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SOME RECENT STUDIES OF THE SKELETAL TRANSFORMATIONS OF ORGANOPOLYSILANES

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Summary

A variety of skeletal transformations of organo (mostly methyl) polysilanes are reviewed, with emphasis on recent results from the author's laboratory. They include: (a) aluminum chloride-catalyzed rearrangements, (b) silyllithium-catalyzed redistribution reactions, and (c) degradation with loss of divalent silicon species under photolysis, thermolysis, and catalysis by Group VIII metal complexes.

Organopolysilanes have been known for over hundred years. However, it is only within the last two decades that numerous organic derivatives of polysilanes of linear, branched-chain, monocyclic, bicyclic and cage types have been synthesized and their chemical and spectral properties examined [1-6]. This review is not comprehensive, but deals with selected aspects of this field of chemistry, with particular emphasis on recent results from my own laboratory.

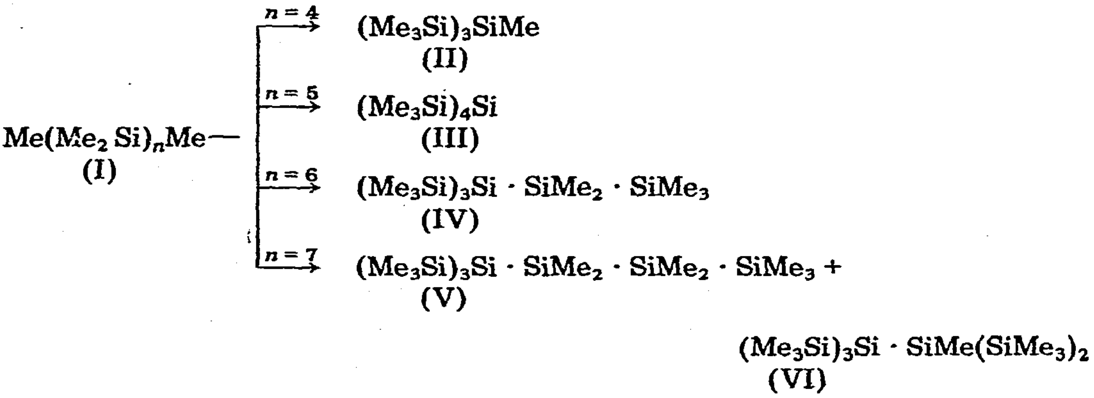
Although there is the closest congeneric relationship between silicon and carbon, the silicon—silicon bond is much more polarizable and hence reactive than the carbon—carbon bond. Therefore, in contrast to hydrocarbons and their derivatives, polysilanes and their inorganic [7-9] and organic derivatives undergo a variety of skeletal transformations under considerably mild conditions. Among others, the topics of aluminum chloride-catalyzed skeletal rearrangements, silyllithium-catalyzed redistribution reactions of the silicon—silicon framework, and degradation reactions with loss of divalent silicon (silylene) species under photolysis, thermolysis or catalysis by Group VIII metal complexes have recently received special attention.

I. Aluminum chloride-catalyzed skeletal rearrangement

In 1968, during the course of systematic studies on aluminum chloride-catalyzed chlorodemethylation reactions of permethylated polysilanes [10] we discovered that dodecamethylcyclohexasilane (XIII) undergoes ring contraction very easily to give an *Si*-silyl substituted cyclopentasilane in good yield [11]. It was soon realized that this novel type of skeletal rearrangement is a general reaction not only for cyclic but also for acyclic methylpolysilanes, and provides a convenient synthetic route to certain organopolysilanes otherwise not readily accessible. For reasons of clarity, the rearrangement of acyclic methylpolysilanes will be described first.

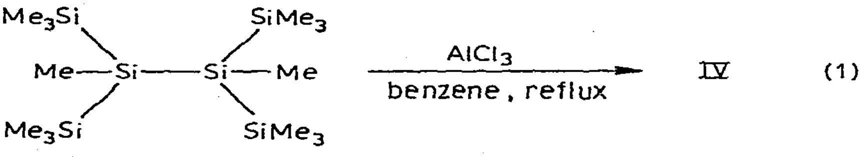
Acyclic methylpolysilanes

Permethylated linear polysilanes of formula I are converted into the corresponding branched-chain isomers II-VI when treated with a catalytic amount of aluminum chloride in boiling benzene for 1 h. In most cases, the yields of the rearrangement products are practically quantitative [12,13].



