odd-electron ions. In (XV), the presence of the ion



(XV)



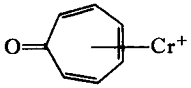
(XVI)



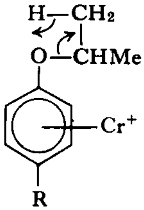
(XVII)

$FeC_6H_6^+$ indicates that the rearrangement shown takes place as it does in the free ligand. In addition, ions formulated as, e.g., [dimedone-Fe]$^+$ indicate migration of the dimedone group to the iron in an analogous manner to the migration of groups from the ring to the metal already discussed. In the corresponding acetylacetone complex, this type of ion was favored, perhaps due to the ability of the acetylacetone fragment to chelate with the metal. In other cyclohexadiene complexes, the same tendency for the ring to aromatize was noted, with the production of ions similar to those formed from the corresponding aromatic tautomers, e.g., (XVI) gave ions similar to those found with *p*-hydroxyanisole. Complex (XVII) fragmented in a similar manner to the tropolone, losing CO to give cyclohexadienoneFe$^+$ followed by loss of 2 H and HCHO to give cyclopentadienoneFe$^+$, which lost a further molecule of CO to give $FeC_4H_4^+$, presumably a cyclobutadiene species.

Substituted arene $Cr(CO)_3$ complexes show little further fragmentation of the $(P-3CO)^+$ ion (*117*). Loss of 2 H from the anisole complex gave stable $C_7H_6OCr^+$, possibly (XVIII), and the analogous isopropoxy complex



(XVIII)



(XIX)

loses propylene, probably by rearrangement (XIX) to give ions containing the phenol. If R = Me, loss of H also occurs, probably to give a hydroxytropylium ion.

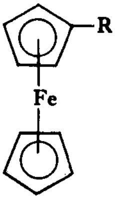
The formation of Cr_2^+, $FeCr^+$, $FeMn^+$, and Mn_2^+ has been reported in the spectra of π complexes containing two or more metal atoms (*176*). The loss of carbonyl groups from such compounds is not straightforward. The diene-$Fe(CO)_3$ complexes do not lose CO stepwise, and in some arene-$Cr(CO)_3$ complexes only arene-$Cr(CO)_n^+$ ($n = 0$, 1 and 3) were seen. Some derivatives of $CpMn(CO)_3$ lose all three CO groups at once, and if a second of these groups is present on a ferrocene moiety, the next three CO groups are also lost simultaneously.

TABLE II

METALLOCENES AND RELATED COMPOUNDS WHICH HAVE BEEN STUDIED USING MASS SPECTROMETRIC TECHNIQUES

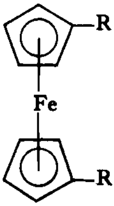
(a) *Ferrocenes*

(i) *Monosubstituted ferrocenes*

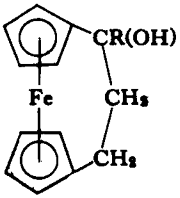


R = CN (*201*), Me (*201*), CH_2OH (*92, 178*), CD_2OH (*92*), $(CH_2)_2OH$ (*92*), CH(OH)Me (*92, 201*), CD(OH)Me (*92*), $CD(OH)CH_2D$ (*92*), CH(OH)Ph (*92*), $(CH_2)_3OH$ (*92*), $(CH_2)_4OH$ (*92*), C(OH)EtPh (*92*), $C(OH)Me.CH_2Ph$ (*92*), $CH(OH)CH_2CH{=}CH_2$ (*178*), $—CH(CH_2)_2COO$ (*178*), *cis* and *trans* $—CHCH_2CHCH_2OH$ (*178*), *cis-* and *trans-* $CHCH_2CHCO_2Et$ (*178*), CPh_2OH (*218*), CO_2H (*73, 174*), CO_2D (*174*), CO_2Me (*174*), COMe (*174*), $CO(CH_2)_2CO_2H$ (*201*), $CO(CH_2)_2CO_2Me$ (*201*), COPh (*174*), COC_6H_4-OMe-*p* (*174*), CONHMe (*174*), $NHCO_2Me$ (*201*), CH_2NMe_2 (*218*), cyclopentadienyl (*221*), $CH_2C_6H_5$ (*221*), C_6H_5 (*201*), C_6H_4Cl-*p* (*201*), $C_6H_4NO_2$-*p* (*201*), PhN_2O (*185*), SO_3H (*72*), SO_2NH_2 (*201*), $B(OH)_2$ (*72*), $SiMe_3$ (*72*), $SiMe_2(OEt)$ (*72*), $SiMe_2CH{:}CH_2$ (*72*), $SiPh_3$ (*72*).

(ii) *1,1′-Disubstituted ferrocenes*



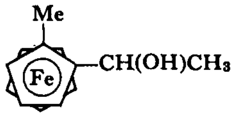
R = R′ = Cl (*72*), CH_2OH (*92*), CD_2OH (*92*), CHMeOH (*92*), C_2H_5 (*72*), C_4H_9 (*72*), $COCH_2CH_2CH_3$ (*72*), $SiMe_3$ (*72*), $SiMe_2(OEt)$ (*72*), $SiMe_2CH{:}CH_2$ (*72*).
R = CH_2NMe_2, R′ = CPh_2OH (*218*).



