

RECENT RESEARCH ON ORGANOPOLYSILANES

MAKOTO KUMADA

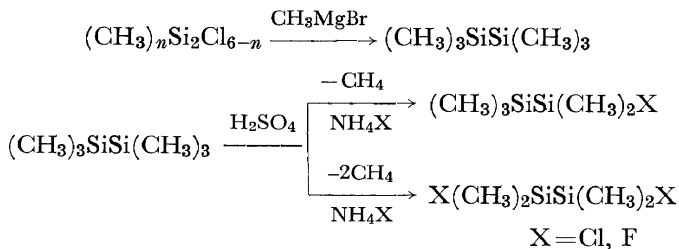
*Department of Synthetic Chemistry, Faculty of Engineering,
Kyoto University, Kyoto, Japan*

In recent years, the chemistry of organopolysilanes has made such remarkable progress that it is now possible to synthesize a variety of silicon-silicon compounds (both silicon-functional and carbon-functional) and to elucidate the mechanisms of some of their reactions. The main purpose of this lecture is to summarize our own work in organopolysilane chemistry which has been done during the past several years and is now in progress. The work can be classified as follows: (i) Silicon-functional methylpolysilanes; (ii) Permethylated linear polysilanes; (iii) Aliphatic carbon-functional organodisilanes, and trisilanes; (iv) Electrophilic and oxidative cleavage of the silicon-silicon bond; and (v) Ultraviolet properties of some organopolysilanes.

SILICON-FUNCTIONAL METHYLPOLYSILANES

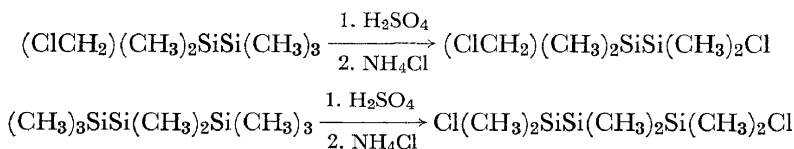
In 1954, during studies aimed at the utilization of the distillation residue from the "direct synthesis" of methylchlorosilanes, we found¹ that the residue is composed essentially of three types of compounds having the frameworks: SiOSi, SiSi, and SiCH₂Si. Of these three, we were most interested in the second type of compounds which constitute a fraction distilling at 150–160° (hereafter called the disilane fraction), because comparatively little had been known about the chemistry of aliphatic organodisilanes at that time. The disilane fraction soon proved to be a mixture of some methylchlorodisilanes (CH₃)_nSi₂Cl_{6-n}, which could not be separated from one another even by time-consuming fractional distillation. It therefore became necessary to develop an advantageous method for obtaining silicon-functional methyldisilanes in a pure state, as intermediates for further syntheses. In 1956, we presented two approaches particularly convenient for this purpose².

The first method involves the preparation of hexamethyldisilane and demethylation of it by conc. sulphuric acid, followed by treatment with ammonium chloride or fluoride.

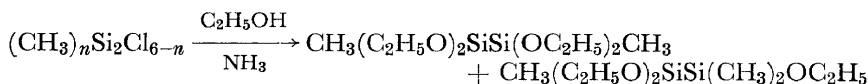


Demethylation of hexamethyldisilane proceeds in two distinct steps: (i) a heterogeneous but fast step, and (ii) a homogeneous but slow step. The first step corresponds to cleavage of one methyl from one silicon, while the second involves cleavage of the second methyl from another silicon. Treatment of the resulting sulphuric acid solution with ammonium chloride or fluoride (or hydrogen fluoride) at the point of the first or the second end of methane evolution gives chloro(or fluoro)pentamethyldisilane or 1,2-dichloro(or difluoro)tetramethyldisilane, respectively, in good yields. Only a small percentage of the reaction gives cleavage of the silicon-silicon bond here.

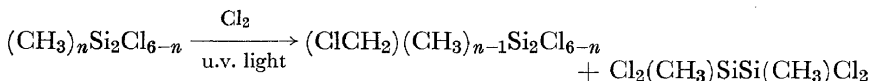
Recently, demethylation by sulphuric acid has been applied successfully to other compounds containing the silicon-silicon bond, although extensive cleavage of this bond takes place sometimes, e.g. in higher polysilanes. Thus (chloromethyl)-pentamethyldisilane was converted to 1-chloromethyl-2-chlorotetramethyldisilane³ in 70 per cent, while octamethyltrisilane to 1,3-dichlorohexamethyltrisilane in about 40 per cent yield^{4, 5}.



The second method for the preparation of silicon-functional methylsilanes comprises ethanolysis of the disilane fraction, giving a mixture of ethoxymethyldisilanes, $(\text{CH}_3)_n\text{Si}_2(\text{OC}_2\text{H}_5)_{6-n}$, much more easily separable from one another by fractional distillation². In general, two compounds, viz. 1,1,2,2-tetraethoxydimethyldisilane and 1,1,2-triethoxytrimethyldisilane are isolated as main products. This observation indicates that the disilane fraction



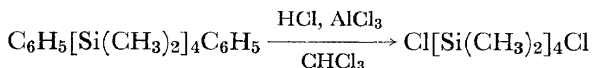
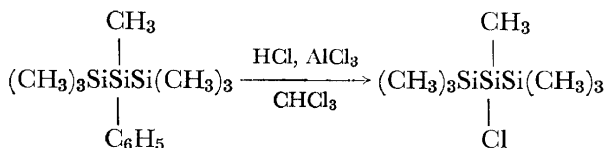
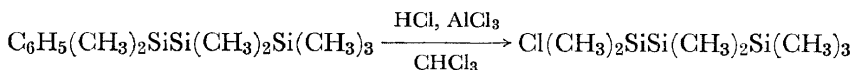
consists mainly of two kinds of methylchlorodisilanes: 1,1,2-tetrachlorodimethyl- and 1,1,2-trichlorotrimethyldisilane. More recently, 1,1,2,2-tetrachlorodimethyldisilane has been obtained in a reasonably pure state, by fractional distillation, from the disilane fraction, from which 1,1,2-trichlorotrimethyldisilane was removed previously through photochemical chlorination⁵. Here, the faster chlorination of 1,1,2-trichlorotrimethyldisilane relative to that of 1,1,2,2-tetrachlorodimethyldisilane is the basis of the method for purification of the latter compound.



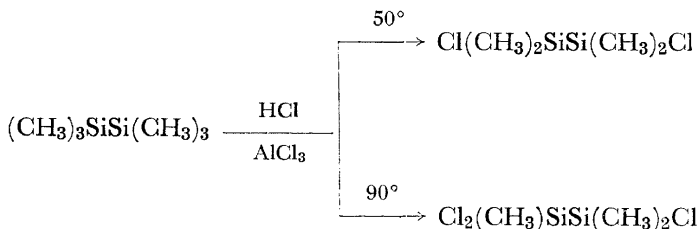
In addition to the two methods mentioned above, we have recently established⁵ that chlorodephenylation reaction of phenylmethylpolysilanes by hydrogen chloride in chloroform in the presence of anhydrous aluminium chloride affords a very convenient method generally applicable to the pre-

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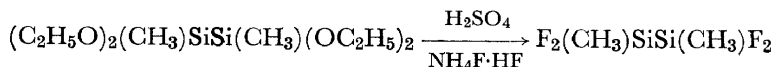
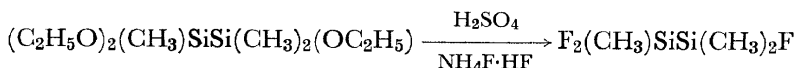
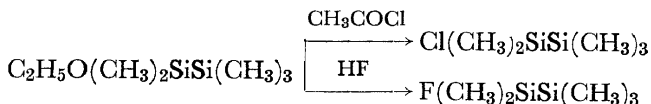
paration of methylchloropolysilanes, except in those instances where a silicon atom in the phenylmethylpolysilanes bears more than one phenyl group. Thus, from 1- and 2-phenylheptamethyltrisilane, and 1,4-diphenyloctamethyltetrasilane were obtained, respectively, 1- and 2-chloroheptamethyltrisilane, and 1,4-dichlorooctamethyltetrasilane in good yields. No appreciable cleavage of the silicon-silicon bond took place. It is to be noted that the use of chloroform as solvent makes the chlorodephenylation proceed as one wishes. Without chloroform, cleavage of the methyl-silicon bond



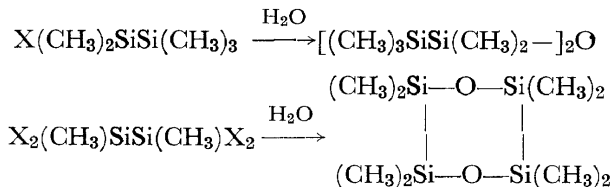
concurrently occurs. On the basis of this observation we have developed a convenient method for the synthesis of certain methylchlorodisilanes⁶. Thus, one can obtain either 1,2-dichlorotetramethyldisilane or 1,1,2-trichlorotrimethyldisilane in about 80 per cent yield from hexamethyldisilane depending upon the reaction conditions.