$$\underset{(\mathrm{I})}{\mathrm{Me(Me_2Si)_{\mathit{n}}Me}} - \begin{cases} \xrightarrow{n=4} \underset{(\mathrm{II})}{\mathrm{(Me_3Si)_3SiMe}} \\ \xrightarrow{n=5} \underset{(\mathrm{III})}{\mathrm{(Me_3Si)_4Si}} \\ \xrightarrow{n=6} \underset{(\mathrm{IV})}{\mathrm{(Me_3Si)_3Si \cdot SiMe_2 \cdot SiMe_3}} \\ \xrightarrow{n=7} \underset{(\mathrm{V})}{\mathrm{(Me_3Si)_3Si \cdot SiMe_2 \cdot SiMe_2 \cdot SiMe_3}} + \underset{(\mathrm{VI})}{\mathrm{(Me_3Si)_3Si \cdot SiMe(SiMe_3)_2}} \end{cases}$$

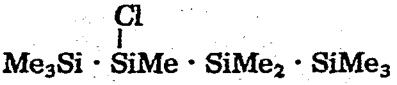
The rearrangement of I (n = 6) can be assumed to proceed via the intermediacy of a branched-chain isomer IVa, since even though this compound is, not detectable, it is when prepared independently, readily transformed into IV under the usual rearrangement conditions (eqn. 1).



(IVa)

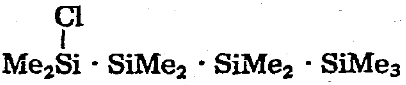
These results indicate clearly that the reaction, in general, tends to proceed towards formation of the most highly-branched chain, probably the most thermodynamically stable, isomers. However, from I (n = 7), an equilibrium mixture is formed containing the intermediate rearrangement product V and the final product in a 2/1 ratio. Structure V may be favored over structure VI for steric reasons.

With a view to providing insight into the mechanism of the rearrangement, the behavior of some chloro derivatives of polysilanes toward aluminum chloride catalyst has been examined [13].



$$\mathrm{Me_3Si \cdot \overset{Cl}{\overset{|}{Si}}Me \cdot SiMe_2 \cdot SiMe_3}$$

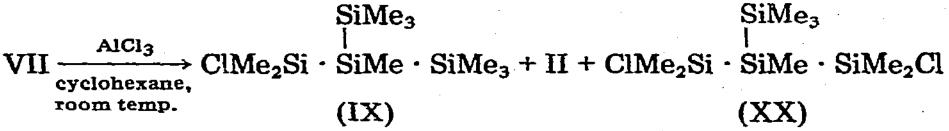
(VII)



$$\mathrm{Me_2\overset{Cl}{\overset{|}{Si}} \cdot SiMe_2 \cdot SiMe_2 \cdot SiMe_3}$$

(VIII)

In cyclohexane at room temperature, under which conditions no permethylated polysilanes interact appreciably with this catalyst, 2-chlorononamethyltetrasilane (VII) undergoes complete rearrangement in 4.5 h to IX in 90% yield and to very small amounts of II and X.



$$\text{VII} \xrightarrow[\text{cyclohexane, room temp.}]{\text{AlCl}_3} \underset{\text{(IX)}}{\text{ClMe}_2\text{Si}\cdot\overset{\text{SiMe}_3}{\overset{|}{\text{SiMe}}}\cdot\text{SiMe}_3} + \text{II} + \underset{\text{(XX)}}{\text{ClMe}_2\text{Si}\cdot\overset{\text{SiMe}_3}{\overset{|}{\text{SiMe}}}\cdot\text{SiMe}_2\text{Cl}} \qquad (2)$$

In contrast, the 1-chloro isomer VIII forms practically no rearrangement products in cyclohexane at room temperature even after 24 h. At reflux temperature however, it is completely converted into IX (60% yield), II and X in 2h (eqn. 2).

The reaction with aluminum chloride of a simpler system, 2-chloroheptamethyltrisilane, in which there is no possibility of the skeletal rearrangement should be noted. It undergoes a complete transformation to octamethyltrisilane (15%), 1-chloroheptamethyltrisilane (64%) and 1,2-dichlorohexamethyltrisilane (21%) in refluxing cyclohexane.

From these findings it can be concluded that the skeletal rearrangement of the permethylated acyclic polysilanes I involves the following steps. Initially, a compound having a silicon—chlorine bond at an internal position of the molecular skeleton (XI) is formed as a result of the reaction on the starting substance I of aluminum chloride, either alone or in association with hydrogen chloride possibly contained in traces in the catalyst. This intermediate XI then undergoes intramolecular rearrangement to a more highly branched-chain isomer XII. Finally chlorine/methyl interchange occurs between this rearranged intermediate XII and the starting permethylated compound I to give the observed final product, with regeneration of the intermediate XI.