R = H, D (*92*)

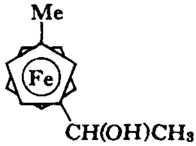
TABLE II—*continued*

(iii) *Other substituted ferrocenes*



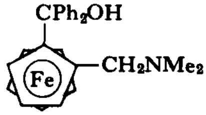
endo and exo

(*92*)

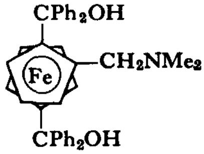


endo and exo

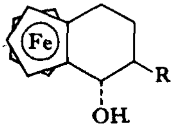
(*92*)



(*218*)

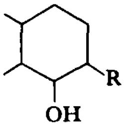


(*218*)



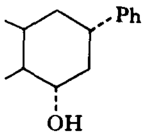
endo R = H, Ph

(*92*)



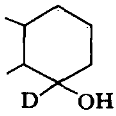
exo R = H, Ph

(*92*)



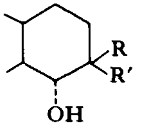
endo

(*92*)



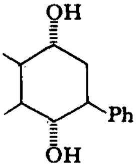
endo and exo

(*92*)

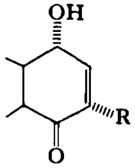


R = R′ = D
R = Ph; R′ = D

(*92*)

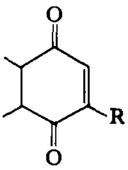


(*94*)



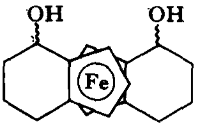
R = H, Ph, cyclohexyl

(*94*)



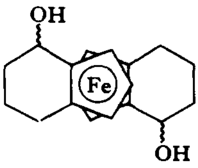
R = H, Ph cyclohexyl

(*94*)



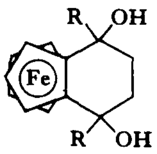
exo/endo
endo/endo

(*92, 93*)



endo/endo
exo/endo

(*92, 93*)

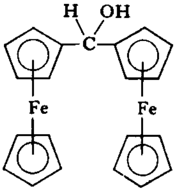


endo/endo } R = H, D
exo/endo }

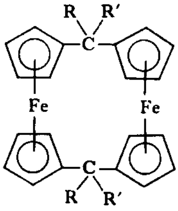
(*92*)

TABLE II—*continued*

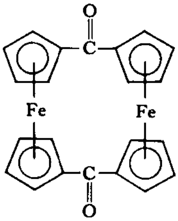
(iv) *Polynuclear ferrocenes*



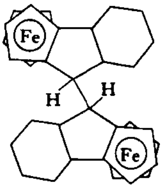
(*92*)



R, R′ = H, H; Me, Me; H, Ph (*235*)
H, Me (*234*)



(*235*)

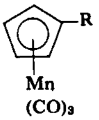


(*58*)

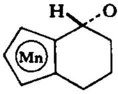
Biferrocenyl (*73*, *221*), diethylbiferrocenyl (*221*), diferrocenylmercury (*199*), terferrocenyl (*221*).

Polyferrocenylenes (*221*), poly(ferrocenyl ketone) (*221*), poly(ferrocenyl-mercury) (*199*).

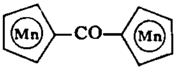
(b) *Cymantrene derivatives*



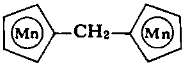
R = CHO (*226*), CH_2OH (*226*), $(CH_2)_2CO_2H$ (*176*), CH:$CHCO_2H$ (*176*), CO_2H (*176*)



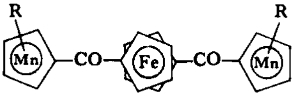
endo (*92*)



(*176*)



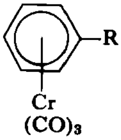
(*176*)



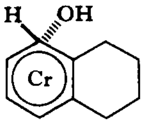
(*176*) (R = H, Me)

TABLE II—*continued*

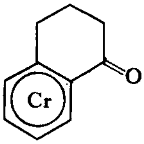
(c) *Benzenechromium tricarbonyl derivatives*



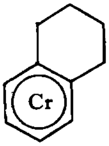
R = OMe (*117*), OCHMe$_2$ (*117*), COPh (*176*), $C_6H_4C_6H_5$ (*176*).
Complexes of *p*-isopropoxytoluene (*117*), *m*-anisic acid (*176*).



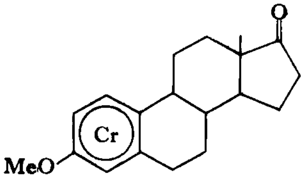
endo
(*92*)



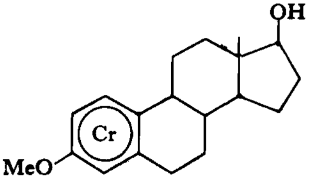
(*176*)



(*176*)



(*117*)



(*117*)

Polynuclear complexes (*176*):

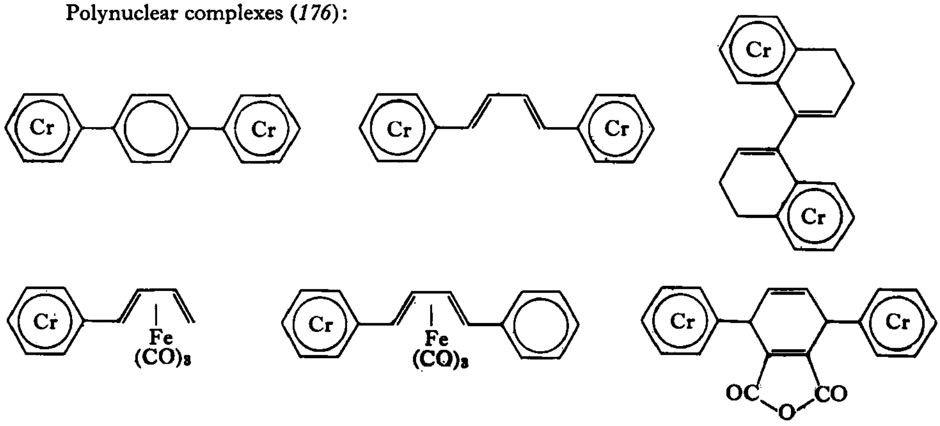
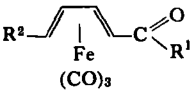