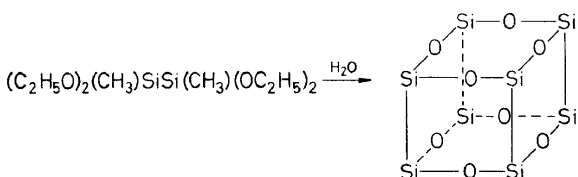
Silicon-functional organopolysilanes react with various reagents in normal ways with the silicon-silicon bond intact in many cases. Thus, ethoxy-pentamethyl-, 1,2-diethoxytetramethyl-, 1,1,2-triethoxytrimethyl- and even 1,1,2,2-tetraethoxydimethyldisilane are converted to the corresponding chloro- and/or fluorodisilanes under appropriate conditions, in good yields^{2, 7}:



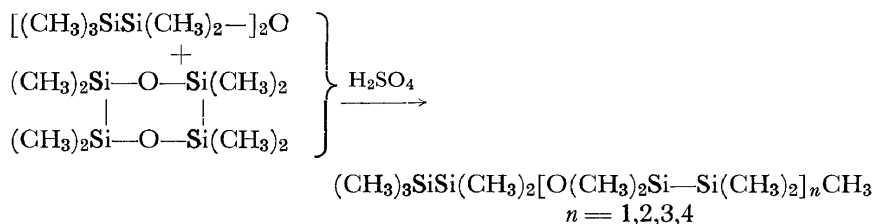
Hydrolysis of mono- and 1,2-difunctional methyl-disilanes gives the disilanyl oxide $[(\text{CH}_3)_3\text{SiSi}(\text{CH}_3)_2-]_2\text{O}$ and the cyclic compound $[-\text{O}(\text{CH}_3)_2\text{SiSi}(\text{CH}_3)_2-]_2$, respectively:



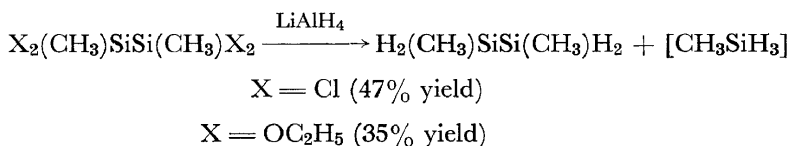
Hydrolysis of 1,1,2,2-tetraethoxydimethyl-disilane leads to the formation of the cubic dehydration tetramer of 1,2-dimethyl-disilane-tetraol⁸:



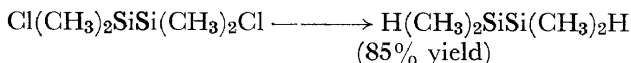
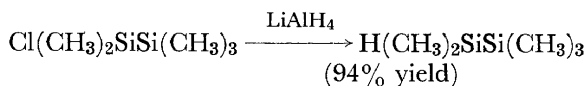
Equilibration reaction between $[(\text{CH}_3)_3\text{SiSi}(\text{CH}_3)_2-]_2\text{O}$ and $[-\text{O}(\text{CH}_3)_2-\text{SiSi}(\text{CH}_3)_2-]_2$ in the presence of sulphuric acid as catalyst proceeds at room temperature as smoothly as that between hexamethyl-disiloxane and octamethylcyclotetrasiloxane, giving a homologous series of linear disilylene-siloxanes⁸:



Extensive cleavage of the silicon-silicon bond, however, has occasionally been observed in the reactions of silicon-functional polysilanes, especially when they contain a large number of electronegative substituents on silicon and are allowed to react with nucleophilic reagents. Thus, the reduction of both 1,1,2,2-tetrachloro- and 1,1,2,2-tetraethoxydimethyl-disilane by lithium aluminium hydride gives the 1,2-dimethyl-disilane only in 47 and 35 per cent yield, respectively, whereas chloropentamethyl- and 1,2-dichlorotetra-methyl-disilane are reduced to the corresponding hydrides in 94 and 85 per cent yield, respectively⁵.



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Dependence of the ease of cleavage of the silicon-silicon bond by nucleophilic reagents upon the number of electronegative substituents on silicon is obvious from *Table 1*, which lists part of the results of kinetics of reaction of certain ethoxymethyldisilanes with ethanol in the presence of sodium ethoxide⁹:

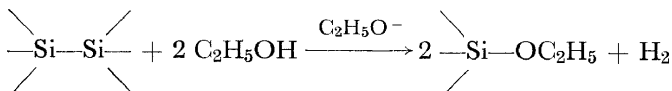
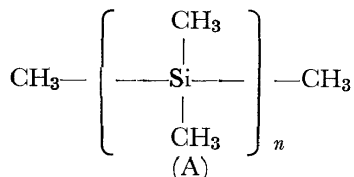


Table 1. Reaction of ethoxymethyldisilanes with sodium ethoxide-ethanol

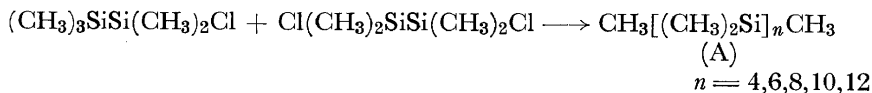
<i>Compound</i>	[Disilane] (mole/l)	[Sodium ethoxide] (mole/l)	<i>Temp.</i> (°C)	<i>k</i> ₂ (l/mole sec)
(CH ₃) ₃ SiSi(CH ₃) ₃	---	High	Reflux	No reaction
(C ₂ H ₅ O)(CH ₃) ₂ Si—Si(CH ₃) ₃	---	2.7	Reflux	Very slow
(C ₂ H ₅ O)(CH ₃) ₂ Si—Si(CH ₃) ₂ (OC ₂ H ₅)	0.0910	11.0	30	1.20 × 10 ⁻⁶
(C ₂ H ₅ O) ₂ (CH ₃)Si—Si(CH ₃) ₂ (OC ₂ H ₅)	0.180	0.0105	30	4.83 × 10 ⁻³
(C ₂ H ₅ O) ₂ (CH ₃)Si—Si(CH ₃)(OC ₂ H ₅) ₂	0.117	0.0060	30	1.07 × 10 ⁻¹

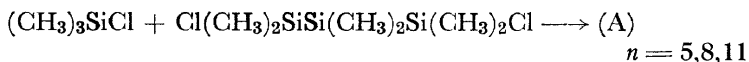
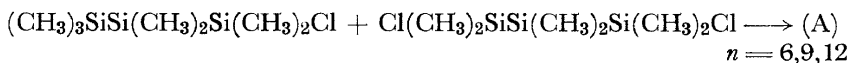
PERMETHYLATED LINEAR POLYSILANES