Cyclic methylpolysilanes

Treatment of dodecamethylcyclohexasilane (XIII) with aluminum chloride as catalyst in benzene at room temperature or in refluxing cyclohexane produces (trimethylsilyl)nonamethylcyclopentasilane (XIV) in almost quantitative yield [11]. If the reaction is carried out in the presence of a large excess of trimethylchlorosilane, (chlorodimethylsilyl)nonamethylcyclopentasilane (XVI) is obtained in ca. 60% yield along with XIV and other by-products. Evidence for the structure of these ring-contraction products comes from chemical transformations (see Fig. 1) as well as spectroscopic studies [14].

Thus, treatment of XVI with phenylmagnesium chloride in tetrahydrofuran (THF) gives (phenyldimethylsilyl)nonamethylcyclopentasilane (XVII) in excellent yield, and this in turn can be converted into ethoxynonamethylcyclopentasilane (XVIII) (65% yield) by treatment with 0.1 *N* sodium ethoxide in ethanol at room temperature. The ethoxycyclopentasilane XVIII is transformed into the known decamethylcyclopentasilane (XIX) by treatment with methyllithium, and into chlorononamethylcyclopentasilane (XX) (94% yield) on refluxing with an excess of acetyl chloride (AcCl).

Chlorodemethylation without ring contraction of XIII can be effected by passing dry hydrogen chloride at room temperature through its solution in

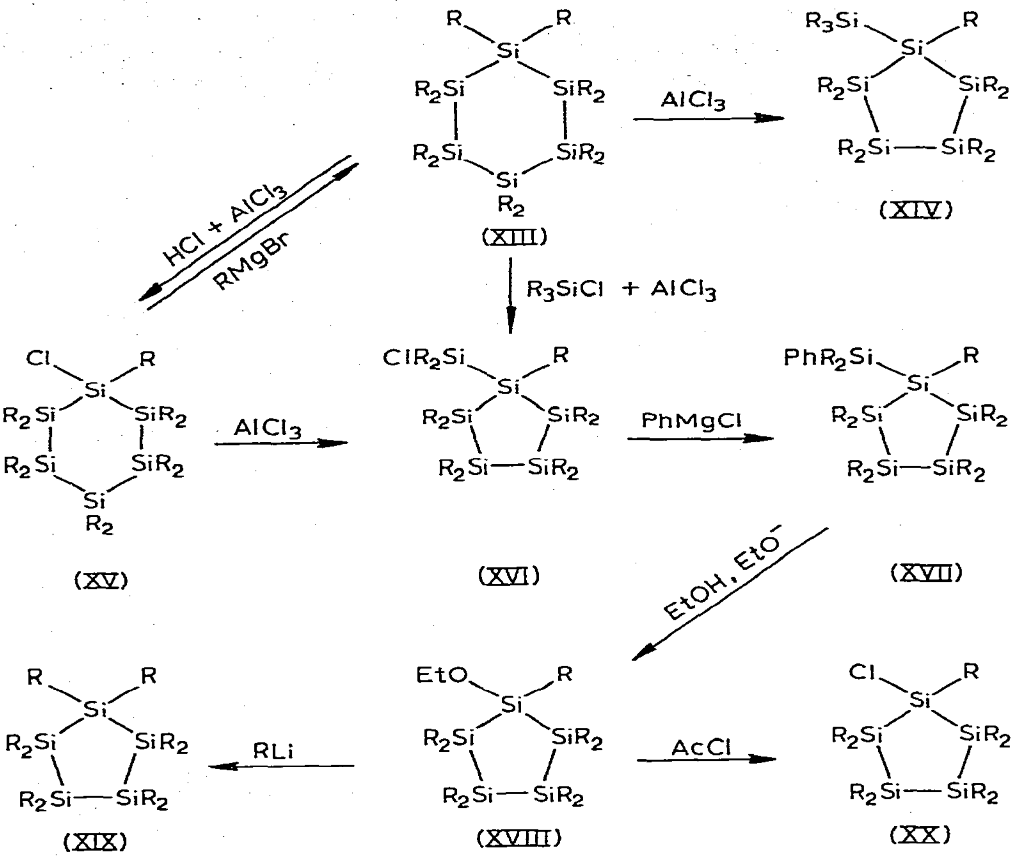
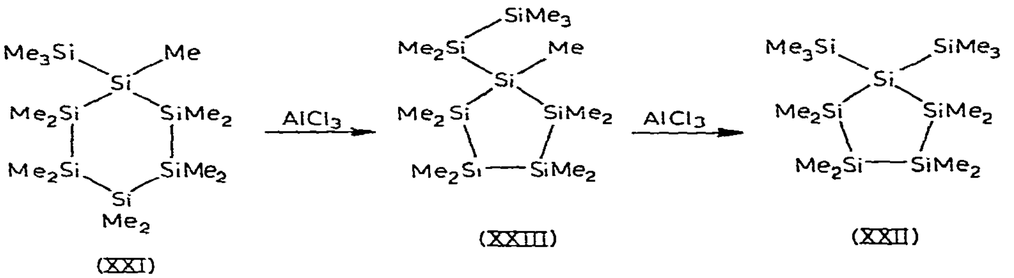