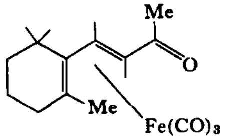
TABLE II—*continued*

(d) *Butadieneiron tricarbonyl derivatives*

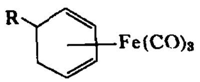


R^1 = OH ; OD ; NH_2 ; NH_2 ; OH ; OMe (*57*)
R^2 = Me ; Me ; Me ; Me ; CO_2H ; CO_2Me

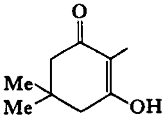
Complexes of β-ionone (*57*), *retro*-ionylidene acetate (*57*), β-ionylidene acetate (*57*), vitamin A aldehyde (*38*),



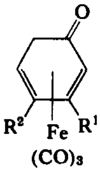
(*57*)



R = $(CH_3CO)_2CH$,

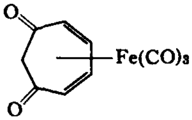


(*117*)

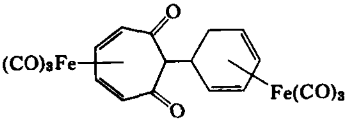


(*117*)

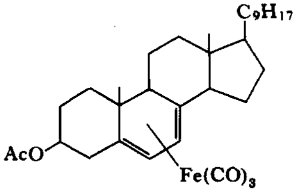
R^1 = Me ; H ; H
R^2 = H ; OMe ; H



(*117*)



(*117*)



Acetylergosterol (*117*)

VIII

MAIN GROUP ORGANOMETALLIC COMPOUNDS

In this section, a short account will be given of the scope of the major references dealing with main group organometallic compounds, although no claim to completeness is made here.

In the spectrum of ethyllithium vapor, the major ions observed were $Li_6R_5^+$ and $Li_4R_3^+$, and fragments derived from these (*30*, *46*, *47*). One alkyl group was found to dissociate from HgR_2 (R = Me, Et, or *n*-Bu) and hydride and hydrocarbon ions formed by intramolecular rearrangement were observed (*87*). Appearance potentials of R^+, HgR^+, and $R'HgR^+$ were measured in RHgR′ (R and R′ = Me_2; Me, Cl; Et_2; iso-Pr_2; *n*-Bu_2) by Gowenlock *et al.* (*116*) and the mass spectrum of dimethylmercury was examined in detail (*127*).

The mass spectra of various boron compounds have attracted considerable attention. Boron trialkyls studied include BMe_3 (*162, 210, 227*), BEt_3 (*162, 210*), BPr_3 (*210*), and BBu_3 (*210*) and combinations of these groups (*121, 142*); various substituted alkenylboranes (*114*); and some fluoroboranes, such as $MeBF_2$, $CH_2{:}CHBF_2$, and Me_2BF (*45, 222*). In the latter case, evidence for the existence of RBXY-type compounds (X = F, Y = Cl or Br) was found. Several methyl- and ethyldiboranes and their deuterated analogs were found to give all of the anticipated fragments (*241*), and methyl-substituted tetra- and pentaboranes (*168*) and various alkylpolyboranes (*216*) have also been studied. Some of the spectra of carboranes that have been reported include those of isomers of $B_2C_4H_{12}$ (*236*), of $B_3C_2H_5$ and $B_3C_2D_3H_2$ (*215*), of normal and deuterated derivatives of $B_4C_2H_6$ (*214*), of $Me_2C_2B_6H_6$ and $B_6H_{10}PPh_3$ (*240*), and of *p*-carborane, $B_{10}C_2H_{12}$ (*188, 189*). Schaeffer (*209*) has reported the spectrum of borane-8 carbonyl (B_4H_8CO). Trimethylboroxines were studied by Lehmann *et al.* (*163*). Examples of boron–nitrogen compounds that have been examined by this technique include triborylamines (*160*), a tert-butyl-substituted boron–nitrogen cyclobutadiene analog (diazaboratane) (*159*), isocyanide-borane adducts (*65, 66*) and their rearrangement products, the 1,3-diaza-2,4-diboretidines (*66*), tetrakis(triethylsilylamino)diborane (*2*) and some aryl dimethyl-aminoboranes which were found to give intense doubly charged peaks (*84*). Tri-*N*-phenylborazoles with various alkyl or aryl substituents on the boron atoms gave ions at one-third and two-thirds the molecular weight (*219*) and other substituted borazoles have been studied (*161, 166, 173*). Two reports concerning dimethylaminoalanes have appeared (*44, 250*).

Many investigations of alkyl and aryl chlorosilanes have been reported (*125, 220, 225, 254*). The probability of cleavage of the R—Si bond is found to decrease with increase in the size of R (*220*). Methylsilanes (*143*) and hydrocarbons with trialkylsilyl groups (*145*) are discussed and extensive studies of linear and cyclic silicon–methylene compounds are also available (*22–24, 105–107, 225*). Russian workers have looked at alkylsilanes (*68*), silacycloalkanes (*69*), and silylvinylacetylenes (*144, 195*). Silicon–carbon bond dissociation energies were reported by Steele *et al.* (*223*). Silicon–oxygen compounds which have been reported include hexamethyldisiloxane (*88*, *217*), octamethyltrisiloxane (*88*), and tetramethyldiphenyldisiloxane (*172*) and several papers have appeared which describe the characteristic mass spectra of trimethylsilyl derivatives of alcohols (*158*, *217*, *252*), thiols (*217*), phenols (*217*), and macrolides (*113*). The mass spectra of hexamethyldisilazane (*217*) and other silazanes (*255*) have also been discussed.

The mass spectra of some propylgermanes and their oxides (*63*), and a brief account of a variety of organogermanes (*67*), have recently been published, as have those of some organogermanium-1,3-enynes, such as 3-buten-1-ynyl- and 3-methyl-3-buten-1-ynyltriethylgermanes (*146*). The interesting compounds originally thought to have been substituted germirenes were shown conclusively to be derivatives of the six-membered 1,4-digermin ring system by mass spectral studies (*115*, *139*, *230*), as also were similar silicon compounds (*140*).