Only a limited number of permethylated linear polysilanes of the formula (A) are known. Wilson and Smith¹⁰, and Stolberg¹¹ prepared the trisilane



and tetrasilane derivatives by condensation of chlorosilanes using sodium-potassium alloy as condensing agent. In our earlier work⁴, we prepared six lower members, from the disilane to the heptasilane, by sodium condensation with appropriate chlorosilanes. Recently, we have synthesized a further five higher homologues, from the octasilane to the dodecasilane, using sodium-potassium alloy in a benzene-ligroin or benzene-*n*-heptane mixture¹². In order to facilitate the separation of products by fractional distillation, we selected a combination of two kinds of chlorosilanes to be condensed so as to produce polysilanes which differ from one another at least by two silicon atoms. The following equations illustrate the reactions carried out:





Permethylated linear polysilanes are colourless liquids or white crystalline substances, melting points of which are plotted against the number of silicon atoms (*Figure 1*). It is seen that the alternating effect of odd and even

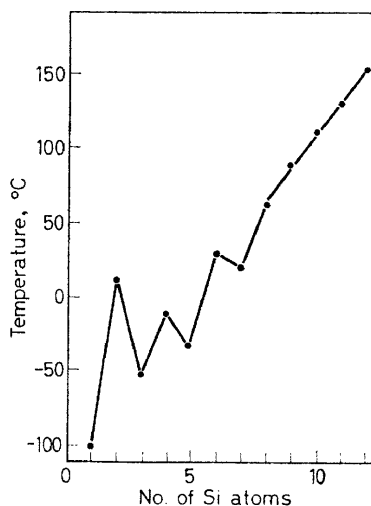


Figure 1. Variation of melting point with the number of silicon atoms in the case of permethylated linear polysilanes

numbered structures on the melting point exists up to the octasilane, but afterwards, the melting points display a regular progression as the molecular weight increases.

In *Figure 2* is plotted the variation of viscosity with the number of silicon atoms of linear methylpolysilanes and methylpolysiloxanes¹³. The figure shows that both 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 polysilanes and polysiloxanes are plotted against the number of silicon atoms in *Figure 3*. The former values were calculated from the viscosities at 30° and 75° by means of the Arrhenius equation

$$\eta = A \cdot \exp(E_{vis}/RT)$$

while the latter values are those reported by Hurd¹⁴. For the permethylated linear polysilanes, the value of E_{vis} increases as a linear function of the number of silicon atoms.

Further studies of the permethylated linear polysilanes along various lines, particularly physico-chemical studies including chemical reactions are in progress.

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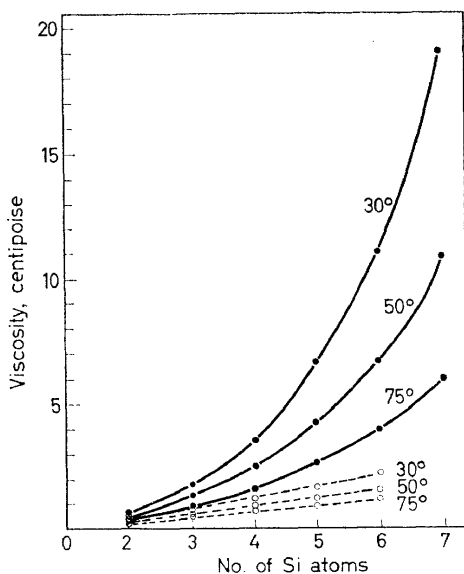


Figure 2. Viscosities of permethylated linear polysilanes and polysiloxanes at different temperatures [●, polysilanes; ○, polysiloxanes]

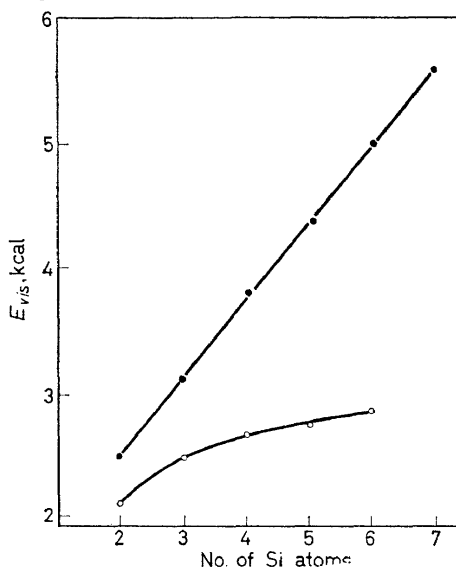
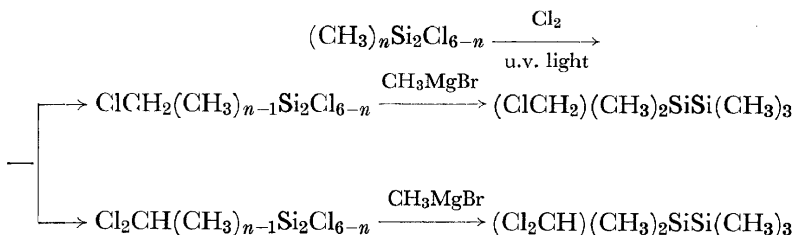


Figure 3. Relation between E_{vis} and the number of silicon atoms in the permethylated linear polysilanes and polysiloxanes [●, polysilanes; ○, polysiloxanes]

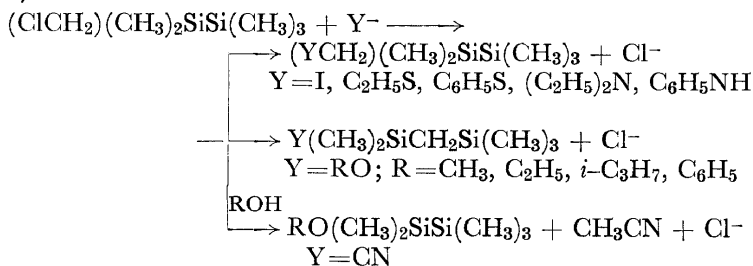
ALIPHATIC CARBON-FUNCTIONAL ORGANO DI- AND TRISILANES

Two of the most basic carbon-functional organodisilanes, viz. (chloromethyl)- and (dichloromethyl)pentamethyldisilane were prepared most conveniently by photochemical chlorination of the disilane fraction followed by methylation^{3, 15}.

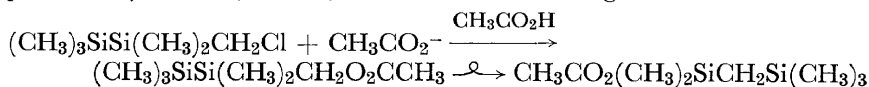


In contrast to hexamethyldisilane and methylchlorodisilanes of lower chlorine content, the disilane fraction is so stable to silicon-silicon cleavage that photochemical chlorination can be carried out as successfully as in the case of methylchlorosilanes.

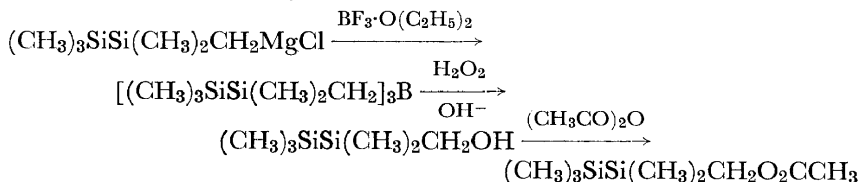
(Chloromethyl)pentamethyldisilane undergoes three different types of nucleophilic reactions, depending upon the nature of the reagent used¹⁶. Thus, substitution of the chlorine exclusively takes place by sodium iodide in acetone, sodium mercaptides in mercaptans or amines; only intramolecular rearrangement proceeds with sodium alkoxides in alcohols; while only silicon-carbon cleavage is found to occur with sodium (or potassium) cyanide in alcohols.



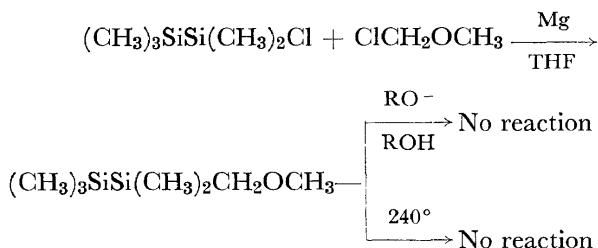
The reaction with acetate ions in acetic acid was found to take place in two steps: first, substitution leading to the formation of (acetoxymethyl)pentamethyldisilane; second, intramolecular rearrangement of the latter.