Fig. 1. Ring contraction of dodecamethylcyclohexasilane (XIII) and subsequent reactions, R = Me).

cyclohexane containing a catalytic amount of aluminum chloride. Chloroundecamethylcyclohexasilane (XV) is thus produced in 66% yield and can be identified by its reconversion into the permethylated cyclohexasilane XIII by treatment with the methyl Grignard reagent. The chloro compound XV undergoes almost complete rearrangement to XVI with aluminum chloride catalyst in cyclohexane at room temperature, under which conditions XIII itself remains substantially unchanged.

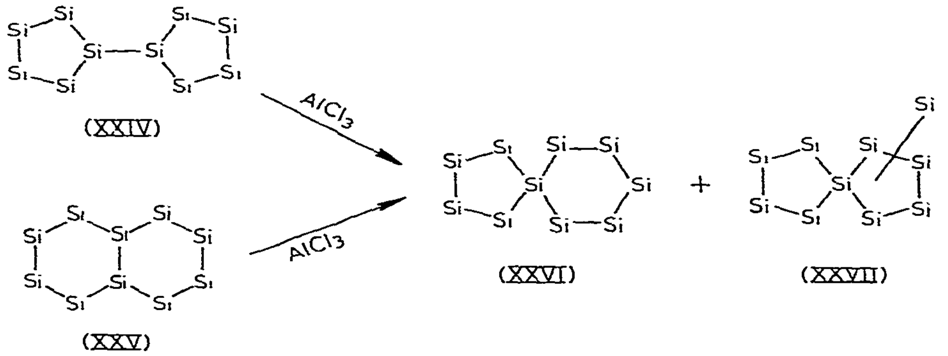
These results suggest that the mechanism for the ring contraction of XIII must be closely analogous to that described for the skeletal rearrangement of the acyclic compounds, and involve the initial formation of XV, followed by its rearrangement to XVI and finally Si—Cl/Si—Me interchange between XVI and XIII. Here again, we find that the reaction tends to proceed towards the formation of an isomer containing a most highly branched silicon atom.

In agreement with this view, the ring contraction of (trimethylsilyl)undecamethylcyclohexasilane (XXI) proceeds with formation of 1,1-bis(trimethylsilyl)-octamethylcyclopentasilane (XXII) as a sole final product [15]. Monitoring the progress of this reaction by GLC, and also an experiment starting with preformed (pentamethyldisilanyl)nonamethylcyclopentasilane (XXIII), demonstrate that XXII is formed via XXIII (eqn. 3).



(XXI) (XXIII) (XXII) (3)

Finally, it is interesting that both bi(nonamethylcyclopentasilanyl) (XXIV) and octadecamethylbicyclo[4.4.0]decasilane (XXV) are transformed into an identical mixture of two isomers, the spiro compounds XXVI (m.p. 151°) and XXVII (m.p. 136°) in a ratio of 3/7 (for simplicity, methyl groups are omitted in equation 4) [16].



(XXIV) (XXV) (XXVI) (XXVII) (4)

II. Silyllithium-catalyzed redistribution reaction

The discovery of this reaction stems from a study aimed at clarifying pathways for a rather unexpected reaction between triphenylsilyllithium and hexamethyltrisilanylene sulfate, which afforded dodecamethylcyclohexasilane (XIII) and hexaphenyldisilane in good yield [17].