Various organotin compounds, including alkylstannanes, have been investigated. The series Me_nSnEt_{4-n} (*118*) and Ph_nSnEt_{4-n} (*67*) ($n = 0$–4) have been studied and the results used to interpret the spectra of the products of radiolysis of Me_2SnEt_2 (*119*). Mass spectra of various trimethyltin compounds with bond dissociation energies (*253*) and appearance potentials for the principal ions from Me_3SnR (R = Me, Et, *n*-Pr, or $SnMe_3$) (*251*) and SnR_4 (R = Me, Pr, or Ph) (*187*) have been measured. One and three alkyl groups are lost from tetramethyl- and tetraethyllead (*87*, *109*), and principal ions from various mixed compounds of this type have also been reported (*197*).

Alkylphosphines have been studied (*99*, *231*), as have cyclopolyphosphines (*120*). The reaction products of phosphorus with various olefins were investigated using mass spectral methods (*108*), and a large number of phospholines have been reported (*181*, *237*). The mass spectrum of the trimer of tetramethylphosphinoborine showed that B—P, C—B, and C—P bonds were broken first, and with the pentamer of the dimethyl compound, B—H, B—P, and C—P bonds were broken (*101*, *232*). The spectra of thiophosphorustri-*N*-methylimide and its arsenic analog were reported by Holmes and Forstner (*130*). Ionization potentials have been recorded for many perfluoroalkylarsines and some of the related alkyl compounds (*79*).

Comparative studies of the mass spectra of series of compounds have been made for tetramethyl derivatives of Group IV (*85*, *86*, *126*), where the main ions observed were due to loss of methyl groups. The ionization and dissociation processes occurring in the spectra of $HgMe_2$, Me_3SiH, and Me_4Ge have been compared, and the appearance potentials of the principal ions recorded (*127*). In a study of the vinyl and perfluorovinyl derivatives of mercury, phosphorus, arsenic, and antimony, the principal ions from the fluorinated Group V compounds were $C_2F_3M^+$; the vinyl phosphorus and antimony compounds were more stable, $SbVi_3^+$ having 20.6% relative abundance. In the spectrum of the mercury compound, the main ions were produced by rupture of the weak mercury–carbon bonds (*90*).

Early experiments in mass spectroscopy were directed towards determining the isotopic composition of the elements. For this purpose, volatile compounds were sought, and this resulted in many main group elements being investigated using some organometallic compound. It is mainly of historical interest to list these, most of which were used by F. W. Aston. Thus he describes the use of $ZnMe_2$ (*8*, *11*, *16*), $CdMe_2$ (*19*), $TlEt_3$ (*15*), germanium alkyls (*6a*), tetramethyltin (*8*, *10*, *20*, *21*), and $TeMe_2$ (*7*) and observed some fragmentation of $SbMe_3$ to give ions such as $SbMe^+$ and $SbMe_2^+$ (*8*). A particularly useful compound was tetramethyllead, which was used in a number of mass spectral investigations of the distributions of the various lead isotopes of radiogenic origin (*9*, *12*, *18*, *177*, *186*, *204*).

IX

APPEARANCE POTENTIALS

Table III summarizes the reported appearance potentials of positively charged organometallic ions, together with the heat of formation of the ion, where this has been determined. Some caution has to be exercised in the interpretation of these figures, as excess energy over that of ionization may well be included (*224*). Appearance potentials for M^+ from metal carbonyls are appreciably higher than currently accepted values for the ionization potentials; excited states are probably produced. Similarly, a comparison of $D[\text{Ni—CO}]$ and $D[\text{Fe—CO}]$ values obtained by thermochemical (*76*, *100*) and mass spectrometric methods (*243*) shows that the molecular ions have an excess energy of some 1–2 eV. On the other hand, the metal–metal bond dissociation energy $D[\text{Mn–Mn}]$ in manganese carbonyl has been estimated as 34 ± 13 kcal mole^{-1} by conventional means (*77*), but a lower value (18.9 ± 1.4 kcal mole^{-1}) was found from the difference in ionization potential of $Mn(CO)_5$ and appearance potential of $Mn(CO)_5^+$ (*35*), which is in agreement with the very long Mn—Mn bond length (2.93 Å) in $Mn_2(CO)_{10}$

(*80*). A similar experiment using $Co_2(CO)_8$ gave a value for *D*[Co—Co] of 11.5 ± 4.6 kcal mole^{-1}) (*36*). This is to be compared with the value of 76 kcal mole^{-1} found by Winters and Kiser (*247*), who included an estimated heat of formation of $Co_2(CO)_8$ vapor in their calculations. Measurements of the ionization potentials of $Fe(CO)_4$ (8.48 eV) and the appearance potential of $Fe(CO)_4^+$ from $Fe(CO)_5$ in a "cold" ion source (9.10 eV), gives a value for the apparent D [$Fe(CO)_4$—CO] of 0.7 ± 0.3 eV (*192*). It is evident that much work remains to be done on this subject.

Replacement of CO in a metal carbonyl by a ligand, L, having a lower ionization potential (I.P.) than CO, results in a decrease in the I.P. of the complex. Since the donor ability of L increases as the I.P. decreases, it is not surprising that fragmentation of these complexes occurs by loss of CO rather than of L, and that the relative abundances of M^+ are lower (*184*).

ACKNOWLEDGMENTS

I am very grateful for permission to use much unpublished data which many people have kindly sent in response to my request for information.