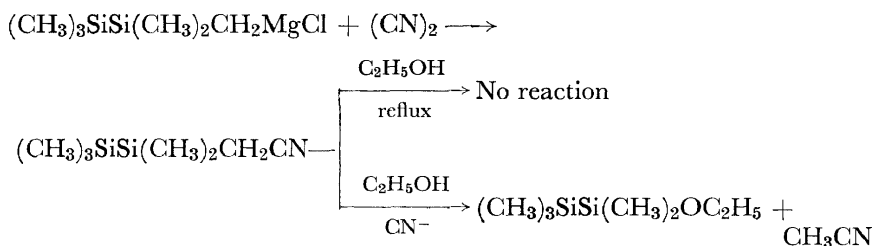
In fact, (acetoxymethyl)pentamethyldisilane, which we prepared by the following sequence of reactions, was converted completely to the rearrangement product on refluxing for 6 h.



In marked contrast to the acetate (methoxymethyl)pentamethyldisilane, which could be prepared merely by reaction of chloropentamethyldisilane with monochloromethyl ether in the presence of magnesium in tetrahydrofuran, did not undergo any change on refluxing with alkoxide ions in alcohols as well as on heating to 240° for 8 h in a sealed tube.



(Cyanomethyl)pentamethyldisilane can be prepared successfully through the reaction of pentamethyldisilanylmethylmagnesium chloride with cyanogen. This compound was found to be stable in refluxing (pure) ethanol, but it underwent complete cleavage of the cyanomethyl group on heating in an ethanolic solution containing a catalytic amount of cyanide ion.



Doubtless, the ease of cleavage is because of the high electronegative nature of the cyanomethyl group.

(Chloromethyl)pentamethyldisilane itself undergoes complete intramolecular rearrangement at 200° within 8 h to give chloropentamethyldisilmethylene¹⁷. Anhydrous aluminium chloride catalyzes the intramolecular rearrangement, making it proceed vigorously at or below room temperatures³.

Table 2 lists the differences in the sum of bond energies between the rearrangement product SiCH_2SiX and the substitution product SiSiCH_2X . The relatively large difference in the sum of bond energies for $\text{X} = \text{OR}$

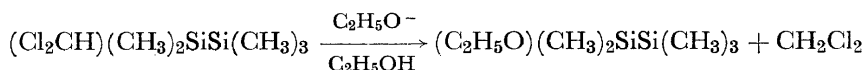
Table 2. Differences in the sum of bond energies between SiCH_2SiX and SiSiCH_2X

<i>X</i>	<i>Difference</i> (kcal/mole)
CN	14.1
I	27.0
NR ₂	28.0
SR	34.0
Cl	36.4
OR	49.1

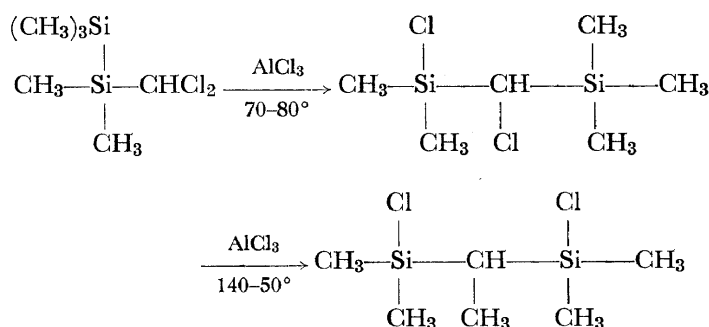
seems to favour the formation of the rearrangement product in the reaction of (chloromethyl)pentamethyldisilane with alkoxide ions. However, more satisfactory elucidation of the reaction requires further information from the

mechanistic investigation, because the simple considerations on the basis of bond energy difference cannot explain the high stability of (methoxymethyl) pentamethyldisilane, once formed.

(Dichloromethyl) pentamethyldisilane is cleaved with sodium ethoxide in ethanol to give ethoxypentamethyldisilane in 57 per cent and methylene chloride in 72 per cent yield¹⁵. This reaction provides evidence for the structure of the disilane.

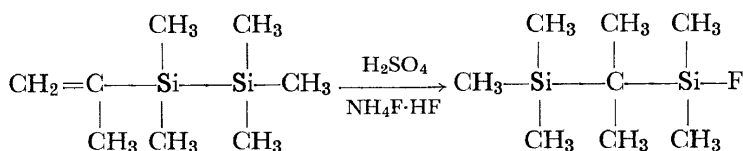


Interestingly, (dichloromethyl)pentamethyldisilane undergoes two successive and discrete intramolecular rearrangements with anhydrous aluminium chloride¹⁵. Under mild conditions, only migration of the trimethylsilyl group from silicon to carbon takes place to give (trimethylsilyl)(chlorodimethylsilyl)chloromethane in 83 per cent yield. At higher temperatures 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 per cent overall yield.

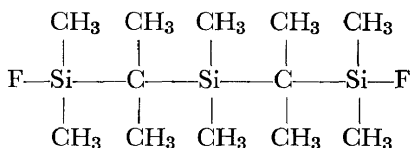
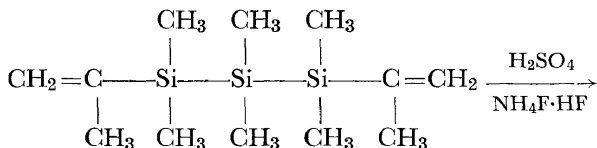
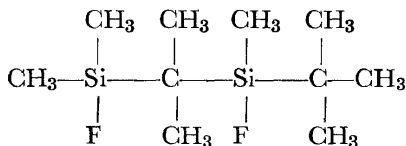
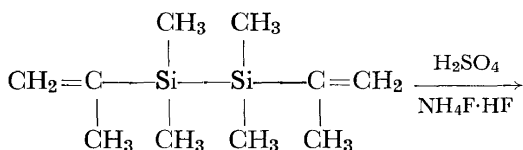


Thermal rearrangement of (dichloromethyl)pentamethyldisilane is effected by heating at 200° for 8 h to give (trimethylsilyl)(chlorodimethylsilyl)-chloromethane as a single product¹⁷.

The phenomena of intramolecular rearrangement in organopolysilanes are also observed with isopropenyl derivatives of disilane and trisilane, which readily undergo rearrangement with conc. sulphuric acid in the cold to give, after treatment with ammonium hydrogen fluoride, fluorosilanes with the SiC(CH₃)₂Si grouping as a framework of the molecule in good yields¹⁸.

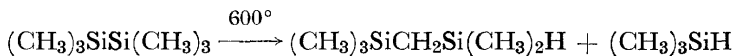


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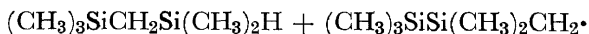
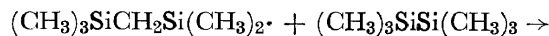
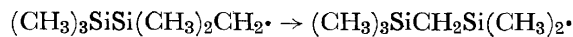
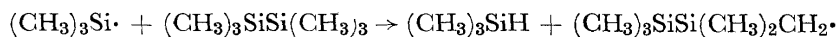
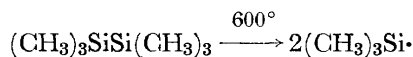


Evidence for structures of these rearrangement products is provided by their inertness to the action of bromide and by n.m.r. spectra of them as well as those of the hydrides derived therefrom.

Incidentally, we refer to the intramolecular rearrangement of hexamethyldisilane¹⁹, which produces pentamethyldisilmethylene together with a small amount of trimethylsilane when passed in quartz tube heated to 600°.