It was found that each member of the homologous series of α,α,α,ω,ω,ω,-hexaphenylpolymethylpolysilanes of the formula XXVIII undergoes redistribution when treated with a catalytic amount of triphenylsilyllithium in THF to produce hexaphenyldisilane as precipitate and two of the permethylated cyclopolysilanes, XIX and XIII, in solution, which are present in a ratio of ca. 1/9 in the final stages of reaction (after ca. 100 h) [18]. The overall reaction is represent by eqn. 5.

$$\underset{(n = 1\text{-}6)}{\underset{\text{(XXVIII)}}{Ph_3Si(Me_2Si)_nSiPh_3}} \xrightarrow[THF]{Ph_3SiLi} Ph_3SiSiPh_3 + \frac{n\cdot x}{5}\underset{\text{(XIX)}}{(Me_2Si)_5} + \frac{n\cdot y}{6}\underset{\text{(XIII)}}{(Me_2Si)_6} \qquad (5)$$

$$x + y = 1$$

A kinetic study of the reaction (eqn. 5) suggested that the cyclopolysilanes

XIX and XIII might be interconvertible under these conditions, and it has been confirmed that this is indeed the case (eqn. 6).

$$\underset{\text{(XIX)}}{6(Me_2Si)_5} \xrightarrow[\text{THF}]{Ph_3SiLi} \underset{\text{(XIII)}}{5(Me_2Si)_6} \qquad (6)$$

Similarly, all the members of the homologous series of α,ω-diphenylpolymethylpolysilanes of formula XXIX undergo redistribution with phenyldimethylsilyllithium as catalyst in THF at room temperature (eqn. 7), except for 1,2-diphenyltetramethyldisilane (XXIX, n = 0) [19]. The reaction mixture remains homogeneous throughout the reaction. Irrespective of which homolog of XXIX is employed as starting material, after ca. 10 h an equilibrium is always established among all the lower homologs of XXIX and dodecamethylcyclohexasilane (XIII).

$$\underset{\text{(XXIX)}\qquad (n = 1\text{-}3)}{PhMe_2Si(Me_2Si)_nSiMe_2Ph} \xrightarrow[\text{THF}]{PhMe_2SiLi} \underset{\text{(XIII)}}{(Me_2Si)_6} + \underset{x = 0\text{-}3}{\Sigma PhMe_2Si(Me_2Si)_xSiMe_2Ph} \qquad (7)$$

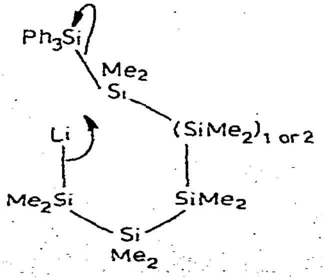
The attainment of equilibrium in each case has been confirmed by performing the reaction between the cyclohexasilane (XIII) and 1,2-diphenyltetramethyldisilane (XXIX, n = 0) in the molar ratio of 1/6, 1/3, and 1/2 in the presence of the silyllithium (eqn. 8), which gives essentially the same equilibrium mixtures as those formed by the redistribution of the polysilanes XXIX with n = 1, n = 2, n = 3, respectively.

$$\underset{\text{(XIII)}}{(Me_2Si)_6} + \underset{m = 6,3,2}{m\,PhMe_2SiSiMe_2Ph} \xrightarrow[\text{THF}]{PhMe_2SiLi} \underset{x = 0\text{-}3}{\Sigma PhMe_2Si(Me_2Si)_xSiMe_2Ph} \qquad (8)$$

It is noteworthy that this type of redistribution reaction formally bears a close resemblance to the well-known acid- and base-catalyzed "equilibration" of polydimethylsiloxanes, and represents a special case of the ring-chain equilibria frequently encountered in "inorganic polymers" [20,21].

$$\underset{\text{(XXVIII)}}{Ph_3Si(SiMe_2)_nSiPh_3} + \underset{z = 0-4}{Li(SiMe_2)_zSiPh_3} \longrightarrow$$

$$\underset{x = 0-6}{\Sigma\, Ph_3Si(SiMe_2)_xSiPh_3} + \underset{y = 0-6}{\Sigma\, Li(SiMe_2)_ySiPh_3} \qquad (9)$$



$$\longrightarrow Ph_3SiLi + (Me_2Si)_{5\text{ or }6} \qquad (10)$$

In the light of the reaction pathway proposed by Gilman and Tomasi [22] for the formation of dodecamethylcyclohexasilane (XIII) in lithium coupling of Me_2SiCl_2 in the presence of Ph_3SiLi as catalyst in THF, a mechanism can be suggested for the Ph_3SiLi-catalyzed redistribution of XXVIII. This involves a relatively fast initial formation of a dynamic equilibrium mixture among several lower members of the homologous series of XXVIII as a result of a sequence of Si—Si/Si—Li redistributions (eqn. 9). The polysilanyllithium compounds $Li(SiMe_2)_ySiPh_3$ having $y = 5$ or 6 are then capable of undergoing cyclization (eqn. 10). The insolubility of hexaphenyldisilane, which precipitates completely as it forms during reaction, serves to make the overall reaction (eqn. 5) proceed irreversibly.