TABLE III

APPEARANCE POTENTIALS AND HEATS OF FORMATION OF SOME IONS

Ion	Appearance potential* (eV)	ΔH_{ion} (kcal mole^{-1})	Reference†
Mg^+	14.36 ± 0.2	—	*104*
$MgCp^+$	10.98 ± 0.1	—	*104*
$MgCp_2^+$	7.76 ± 0.1	—	*104*
V^+	15.5 ± 0.2^a	—	*36a*
	18.32 ± 0.2^b	—	*104*
	19.4 ± 0.4^c	—	*246*
VC^+	23.8 ± 0.8	—	*36a*
$V(CO)^+$	13.8 ± 0.2	—	*36a*
$V(CO)_2^+$	12.3 ± 0.2	—	*36a*
$V(CO)_3^+$	10.98 ± 0.15	—	*36a*
$V(CO)_4^+$	9.70 ± 0.2	—	*36a*
$V(CO)_5^+$	8.24 ± 0.15	—	*36a*
$V(CO)_6^+$	7.53 ± 0.15	—	*36a*
$VC_3H_3^+$	18.9 ± 0.3	348	*246*
VCp^+	12.68 ± 0.1^b	—	*104*
	14.2 ± 0.2^c	294	*246*

TABLE III—*continued*

Ion	Appearance potential (eV)	ΔH_{ion} (kcal mole^{-1})	Reference
$\mathrm{VCp_2^+}$	7.56 ± 0.1	—	*104*
$\mathrm{VCp(CO)^+}$	10.7 ± 0.3	187	*246*
$\mathrm{VCp(CO)_2^+}$	9.7 ± 0.3	137	*246*
$\mathrm{VCp(CO)_4^+}$	8.2 ± 0.3	50	*246*
$\mathrm{Cr^+}$	14.7 ± 0.1[d]	—	*102*
	15.1 ± 0.2[d]	—	*36a*
	16.15 ± 0.3[e]	—	*104*
	17.07[d]	311	*140a*‡
	17.7 ± 0.3	326	*244*
$\mathrm{CrC^+}$	23.15 ± 0.3	—	*36a*
	(24.7)†	(530)†	*244*
$\mathrm{Cr(CO)^+}$	13.3 ± 0.2	—	*102*
	13.63 ± 0.2	—	*36a*
	14.12	216	*140a*
	14.9 ± 0.2	235	*244*
$\mathrm{Cr(CO)^{2+}}$	30.8 ± 1.0	—	*36a*
$\mathrm{Cr(CO)_2^+}$	11.56 ± 0.2	—	*102*
	11.94 ± 0.1	—	*36a*
	12.56	154	*140a*
	13.1 ± 0.2	167	*244*
$\mathrm{Cr(CO)_3^+}$	10.42	79	*140a*
	10.62 ± 0.15	—	*102*
	11.1 ± 0.2	—	*36a*
	(12.0)†	(115)†	*244*
$\mathrm{Cr(CO)_4^+}$	9.52	31	*140a*
	9.64 ± 0.1	—	*36a*
	9.97 ± 0.04	—	*102*
	(10.7)†	(60)†	*244*
$\mathrm{Cr(CO)_5^+}$	8.95 ± 0.1	—	*36a*
	9.17 ± 0.04	—	*102*
	9.32	0	*140a*
	(9.5)†	(5)†	*244*
$\mathrm{Cr(CO)_6^+}$	8.03 ± 0.03	—	*229*
	8.15 ± 0.17	−52	*244*
	8.18 ± 0.07	—	*102*
$\mathrm{CrO^+}$	23.45 ± 0.3	—	*36a*
$\mathrm{Et_3PCr(CO)_5^+}$	7.63	—	*89a*
$\mathrm{Bu_3PCr(CO)_5^+}$	7.37	—	*89a*
$\mathrm{(BuO)_3PCr(CO)_5^+}$	7.63	—	*89a*
$\mathrm{CrCp^+}$	13.6 ± 0.1	—	*104*
$\mathrm{CpCp_2^+}$	6.91 ± 0.2	—	*104*

TABLE III—*continued*

Ion	Appearance potential (eV)	ΔH_{ion} (kcal mole^{-1})	Reference
$Cr(C_6H_6)^+$	9.2^f	—	*192*
	10.8^g	—	*192*
Mo^+	18.3 ±0.3	—	*102*
	18.6±0.2	—	*36a*
	19.63	391	*140a*
	20.7 ±0.5	417	*244*
MoC^+	24.3 ±1	—	*36a*
	27.2 ±0.4	608	*244*
$MoCO^+$	15.61	273	*140a*
	15.7 ±0.2	—	*36a*
	15.8 ±0.06	—	*102*
	18.1 ±0.3	331	*244*
$Mo(CO)^{2+}$	34.5 ±0.5	709	*244*
	35.7 ±1	—	*36a*
$Mo(CO)_2^+$	13.90±0.3	—	*102*
	14.5 ±0.1	—	*36a*
	14.76	226	*140a*
	15.6 ±0.3	247	*244*
$Mo(CO)_2^{2+}$	30.8 ±0.5	597	*244*
	31.6 ±1	—	*36a*
$Mo(CO)_3^+$	12.36±0.12	—	*102*
	12.82±0.12	—	*36a*
	13.18±0.1	164	*140a*
	13.7 ±0.3	177	*244*
$Mo(CO)_3^{2+}$	29.1 ±1.2	532	*244*
$Mo(CO)_4^+$	10.63±0.15	—	*36a*
	10.72	81	*140a*
	11.28±0.14	—	*102*
	11.9 ±0.2	109	*244*
$Mo(CO)_5^+$	9.14	18	*140a*
	9.43±0.1	—	*36a*
	9.64±0.05	—	*102*
	9.80±0.15	34	*244*
$Mo(CO)_6^+$	8.12±0.03	—	*229*
	8.23±0.12	−29	*244*
	8.30±0.03	—	*102*
MoO^+	24.3 ±1	—	*36a*
$CpMo(CO)_2NO^+$	8.1 ±0.2	—	*248*
$BuNCMo(CO)_5^+$	7.65	—	*89a*
$Et_3PMo(CO)_5^+$	7.72	—	*89a*
$Bu_3PMo(CO)_5^+$	7.51	—	*89a*