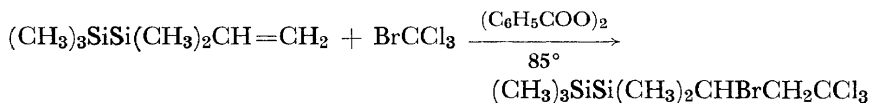


The reaction probably involves a free radical chain mechanism and may be presented as follows:



In connection with intramolecular rearrangement by free radical mechanisms, it was of interest to know whether the addition of bromotrichloromethane to vinylpentamethyldisilane in the presence of peroxide will be accompanied by intramolecular rearrangement or not. Experiments showed

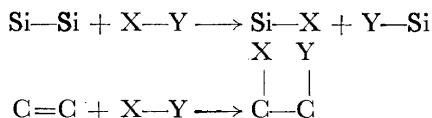
that only normal addition occurs to give γ , γ , γ -trichloro- α -bromopropyl-pentamethyldisilane in 85 per cent yield²⁰.



This result is analogous to that reported by Nesmeyanov and co-workers²¹ for the addition of bromotrichloromethane to compounds $\text{R}(\text{C}_6\text{H}_5)_2\text{ECH}=\text{CH}_2$, where $\text{R}=\text{C}_6\text{H}_5$, CH_3 and $\text{E}=\text{Sn}$, Si , C .

ELECTROPHILIC AND OXIDATIVE CLEAVAGE OF Si—Si BONDS

The silicon-silicon bond undergoes a variety of electrophilic and oxidative cleavage reactions. Many examples suggest that the cleavage reactions of this type, in a certain sense, resemble the corresponding electrophilic addition reactions to the carbon-carbon double bonds:



Hexaalkyldisilanes and alkylchlorodisilanes of lower chlorine content are cleaved by halogens²². Hexaaryldisilanes, and alkyl-chlorodisilanes of higher chlorine content such as $(\text{CH}_3)_3\text{Si}_2\text{Cl}_3$ and $(\text{CH}_3)_3\text{Si}_2\text{Cl}_4$ are quite resistant to cleavage by halogens. The relative reactivity of halogens for cleavage of a given silicon-silicon bond decreases in the order $\text{Cl}_2 > \text{Br}_2 \gg \text{I}_2$. A study of kinetics of the cleavage of several alkyldisilanes by iodine and by bromine indicates that the reaction is of the first order both in disilane and iodine (or bromine)²³. Table 3, which lists part of the results obtained, shows that the substitution of methyl groups by chlorine on the silicon-silicon linkage considerably reduces the rate of cleavage.

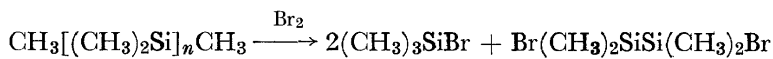
Table 3. Reactions of disilanes with iodine and bromine

Compound	Halogen	$k_2(30^\circ) \times 10^4$ (1/mole sec)	E_{app} (kcal/mole)	$\Delta S^\ddagger(30^\circ)$ (e.u.)
$(\text{CH}_3)_3\text{SiSi}(\text{CH}_3)_3$	I_2	6.35	10.5 ± 0.8	-39 ± 3
$(\text{C}_2\text{H}_5)_2\text{CH}_3\text{SiSiCH}_3(\text{C}_2\text{H}_5)_2$	I_2	4.93	11.7 ± 0.5	-35 ± 2
$(n\text{-C}_3\text{H}_7)(\text{CH}_3)_2\text{SiSi}(\text{CH}_3)_3$	I_2	6.93	7.9 ± 1.8	-47 ± 6
$\text{Cl}(\text{CH}_3)_2\text{SiSi}(\text{CH}_3)_3$	I_2	0.7	—	—
$\text{Cl}(\text{CH}_3)_2\text{SiSi}(\text{CH}_3)_2\text{Cl}$	I_2	Very slow	—	—
$(\text{C}_2\text{H}_5)_2\text{CH}_3\text{SiSiCH}_3(\text{C}_2\text{H}_5)_2$	Br_2	3880(25°)	5.2 ± 0.1	-43 ± 1
$\text{Cl}(\text{CH}_3)_2\text{SiSi}(\text{CH}_3)_3$	Br_2	970	9.2 ± 0.2	-33 ± 1
$\text{Cl}(\text{CH}_3)_2\text{SiSi}(\text{CH}_3)_2\text{Cl}$	Br_2	59	11.9 ± 0.2	-29 ± 1

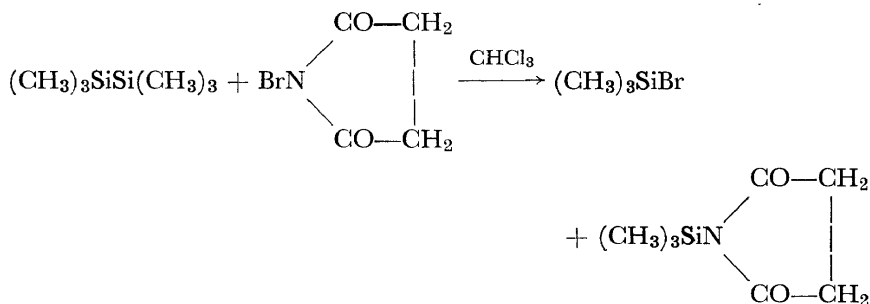
Rates of electrophilic additions to $\text{C}=\text{C}$ double bonds are also decreased by electron-withdrawing groups.

RECENT RESEARCH ON ORGANOPOLYSILANES

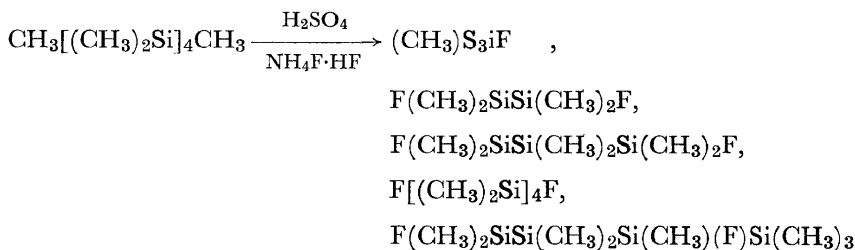
Successful synthesis of 1,2-dibromotetramethyldisilane, which was attained by the action of bromine on a mixture of permethylated linear polysilanes in the cold, is based on taking advantage of the results of the kinetic study⁸.



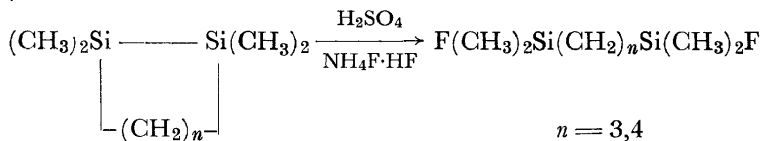
N-Bromosuccinimide attacks hexamethyldisilane with the formation of trimethylbromosilane and N-(trimethylsilyl)succinimide²⁴.



Permethylated trisilane and higher polysilanes much more extensively undergo cleavage of the silicon-silicon bond by conc. sulphuric acid than hexamethyldisilane does. Thus, the demethylation, followed by treatment with ammonium hydrogen fluoride, of decamethyltetrasilane gave several fluoro derivatives of lower polysilanes in addition to a mixture of two isomeric difluorooctamethyltetrasilanes (in nearly the equimolar ratio)²⁵.



Both 1,1,2,2-tetramethyl-1,2-disilacyclopentane and -hexane undergo complete cleavage of the silicon-silicon bond by sulphuric acid to give, after treatment with ammonium hydrogen fluoride, 1,3-bis(fluorodimethylsilyl)propane and 1,4-bis(fluorodimethylsilyl)butane, respectively, in quantitative yield.