III. Photolysis

One of the most striking findings on the physical properties of organopolysilanes is the fact that many of them exhibit intense absorptions in the ultraviolet region. Many papers and reviews on this subject have been published in the past decade [4,5,23].

In 1969, we were prompted by this remarkable property of the silicon—silicon bond to initiate a series of studies of the photolysis of various types of silicon—silicon compounds including cyclic [24] and acyclic [25] polysilanes and cyclic silahydrocarbons containing silicon—silicon linkages in the ring [26].

Cyclic methylpolysilanes

Dodecamethylcyclohexasilane (XIII) has been found to undergo photolysis readily when its solution in cyclohexane is irradiated internally with ultraviolet light (2537 Å) at room temperature for 20-40 h, giving rise to two of the lower permethylated cyclopolysilanes, decamethylcyclopentasilane (XIX) and octamethylcyclotetrasilane (XXX), along with a polymer [24] (eqn. 11).

$$\underset{\text{(XIII)}}{(Me_2Si)_6} \xrightarrow{h\nu} \underset{\text{(XIX)}}{(Me_2Si)_5} + \underset{\text{(XXX)}}{(Me_2Si)_4} + \text{polymer} \qquad (11)$$

The photolysis proceeds with generation of dimethylsilylene species (XXXI). This fact is established by trapping experiments. Thus the irradiation of XIII in the presence of diethylmethylsilane gives compounds XXXIIa and XXXIIb in the ratio of ca. 2.5/1 in high yield, along with a small amount of XIX (eqn. 12). In this case polymeric material is produced only in traces.

$$\text{XIII} \xrightarrow{h\nu} \underset{\text{(XXXI)}}{n(Me_2Si\!:)} \xrightarrow{Et_2MeSiH} \underset{\substack{\text{(XXXIIa) } n = 1 \\ \text{(XXXIIb) } n = 2}}{Et_2MeSi(SiMe_2)_nH} \qquad (12)$$

The photolysis of XIII for a prolonged period of time gives a significant amount of 1,4-dihydrooctamethyltetrasilane (XXXIII) and a small amount of 1,3-dihydrohexamethyltrisilane in addition to the products listed above. The formation of XXXIII can be ascribed to homolytic cleavage of the silicon—silicon linkage in the cyclotetrasilane XXX to give a diradical, which in turn abstracts hydrogen atoms from the solvent or from the methyl groups of the polysilanes.

The dimethylsilylene readily reacts with hydrogen chloride to produce dimethylchlorosilane, Me_2SiHCl, in high yield (72%) [27]. Therefore, photolysis of XIII with dry hydrogen chloride bubbling through provides a convenient laboratory method for preparation of this silane, which is otherwise not easily accessible [28,29].

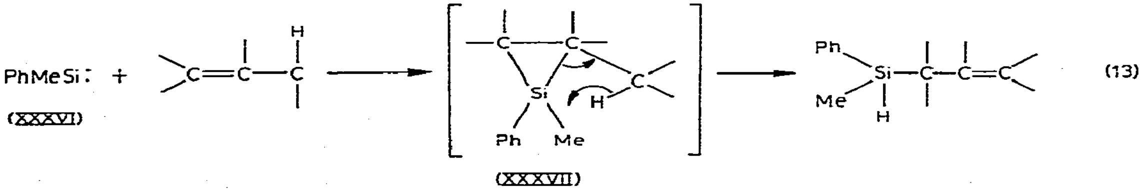
Linear organopolysilanes

The permethylated linear polysilanes (tetra and higher) (I) also undergo photolysis under similar conditions, and after 40 h octamethyltrisilane (I, $n = 3$) is always obtained as the sole volatile product, along with polymeric material. However, the irradiation of the trisilane for a prolonged period results in some formation of hexamethyldisilane. Here again, the generation of dimethylsilylene during the photolysis, which may be largely responsible for the formation of the polymeric material, can be confirmed by trapping it with diethylmethylsilane [25].