TABLE III—*continued*

Ion	Appearance potential (eV)	ΔH_{ion} (kcal mole^{-1})	Reference
$(BuO)_3PMo(CO)_5^+$	7.71	—	*89a*
$PhCl_2PMo(CO)_6^+$	8.03	—	*89a*
W^+	20.6 ±0.2	—	*102*
	21.7 ±0.3	—	*36a*
	22.25	465	*140a*
	22.9 ±0.6	477	*244*
WC^+	28.8 ±0.5	654	*244*
$W(CO)^+$	18.5 ±0.16	—	*102*
	18.51	348	*140a*
	18.7 ±0.3	—	*36a*
	20.2 ±0.3	388	*244*
$W(CO)^{2+}$	31.7 ±1	—	*36a*
$WC(CO)^+$	25.9 ±0.6	561	*244*
$W(CO)_2^+$	15.8 ±0.3	—	*36a*
	16.07±0.04	—	*102*
	16.08	266	*140a*
	17.6 ±0.2	302	*244*
$W(CO)_2^{2+}$	35.0 ±1	—	*36a*
$W(CO)_3^+$	13.60±0.02	—	*102*
	13.7 ±0.15	—	*36a*
	13.87	189	*140a*
	14.9 ±0.2	213	*244*
$W(CO)_4^+$	11.82±0.02	—	*102*
	11.93±0.15	—	*36a*
	12.05	120	*140a*
	12.7 ±0.2	136	*244*
$W(CO)_5^+$	9.21	26	*140a*
	9.80±0.17	43	*244*
	9.86±0.1	—	*36a*
	9.97±0.04	—	*102*
$W(CO)_6^+$	8.18±0.03	—	*229*
	8.43	−16	*140a*
	8.46±0.02	—	*102*
	8.47±0.1	—	*36a*
	8.56±0.13	−12	*244*
$BuNCW(CO)_5^+$	7.60	—	*89a*
$pyW(CO)_5^+$	7.6	—	*89a*
$Et_3PW(CO)_5^+$	7.82	—	*89a*
$Bu_3PW(CO)_5^+$	7.63	—	*89a*
$(BuO)_3PW(CO)_5^+$	7.85	—	*89a*
$PhCl_2PW(CO)_5^+$	8.2	—	*89a*
Mn^+	14.05±0.2^h	—	*104*

TABLE III—*continued*

Ion	Appearance potential (eV)	ΔH_{ion} (kcal mole^{-1})	Reference
	15.9 ± 0.3^{i}	—	*246*
	17.9^{j}	—	*83*
	20.8 ± 0.4^{k}	290	*247*
	22.13^{k}	—	*224a*‡
	25.67^{l}	—	*224a*
$MnCO^+$	17.5 ± 0.2	187	*247*
	18.21^{k}	—	*224a*
	19.05^{l}	—	*224a*
$Mn(CO)_2^+$	14.80	—	*224a*
$Mn(CO)_5^+$	9.40	—	*224a*
$MnCp^+$	11.25 ± 0.2^{h}	—	*104*
	12.0 ± 0.3^{i}	289	*246*
	12.3^{j}	—	*83*
$MnCpC_6H_6^+$	6.8 to 7.1	—	*83*
$MnCp_2^+$	7.25 ± 0.1	—	*104*
$MnCpCO^+$	9.8 ± 0.3	212	*246*
$MnCp(CO)_3^+$	8.3 ± 0.4	124	*246*
$MnHC_6H_6^+$	12.1	—	*83*
Mn_2^+	18.73	309	*224a*
	18.8 ± 0.3	312	*247*
$Mn_2(CO)_2^+$	16.43	201	*224a*
$Mn_2(CO)_3^+$	15.34	152	*224a*
$Mn_2(CO)_4^+$	13.98	94	*224a*
	14.0 ± 0.2	95	*247*
$Mn_2(CO)_5^+$	11.91	20	*224a*
	12.6 ± 0.2	39	*247*
$Mn_2(CO)_{10}^+$	8.55 ± 0.1	−189	*247*
	8.58	−188	*224a*
$MnRe^+$	25.98	314	*224a*
$MnRe(CO)^+$	23.00	219	*224a*
$MnRe(CO)_2^+$	19.75	118	*224a*
$MnRe(CO)_3^+$	16.94	26	*224a*
$MnRe(CO)_4^+$	14.65	−53	*224a*
$MnRe(CO)_5^+$	12.12	−137	*224a*
$MnRe(CO)_{10}^+$	8.16	−360	*224a*
Re^+	37.57	—	*224a*
$Re(CO)_4^+$	13.30	—	*224a*
$Re(CO)_5^+$	10.35^{m}	—	*224a*
	10.80^{l}	—	*224a*
$Re(CO)_6^+$	9.36	—	*224a*
Re_2^+	28.96	319	*224a*
$Re_2(CO)^+$	26.26	231	*224a*