The reaction with 1,2-disilacycloheptane, however, proceeds in a lesser degree of cleavage of the silicon-silicon bond, giving the expected fluorode-

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Recently, we have observed that the silicon-silicon bond adjacent to a ferrocenyl group undergoes cleavage with unusual ease in highly dilute alcoholic solutions of hydrogen chloride²⁸. Thus, 1,1'-bis(pentamethyl-disilanyl)ferrocene is cleaved to give two compounds, ferrocene and 1,3-(1,1'-ferrocenylene)tetramethyl-disiloxane, when refluxed for 2 h in extremely dilute methanolic or ethanolic solutions of hydrogen chloride. The relative yields of these two products depend upon the acid concentration as illustrated in *Figure 4*. The lower concentration of the acid favours the

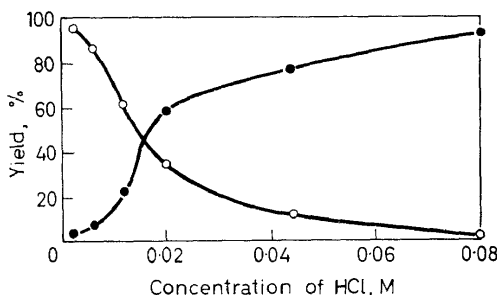
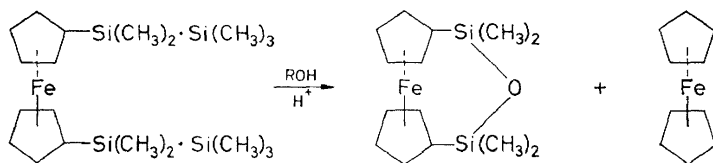
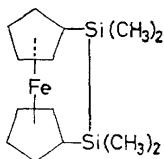


Figure 4. Cleavage of 1,1'-bis(pentamethyl-disilanyl)ferrocene by HCl in methanol [●—● ferrocene; ○—○ 1,3-(1,1'-ferrocenylene)tetramethyl-disiloxane]

formation of the ferrocenylenedisiloxane, i.e. the selective cleavage of the silicon-silicon bond. If the bis-disilanylferrocene is allowed to stand in 10^{-3} M-hydrochloric acid-ethanol solution at room temperatures for two days, the ferrocenylenedisiloxane is obtained in substantially the theoretical yield.



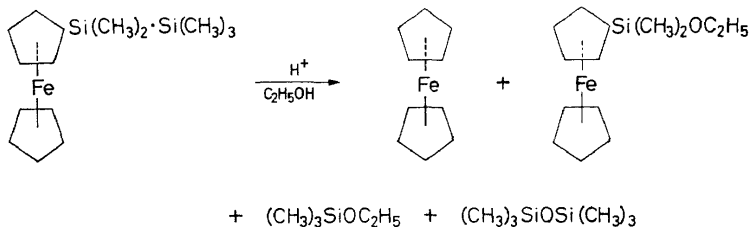
1,2-(1,1'-Ferrocenylene)tetramethyl-disilane seems to be more sensitive to acid-catalyzed cleavage, and gives the same two compounds as above under similar conditions²⁹.



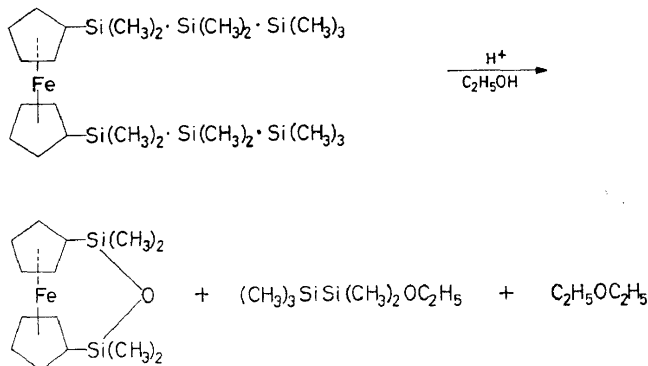
Pentamethyl-disilanylferrocene and 1,1'-bis(heptamethyl-trisilyl)ferrocene also undergo a similar type of cleavage to that mentioned above under the same conditions. From the reaction with pentamethyl-disilanylferrocene in

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ethanol we were able to detect ferrocene, ethoxydimethylsilylferrocene, trimethylethoxysilane and hexamethyldisiloxane by gas chromatography.

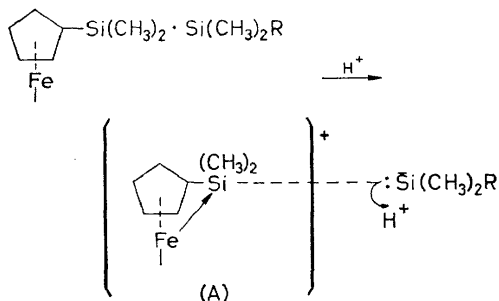


1,1'-Bis(heptamethyltrisilyl)ferrocene gave 1,3-(1,1'-ferrocenylene)tetramethyldisiloxane, ethoxypentamethyldisilane and diethyl ether.

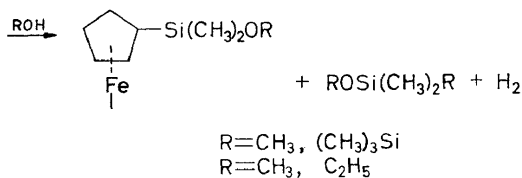


These ferrocenes containing the silicon-silicon bond are very stable to the action of basic reagents. For example, 1,1'-bis(pentamethyldisilyl)ferrocene gave no appreciable reaction when refluxed with 0.012–0.14 M sodium methoxide in methanol for several hours. Cyclopentadienylpentamethyldisilane itself is fairly stable to acid cleavage and was mostly recovered unchanged when it was subjected to the same conditions as used for the ferrocenes containing silicon-silicon linkages.

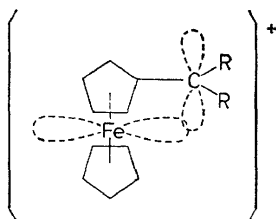
From these observations, the unusual ease with which the silicon-silicon bond adjacent to a ferrocenyl group undergoes acid-catalyzed cleavage in alcohols may be explained by stabilization of the transition state, as symbolized by structure A, which could result from overlap of filled *d*-orbitals of iron with the electron-deficient *p*-orbital of silicon.



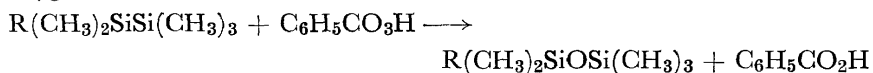
RECENT RESEARCH ON ORGANOPOLYSILANES



Stabilization of carbonium ions adjacent to a ferrocenyl group in a similar way has been proposed by Richard and Hill³⁰, and supported by many other authors³¹:



One of the most interesting electrophilic cleavage of organodisilanes may be their oxidation by perbenzoic acid, which involves direct insertion of an oxygen atom into the silicon-silicon bond³²:



Thus, the oxidation of phenylpentamethyldisilane in methylene chloride gives phenylpentamethyldisiloxane in nearly quantitative yield. Gas chromatographic analysis of the reaction product revealed that neither symmetrical disiloxane (hexamethyl- or diphenyltetramethyldisiloxane) nor compound arising from phenyl-silicon cleavage was formed.