Similar photolysis of 2,3-diphenyloctamethyltetrasilane (XXXIV) or 2-phenylheptamethyltrisilane (XXXV) in cyclohexane generates methylphenylsilylene species (XXXVI) which is trapped by diethylmethylsilane to give the expected 1,1-diethyl-1,2-dimethyl-2-phenyldisilane [30].

It is interesting that the photogenic organosilylene species add to olefins bearing hydrogen atom(s) in the allylic position and produce allylic silanes. Thus the photolysis of XXXIV in the presence of a large excess of cyclohexene for 6 h gives 10% yield of 3-(methylphenylsilyl)cyclohexene. Similarly, with 1-octene, 1-(methylphenylsilyl)-2-octene is formed.

The production of allylic silanes is best explained in terms of initial formation of a silacyclopropane intermediate (XXXVII), followed by rearrangement involving a 1,3-hydrogen shift from carbon to silicon (eqn. 13).



A silacyclopropane system, 7-methyl-7-phenyl-7-silabicyclo[4.1.0]heptane, produced by photolysis of XXXV in the presence of cylcohexene using a low pressure mercury lamp with a Vycor filter, can be stored unchanged for some time in cyclohexane or ether solution. It is converted into the cyclohexylmethoxysilane by treatment with methanol, and into the 3-silylcyclohexene by further photolysis [31]. In this connection it should be noted that Lambert and Seyferth have recently succeeded in isolating stable silacyclopropanes for the first time, and have shown them to be very reactive towards methanolysis and in oxidation [32].

Branched-chain methylpolysilanes

The photolysis of permethylated branched-chain polysilanes II and IVa produces (trimethylsilyl)methylsilylene species, which can also be effectively trapped by diethylmethylsilane [33].

In certain cases, the photolysis can successfully be used as a method for structure determination of organopolysilanes. For example, since no useful information could be obtained from their NMR spectra, identification of the two previously described isomers XXVI and XXVII was best acomplished as follows [16]: Photolysis of one isomer with m.p. 151° in diethylmethylsilane solution gave, after 20 h (99% conversion), $Et_2MeSiSiMe_2H$ (XXXa) alone, while similar photolysis of the other isomer with m.p. 136° gave, after 54 h (99% conversion), both XXXa and $Et_2MeSi \cdot SiMeH \cdot SiMe_3$ in a 4/1 ratio, in reasonable yields. Based on these results, the former isomer is identified as XXVI, and the latter as XXVII.

IV. Thermolysis

Certain types of silicon-functional organo-disilanes and -polysilanes undergo thermal redistribution as exemplified by eqns. 14 and 15.

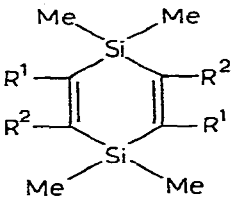
$$Me_3SiSiMe_2Y \rightarrow \Sigma\, Me(Me_2Si)_x Y \tag{14}$$

$$YMe_2SiSiMe_2Y \rightarrow \Sigma\, Y(Me_2Si)_x Y \tag{15}$$

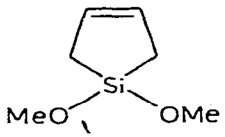
where Y stands for, e.g., OMe [34-37], CN [38], and H [39], and $x = 1,2,3,\ldots$.

For these reactions two different mechanisms are possible: one involves an α-elimination to produce silylene species followed by successive insertion of the silylene into the Si—Y bonds, the other comprises a four-centered transition state without intervention of the silylene.

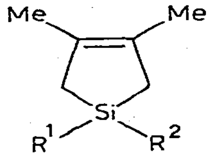
Weyenberg, Atwell and their coworkers have extensively studied the synthetic, kinetic, and mechanistic aspects of thermolysis of methoxy derivatives of di- and tri-silane [34-37]. They succeeded in trapping the silylene species with a variety of unsaturated hydrocarbons such as disubstituted acetylenes, butadiene and 2,3-dimethylbutadiene, obtaining XXXVIII, XXXIX and XL, respectively, and concluded that the thermal redistribution proceeds via intermediacy of the silylenes.