TABLE III—*continued*

Ion	Appearance potential (eV)	ΔH_{ion} (kcal mole^{-1})	Reference
$Re_2(CO)_2^+$	23.55	142	*224a*
$Re_2(CO)_3^+$	21.46	67	*224a*
$Re_2(CO)_4^+$	19.31	−9	*224a*
$Re_2(CO)_5^+$	16.71	−95	*224a*
$Re_2(CO)_6^+$	15.01	−160	*224a*
$Re_2(CO)_7^+$	13.55	−220	*224a*
$Re_2(CO)_8^+$	10.89	−308	*224a*
$Re_2(CO)_9^+$	9.57	−365	*224a*
$Re_2(CO)_{10}^+$	8.27	−421	*224a*
Fe^+	14.7 ±0.1[n]	—	*102*
	15.31 ±0.1[n]	—	*36a*
	15.99[n]	326	*140a*
	16.1 ±0.2[n]	330	*243*
	17.1 ±0.9[o]	—	*104*
FeC^+	23.6 ±0.3	—	*36a*
$Fe(CO)^+$	12.9 ±0.1	—	*102*
	13.39 ±0.07	—	*36a*
	13.76	248	*140a*
	14.0 ±0.2	255	*243*
$Fe(CO)^{2+}$	30.2 ±2	629	*243*
$Fe(CO)_2^+$	10.92 ±0.04	—	*102*
	11.12	161	*140a*
	11.27 ±0.05	—	*36a*
	11.8 ±0.2	178	*243*
$Fe(CO)_3^+$	9.89 ±0.05	—	*102*
	10.01 ±0.04	—	*36a*
	10.04	710	*140a*
	10.3 ±0.3	117	*243*
$Fe(CO)_4^+$	8.34 ±0.12	—	*102*
	8.73 ±0.08	—	*36a*
	9.17	64	*140a*
	10.0 ±0.2	83	*243*
$Fe(CO)_5^+$	7.95 ±0.03	—	*229*
	8.14 ±0.06	—	*102*
	8.16 ±0.05	—	*36a*
	8.40	20	*140a*
	8.53 ±0.2	23	*243*
$Fe(NO)^+$	12.70	—	*192*
$Fe(NO)_2^+$	10.40	—	*192*
$Fe(CO)(NO)^+$	11.10	—	*192*
$Fe(CO)(NO)_2^+$	9.10	—	*192*
$Fe(CO)(NO)P(OEt)_3^+$	7.50	—	*103*

TABLE III—*continued*

Ion	Appearance potential (eV)	ΔH_{ion} (kcal mole^{-1})	Reference
$Fe(CO)(NO)P(OBu)_3^+$	7.57	—	*89a*
$Fe(CO)_2NO^+$	9.30	—	*192*
$Fe(CO)_2(NO)_2^+$	8.40	—	*103*
$Fe(CO)_4PBu_3^+$	7.29	—	*89a*
$Fe(CO)_4P(OMe)_3^+$	7.65	—	*89a*
$Fe(CO)_4P(OEt)_3^+$	7.43	—	*89a*
$Fe(CO)_4PCl_3^+$	8.05	—	*89a*
$FeCp^+$	12.8	—	*192*
	14.38 ± 0.3	—	*104*
$FeCp_2^+$	7.05 ± 0.1	—	*104*
$C_6H_8Fe(CO)_3^+$	8.0 ± 0.2	—	*248*
Co^+	14.60[p]	—	*192*
	16.1 ± 0.6[q]	—	*104*
	16.8 ± 0.3[r]	—	*246*
	16.9 ± 0.4[s]	—	*247*
$CoCO^+$	11.90[p]	—	*192*
	14.4 ± 0.5[s]	202	*247*
	16.5 ± 0.5[r]	254	*246*
$Co(CO)_2^+$	12.35[p]	—	*192*
	12.7 ± 0.4[s]	138	*247*
$Co(CO)_3^+$	10.30[p]	—	*192*
	10.9 ± 0.3[s]	70	*247*
$Co(CO)(NO)^+$	10.60	—	*192*
$Co(CO)_2(NO)^+$	9.30	—	*192*
$Co(CO)_2(NO)PCl_3^+$	8.45	—	*103*
$Co(CO)_2(NO)PEt_3^+$	7.62	—	*89a*
$Co(CO)_2(NO)PBu_3^+$	7.51	—	*89a*
$Co(CO)_2(NO)P(OMe)_3^+$	7.92	—	*89a*
$Co(CO)_2(NO)P(OEt)_3^+$	7.82	—	*89a*
$Co(CO)_3NO^+$	8.75	—	*103*
$CoNO^+$	12.90	—	*192*
$CoC_3H_3^+$	16.8 ± 0.3	371	*246*
	10.8[r]	—	*192*
$CoCp^+$	11.7 ± 0.2[r]	308	*246*
	12.3[q]	—	*192*
	14.20 ± 0.1[q]	—	*104*
$CoCpCO^+$	10.1 ± 0.2	244	*246*
$CoCp(CO)_2^+$	8.3 ± 0.2	176	*246*
$CoCp_2^+$	6.2 ± 0.3	—	*104*
Co_2^+	17.8 ± 0.4	282	*247*
$Co_2(CO)^+$	16.7 ± 0.3	230	*247*
$Co_2(CO)_2^+$	14.7 ± 0.5	157	*247*

TABLE III—*continued*

Ion	Appearance potential (eV)	ΔH_{ion} (kcal mole^{-1})	Reference
$\mathrm{Co_2(CO)_4^+}$	12.2 ±0.3	47	*247*
$\mathrm{Co_2(CO)_5^+}$	10.1 ±0.4	−28	*247*
$\mathrm{Co_2(CO)_6^+}$	9.4 ±0.3	−70	*247*
$\mathrm{Co_2(CO)_7^+}$	8.6 ±0.3	−115	*247*
$\mathrm{Co_2(CO)_8^+}$	8.12±0.22	−153	*247*
$\mathrm{Ni^+}$	14.32±0.2[t]	—	*104*
	15.1 ±0.3[u]	—	*36a*
	15.15[v]	—	*192*
	15.51[u]	317	*140a*
	16.0 ±0.3[u]	330	*243*
$\mathrm{NiC^+}$	24.2 ±0.2	—	*36a*
$\mathrm{NiCO^+}$	12.84	229	*36a*
	12.96±0.10	—	*36a*
	13.5 ±0.2	246	*243*
$\mathrm{Ni(CO)_2^+}$	10.48±0.05	—	*36a*
	10.63	152	*140a*
	10.7 ±0.2	155	*243*
$\mathrm{Ni(CO)_2^{2+}}$	28.3 ±1	560	*243*
$\mathrm{Ni(CO)_3^+}$	9.22±0.1	—	*36a*
	9.34	96	*140a*
	9.36±0.15	97	*243*
$\mathrm{Ni(CO)_4^+}$	8.28±0.03	—	*229*
	8.57±0.10	—	*36a*
	8.64±0.15	54	*243*
	8.75	56	*140a*
$\mathrm{NiC_3H_3^+}$	14.40	—	*192*
$\mathrm{NiCp^+}$	10.40[u]	—	*192*
	11.9[t]	—	*192*
	12.67±0.1[t]	—	*104*
$\mathrm{NiCp_2^+}$	7.06±0.1	—	*104*
$\mathrm{NiCp(NO)^+}$	8.50	—	*103*