Kinetic studies of the reaction of hexamethyldisilane and several ring-substituted phenylpentamethyldisilanes with perbenzoic acid in benzene indicate that the reaction is always of the first order each in the disilane and the peracid. *Table 4* lists the second order rate constants at 45° and activation parameters for the reaction. In *Figure 5* are plotted the logarithms of the rate

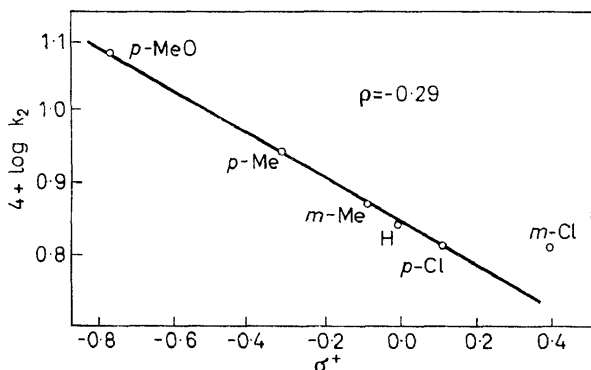


Figure 5. Correlation of $\log k_2 + 4$ and σ^+ for the reaction of phenylpentamethyldisilane with perbenzoic acid in benzene at 45.0°

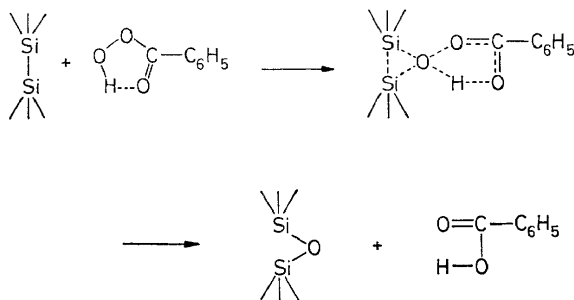
constants against values of σ^+ of Brown and Okamoto³³ for six phenylpentamethyldisilanes. The fairly good linear relationships with negative values in *Figure 5* may indicate that electron-donating substituents on the phenyl ring of the disilane are capable of resonance interaction with the silicon atom possibly through $p_\pi-d_\pi$ conjugation to make the silicon-silicon bond more reactive to the electrophilic cleavage. Substitution of a phenyl

Table 4. Second order rate constants at 45° and activation parameters for oxidation reaction of disilanes with perbenzoic acid in benzene

Disilane	$k_2 \times 10^4 (45^\circ)$ (1/mole sec)	ΔH^\ddagger (kcal/mole)	$-\Delta S^\ddagger$ (e.u.)
$(\text{CH}_3)_5\text{SiSi}(\text{CH}_3)_3$	11.7	13.7	27.3
<i>p</i> - $\text{CH}_3\text{OC}_6\text{H}_4\text{Si}(\text{CH}_3)_2\text{Si}(\text{CH}_3)_3$	11.9	14.2	27.4
<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{Si}(\text{CH}_3)_2\text{Si}(\text{CH}_3)_3$	8.79	14.0	28.7
<i>m</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{Si}(\text{CH}_3)_2\text{Si}(\text{CH}_3)_3$	7.44	13.8	29.6
$\text{C}_6\text{H}_5\text{Si}(\text{CH}_3)_2\text{Si}(\text{CH}_3)_3$	6.93	13.4	31.1
<i>p</i> - $\text{ClC}_6\text{H}_4\text{Si}(\text{CH}_3)_2\text{Si}(\text{CH}_3)_3$	6.46	13.2	31.6
<i>m</i> - $\text{ClC}_6\text{H}_4\text{Si}(\text{CH}_3)_2\text{Si}(\text{CH}_3)_3$	6.55	14.2	29.6
$\text{C}_6\text{H}_5\text{Si}(\text{CH}_3)_2\text{Si}(\text{CH}_3)_2\text{C}_6\text{H}_5$	3.89	17.7	18.6

for a methyl group decreases the reactivity of disilanes towards perbenzoic acid. Qualitatively this is the same tendency as was observed with the series of phenyl substituted ethylenes³⁴.

These results suggest that a possible mechanism for peracid oxidation of organodisilanes is direct insertion of an oxygen atom involving electrophilic attack at the silicon-silicon bond by a cyclic hydrogen-bonded form of the peracid³⁵. (Analogous molecular mechanism involving electrophilic attack by a cyclic hydrogen-bonded form of peracid was first suggested by P. D. Bartlett³⁵.)



ULTRAVIOLET PROPERTIES OF SOME ORGANOPOLYSILANES

Polysilanes with phenyl or vinyl groups exhibit intense absorption in the u.v. region, unlike the corresponding monosilanes. Hague and Prince³⁶ first observed that hexaphenyldisilane absorbs strongly at 246.5 $m\mu$, and described the phenomenon as due to an intense interaction between phenyl groups through the silicon-silicon bond. Gilman *et al.*³⁷ determined the u.v. spectra of the homologous series, $\text{C}_6\text{H}_5[\text{Si}(\text{CH}_3)_2]_n\text{C}_6\text{H}_5$ (where $n=2-6$) and a number of other organopolysilanes, and suggested that the unique spectral properties of polysilanes are due to the silicon-silicon bond acting as a chromophore. Independently, we have studied³⁸ u.v. absorption

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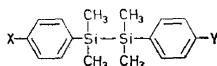
properties of certain phenyl and vinyl disilanes and trisilanes, and made essentially the same suggestion as that of Gilman.

In *Tables 5 and 6* are listed our own experimental results. Hexamethyldisilane, the parent compound, has no absorption in the u.v. region, 210–260 $m\mu$. From *Table 5* it can be seen that phenylpentamethyldisilane exhibit the most striking red shift in the absorption maxima; namely, the introduction of a pentamethyldisilanyl group into benzene gives rise to a red shift to the extent of 28 $m\mu$ in the 200 $m\mu$ -band. This fact suggests that the pentamethyldisilanyl group itself can interact strongly with the phenyl group, possibly by way of p_{π} — d_{π} conjugation. Introduction of the second phenyl group into phenylpentamethyldisilane at the vicinal position results in a rather small shift in absorption maxima, although it makes the absorption intensity increase.

Table 5. Ultraviolet spectra of some polysilanes

<i>Polysilane</i>	λ_{max} ($m\mu$)	$\epsilon_{max} \times 10^{-4}$
$C_6H_5(CH_3)_2SiSi(CH_3)_3$	231.0	1.09
$C_6H_5(CH_3)_2SiSi(CH_3)_2C_6H_5$	238.0	1.85
$(C_6H_5)_2CH_3SiSiCH_3(C_6H_5)_2$	240.0	2.59
$(CH_2=CH)(CH_3)_2SiSi(CH_3)_3$	223.2	0.52
$(CH_2=CH)(CH_3)_2SiSi(CH_3)_2(CH=CH_2)$	227.7	0.97
$(C_6H_5)(CH_3)_2SiSi(CH_3)_2Si(CH_3)_3$	240.0	1.54
	221.3	1.30
$(CH_3)_3SiSi(CH_3)(C_6H_5)Si(CH_3)_3$	243.0	1.3

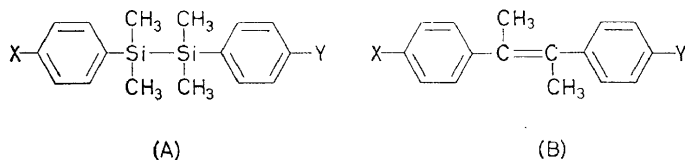
Table 6. Ultraviolet spectra of some 1,2-diphenyltetramethyldisilanes



<i>Substituents</i>		λ_{max} ($m\mu$)	$\epsilon_{max} \times 10^{-4}$
X	Y		
None		238.0	1.85
<i>p</i> -CH ₃	<i>p</i> -H	238.5	2.11
<i>p</i> -CH ₃	<i>p</i> -CH ₃	239.0	2.49
<i>p</i> -CH ₃ O	<i>p</i> -CH ₃ O	242.0	3.26
<i>p</i> -CH ₃ O	<i>p</i> -H	241.0	2.58
<i>p</i> -CH ₃ O	<i>p</i> -CH ₃	241.5	2.82
<i>p</i> -Cl	<i>p</i> -Cl	242.5	2.80
<i>p</i> -CH ₃	<i>p</i> -Cl	240.5	2.46

Almost the same trends are observed for vinylpentamethyl- and 1,2-divinyltetramethyldisilane. Since the trimethylsilyl group has only a small bathochromic effect on benzene or ethylene, it seems reasonable to assume that the silicon-silicon bond is essential as a chromophore to make an enhanced conjugation with benzene and ethylene.