(XXXVIII)



(XXXIX)



(XL)

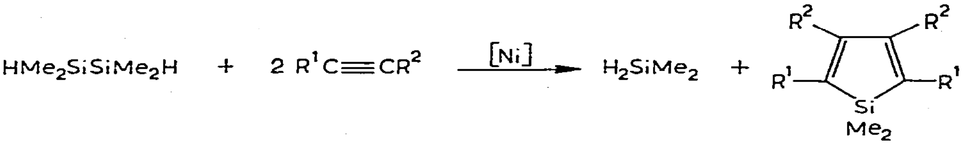
In the presence of lithium methoxide as catalyst, redistribution of 1,2-dimethoxytetramethyldisilane occurs at 100° within 10 h. For this base-catalyzed reaction, a mechanism involving nucleophilic assistance in a four-centered transition state has been proposed [34].

V. Catalysis by transition metal complexes

In 1965 Urenovitch and West attempted to effect the addition of pentamethyldisilane to 1-octene using Speier's catalyst (chloroplatinic acid in isopropyl alcohol), but the reaction led only to decomposition of the disilane into trimethylsilane and isopropoxysilicon compounds [40]. Their failure prompted us to investigate the behavior of some organopolysilanes towards Group VIII metal complexes [41-46].

It has been found that polysilicon hydrides such as pentamethyl- and *sym*-tetramethyldisilane undergo redistribution reactions very easily when heated in a sealed glass tube at 90° with a catalytic amount of a complex of nickel, palladium or platinum having phosphine ligands, giving a mixture of several lower members of the corresponding homologous series (see eqns. 14 and 15, Y = H) [42,43]. These redistribution reactions are, from the evidence of trapping experiments described below, believed to proceed via an α-elimination to generate silylene species (probably complexed with the metal "silylenoid"), followed by successive insertion into the Si—H bonds.

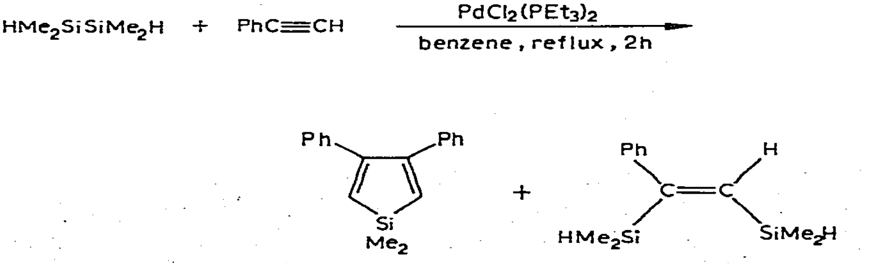
Thus, heating a mixture of pentamethyldisilane and diphenylacetylene in cyclohexane in the presence of *trans*-$[PtCl_2(PEt_3)_2]$ as catalyst at 90° for 24 h gives XXXVIII ($R^1 = R^2 = Ph$) in 5.3% yield [44]. Moreover, very interestingly, an analogous reaction of *sym*-tetramethyldisilane with a disubstituted acetylene in the presence of $NiCl_2(PEt_3)_2$ as catalyst gives a 1,1-dimethyl-2,3,4,5-tetraorgano-1-silacyclopentadiene (XLI) in good yields ($R^1 = R^2 = Ph$, 56%; $R^1 = R^2 = Et$, 95%; $R^1 = Me$, $R^2 = Ph$, 44%; $R^1 = SiMe_3$, $R^2 = Ph$, 30%) [43]. In both cases, none of higher homologs of methylsilanes arising from the redistribution are formed.



(XLI)

(16)

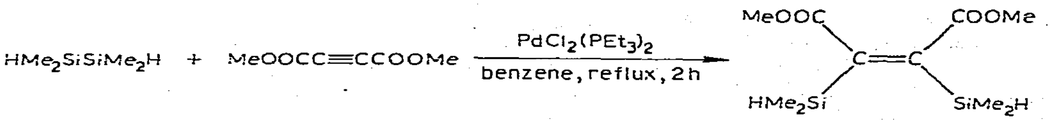
More recently it has been shown [45] that a variety of organosilicon compounds otherwise accessible only with difficulty can be synthesized very conveniently by treating disilicon hydrides with unsaturated compounds or other systems in the presence of an appropriate transition metal complex as catalyst. Examples are shown in eqns. 17 and 18.



(45% yield)

(XLII) (25% yield)

(17)



(18)

(XLIII) (43% yield)

Evidence has been obtained that both the double silylation products XLII and XLIII come from initial addition of the dimethylsilylene species across the triple bond to produce the respective silacyclopropene intermediates, followed by ring opening involving attack of dimethylsilane, Me_2SiH_2, which is formed as a result of α-elimination from the starting disilane.

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