*Ions produced from:

[a] $\mathrm{V(CO)_6}$
[b] $\mathrm{VCp_2}$
[c] $\mathrm{CpV(CO)_4}$
[d] $\mathrm{Cr(CO)_6}$
[e] $\mathrm{CrCp_2}$
[f] $\mathrm{Cr(C_6H_6)_2}$
[g] $\mathrm{C_6H_6Cr(CO)_3}$
[h] $\mathrm{MnCp_2}$
[i] $\mathrm{CpMn(CO)_3}$
[j] $\mathrm{CpMnC_6H_6}$
[k] $\mathrm{Mn_2(CO)_{10}}$
[l] $\mathrm{MnRe(CO)_{10}}$
[m] $\mathrm{Re_2(CO)_{10}}$
[n] $\mathrm{Fe(CO)_5}$
[o] $\mathrm{FeCp_2}$
[p] $\mathrm{Co(CO)_3NO}$
[q] $\mathrm{CoCp_2}$
[r] $\mathrm{CpCo(CO)_2}$
[s] $\mathrm{Co_2(CO)_8}$
[t] $\mathrm{NiCp_2}$
[u] $\mathrm{Ni(CO)_4}$
[v] CpNiNO

† Estimated values.

‡ Values from references *140a* and *224a* have reproducibilities in the range ±0.05–0.2 eV.

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ERRATA

VOLUME 3

Table X, pages 435-437 should appear as follows:

TABLE X

ORGANOTIN-SUBSTITUTED HETEROCYCLES

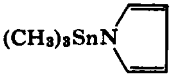
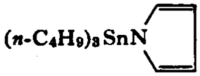
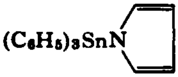
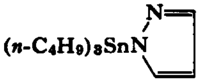
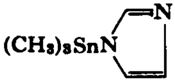
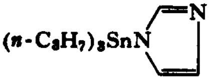
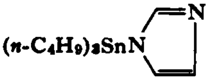
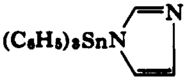
Compound	M.p. (°C)	B.p. (°C/mm)	n_D^{20}	References
	—	101.5°–102°/17	1.5302	*100*
	—	139°–141°/0.62	1.4952	*100*
	203.2°–204°	—	—	*100*
	—	98°–102°/0.04	1.4995	*100*
	234°–236°	—	—	*3, 42*
	235°–238° (dec)	—	—	*100*
	152°–154°	—	—	*3, 42*
	149°–150°	—	—	*100*
	65°–67°	—	—	*3, 42*
	64°–64.5°	—	—	*100*
	304°–305.5°	—	—	*42*
	310°–311°	—	—	*100*

TABLE X—*continued*

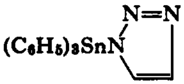
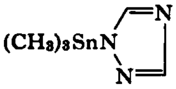
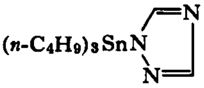
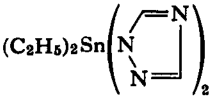
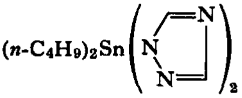
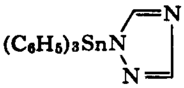
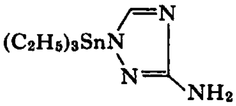
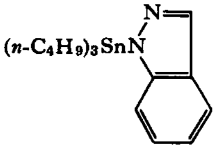
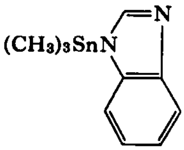
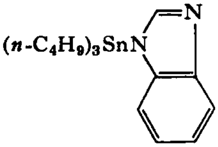
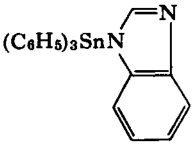
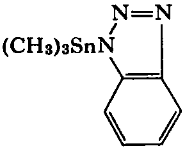
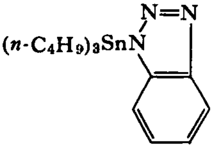
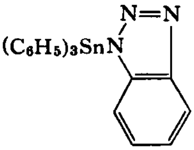
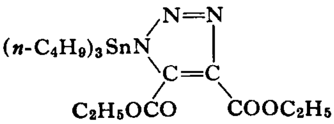
Compound	M.p. (°C)	B.p. (°C/mm)	n_D^{20}	References
	311°–313° (dec)	—	—	*100*
	277°–278°	—	—	*3*
	277°–278° (dec)	—	—	*42, 100*
	66°–71°	—	—	*3, 42, 100*
	Infusible	—	—	*100*
	Dec at 240°	—	—	*100*
	294°–295.5°	—	—	*42, 100*
	196°–197°	—	—	*100*
	—	124°–128°/0.002	1.5376	*100*
	Subl. > 200°	—	—	*3, 42, 100*

TABLE X—*continued*

Compound	M.p. (°C)	B.p. (°C/mm)	n_D^{20}	References
	137.5°–139°	—	—	*3, 42, 100*
	Dec at 298°	—	—	*42, 100*
	221.5°–223°	—	—	*3*
	221.5°–223° (dec)	—	—	*42, 100*
	78°–88°	—	—	*3, 42, 100*
	270.5°–272°	—	—	*42, 100*
	64.5°–67°	—	—	*102*

Author Index

Numbers in parentheses are reference numbers and indicate that an author's work is referred to although his name is not cited in the text. Numbers in italic indicate the page on which the complete reference is listed.

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