It is of considerable interest to compare the u.v. properties of some of 1,2-bis(*p*-substituted phenyl)tetramethyldisilanes (A) in Table 6 with those of the corresponding *p*-substituted *trans*- α,α' -dimethylstilbene (B). Figure 6 shows there is a linear correlation between the absorption maxima of the



disilanes (A) and those of the stilbenes (B).

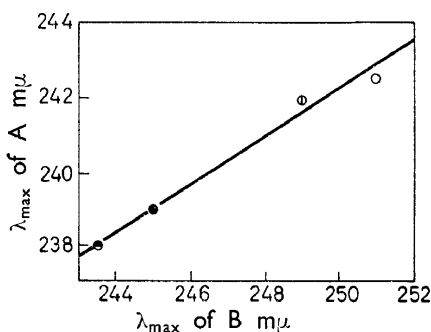


Figure 6. Correlation of λ_{\max} of 1,2-diphenyltetramethyldisilanes (A) with λ_{\max} of α,α' -dimethylstilbenes (B) [○ *p,p'*-dichloro-; ⊙ *p,p'*-dimethoxy-; ● *p,p'*-dimethyl-; ◐ unsubstituted]

CONCLUSION

In this lecture the author has only been able to outline the results of his own work in the chemistry of organopolysilanes, but to refer none of important and excellent results of many other authors' investigations. The chemistry of organopolysilanes is much more extensive than mentioned here and contains innumerable interesting problems to be solved. Among the most important subjects are as follows: elucidation of the nature of the silicon-silicon bond, especially in connection with the unique u.v. properties of organopolysilanes; preparation and reactions of small ring compounds with the silicon-silicon bond; stereochemistry and mechanisms of reactions at the silicon-silicon bond; and the influences of polysilyl substituents on the reactivities of organic portions in the molecules.

Finally the author wishes to express his appreciation to present and past coworkers who have carried out all the experiments described. Particular thanks are due to Professor Kimio Tarama, Dr Mitsuo Ishikawa, Dr Kyo Shiina, Dr Hideki Sakurai, and Dr Keiji Yamamoto. It is a pleasure for the author to acknowledge the support of his research activities in organosilicon chemistry for many years by Tokyo-Shibaaura Electric Co. Ltd., and Nitto Electric Industrial Co. Ltd.

References

- ¹ M. Kumada and M. Yamaguchi. *J. chem. Soc. Japan (Industr. chem. Sec.)* **57**, 175 (1954).
- ² M. Kumada, M. Yamaguchi, Y. Yamamoto, J. Nakajima, and K. Shiina. *J. org. Chem.* **21**, 1264 (1956).
- ³ M. Kumada, J. Nakajima, M. Ishikawa, and Y. Yamamoto. *J. org. Chem.* **23**, 292 (1958).
- ⁴ M. Kumada and M. Ishikawa. *J. organometal Chem.* **1**, 153 (1963).
- ⁵ M. Kumada, M. Ishikawa, and S. Maeda. *J. organometal. Chem.* **2**, 478 (1964).
- ⁶ H. Sakurai, K. Tominaga, and M. Kumada. Unpublished work.
- ⁷ M. Kumada and M. Ishikawa. Unpublished work.
- ⁸ M. Kumada, M. Ishikawa, and B. Murai. *J. chem. Soc. Japan (Industr. chem. Sec.)* **66**, 637 (1963).
- ⁹ A. Taketa, M. Kumada, and K. Tarama. *J. chem. Soc. Japan (Industr. chem. Sec.)* **60**, 201 (1957).
- ¹⁰ G. R. Wilson and A. G. Smith. *J. org. Chem.* **26**, 557 (1961).
- ¹¹ U. G. Stolberg. *Angew. Chem.* **74**, 696 (1962).
- ¹² M. Kumada and M. Ishikawa. *J. organometal. Chem.* **5**, 120 (1966).
- ¹³ M. Kumada and M. Ishikawa. Unpublished work.
- ¹⁴ D. T. Hurd. *J. Am. chem. Soc.* **68**, 364 (1964).
- ¹⁵ M. Kumada and M. Ishikawa. *J. organometal. Chem.* **1**, 411 (1964).
- ^{16a} M. Kumada, M. Ishikawa, and K. Tamao. *J. organometal. Chem.* **5**, 226 (1966);
^b M. Kumada, N. Imaki, and K. Yamamoto. Unpublished work.
- ¹⁷ M. Kumada and M. Ishikawa. Unpublished work.
- ¹⁸ M. Kumada, K. Naka, and M. Ishikawa. *J. organometal. Chem.* **2**, 136 (1964).
- ¹⁹ K. Shiina and M. Kumada. *J. org. Chem.* **23**, 139 (1958).
- ²⁰ M. Kumada and K. Naka. Unpublished work.
- ²¹ R. Kh. Freidlina, G. T. Martirocyan, and A. N. Nesmeyanov. *Doklady Akad. Nauk, SSSR* **137**, 1129 (1961).
- ²² M. Kumada, K. Shiina, and M. Yamaguchi. *J. chem. Soc. Japan (Industr. chem. Sec.)* **57**, 230 (1954).
- ²³ A. Taketa, M. Kumada, and K. Tarama. *J. chem. Soc. Japan (Pure chem. Sec.)* **78**, 999 (1957).
- ^{24a} M. Kumada and J. Nakajima. Preliminary experiments cited in M. Kumada and R. Okawara, *Organosilicon Chemistry*, Maki, Tokyo, 74 (1959);
^b R. Calas, E. Frainnet, and Y. Dentone. *C. R. Acad. Sci. Paris* **259**, 3777 (1964).
- ²⁵ M. Kumada and M. Ishikawa. Unpublished work.
- ²⁶ M. Kumada, M. Ishikawa, and T. Takubo. Unpublished work.
- ²⁷ K. Shiina and M. Kumada. *J. chem. Soc. Japan (Industr. chem. Sec.)* **60**, 1395 (1957).
- ²⁸ M. Kumada, K. Mimura, and M. Ishikawa. *Tetrahedron Lett.* No. 1, 83 (1965).
- ²⁹ M. Kumada, K. Mimura, M. Ishikawa, and H. Tsunmi. Abstracts of Papers presented at the Second International Symposium on Organometallic Chemistry, Madison, Wisconsin, U.S.A. (30th August–3rd September, 1965).
- ³⁰ J. H. Richards and E. A. Hill. *J. Am. chem. Soc.* **81**, 3484 (1959).
- ³¹ For pertinent references, see ^a W. F. Little. In *Survey of Progress in Chemistry, Vol. I*, edited by A. F. Scott, Academic Press, New York 133–210 (1963);
^b M. Rosenblum. *Chemistry of the Iron Group Metalloenes*. Interscience, New York 129–37 (1965).
- ^{32a} H. Sakurai, T. Imoto, N. Hayashi, and M. Kumada. *J. Am. chem. Soc.* **87**, 4001 (1965);
^b H. Sakurai, N. Hayashi, and M. Kumada. Unpublished work.
- ³³ H. C. Brown and Y. Okamoto. *J. Am. chem. Soc.* **80**, 4979 (1958); *J. org. Chem.* **22**, 485 (1957).
- ³⁴ B. M. Lynch and K. H. Pausacker. *J. chem. Soc.* 1525 (1955).
- ³⁵ P. D. Bartlett. *Record Chem. Progr.* **11**, 47 (1950).
- ³⁶ D. N. Hague and R. H. Prince. *Proc. chem. Soc.* 300 (1962).
- ^{37a} H. Gilman, W. H. Atwell, and G. L. Schwebke. *Chem. Ind.* 1063 (1964);
^b H. Gilman, W. Atwell, and G. L. Schwebke. *J. organometal. Chem.* **2**, 369 (1964);
^c H. Gilman and W. H. Atwell. Private communication.
- ^{38a} H. Sakurai and M. Kumada. *Bull. chem. Soc. Japan* **37**, 1894 (1964);
^b H. Sakurai, H. Yamamori, and M. Kumada. *Bull. Chem. Soc. Japan* **38**, 2024 (1965).