RECENT RESEARCH ON ORGANOPOLYSILANES

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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 found\(^1\) that the residue is composed essentially of three types of compounds having the frameworks: SiOSi, SiSi, and SiCH\(_2\)Si. Of these three, we were most interested in the second type of compounds which constitute a fraction distilling at 150–160\(^\circ\) (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 \((\text{CH}_3)_n\text{Si}_2\text{Cl}_{6-n}\), 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 purpose\(^2\).

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

\[
\begin{align*}
(\text{CH}_3)_n\text{Si}_2\text{Cl}_{6-n} &\xrightarrow{\text{CH}_3\text{MgBr}} (\text{CH}_3)_3\text{SiSi}((\text{CH}_3)_3 \\
(\text{CH}_3)_3\text{SiSi}(\text{CH}_3)_3 &\xrightarrow{\text{H}_2\text{SO}_4, \text{NH}_4\text{X}} (\text{CH}_3)_3\text{SiSi}((\text{CH}_3)_2\text{X} \\
 &\xrightarrow{-2\text{CH}_4, \text{NH}_4\text{X}} X(\text{CH}_3)_3\text{SiSi}((\text{CH}_3)_2\text{X} \\
 &\text{X = Cl, F}
\end{align*}
\]
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-chlorotetramethyldisilane in 70 per cent, while octamethyltrisilane to 1,3-dichlorohexamethyltrisilane in about 40 per cent yield

\[
\begin{align*}
\text{(ClCH}_2\text{(CH}_3\text{)}_2\text{SiSi(CH}_3\text{)}_3 & \xrightarrow{1. \text{H}_2\text{SO}_4} \text{(ClCH}_2\text{(CH}_3\text{)}_2\text{SiSi(CH}_3\text{)}_3\text{Cl)} \\
& \xrightarrow{\text{2. NH}_4\text{Cl}} \text{Cl(CH}_3\text{)}_2\text{SiSi(ChH}_3\text{)}_3\text{Cl)\
\end{align*}
\]

The second method for the preparation of silicon-functional methyldisilanes comprises ethanalysis of the disilane fraction, giving a mixture of ethoxymethylsilanes, \((\text{CH}_3)_n\text{Si(OC}_2\text{H}_5)_6-n\), much more easily separable from one another by fractional distillation. In general, two compounds, viz. 1,1,2,2-tetraethoxydimethylsilane and 1,1,2-trioethoxytrimethylsilane are isolated as main products. This observation indicates that the disilane fraction

\[
\text{(CH}_3\text{)}_n\text{Si}_2\text{Cl}_{6-n} \xrightarrow{\text{C}_2\text{H}_5\text{OH, NH}_3} \text{CH}_3\text{(C}_2\text{H}_5\text{)}_2\text{SiSi(OCC}_2\text{H}_5\text{)}_2\text{CH}_3
\]

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

\[
\text{(CH}_3\text{)}_n\text{Si}_2\text{Cl}_{6-n} \xrightarrow{\text{Cl}_2, \text{u.v. light}} \text{(ClCH}_2\text{(CH}_3\text{)}_n\text{SiCl}_{6-n}) + \text{Cl}_2\text{(CH}_3\text{)}_2\text{SiSi(ChH}_3\text{)}_3\text{Cl}_2
\]

In addition to the two methods mentioned above, we have recently established 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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Preparation 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-diphenyl-octamethyltetrasilane 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

\[
C_6H_5(CH_3)_2SiSi(CH_3)_2Si(CH_3)_3 + HCl, AlCl_3 \xrightarrow{CHCl_3} Cl(CH_3)_2SiSi(CH_3)_2Si(CH_3)_3
\]

\[
\text{CH}_3 \quad \text{CH}_3
\]

\[
(\text{CH}_3)_3SiSi(\text{CH}_3)_3 + HCl, AlCl_3 \xrightarrow{CHCl_3} (\text{CH}_3)_3SiSi(\text{CH}_3)_3
\]

\[
\text{C}_6\text{H}_5 \quad \text{Cl}
\]

\[
C_6H_5[Si(CH_3)_2]_4C_6H_5 + HCl, AlCl_3 \xrightarrow{CHCl_3} Cl[Si(CH_3)_2]_4Cl
\]

concurrently occurs. On the basis of this observation we have developed a convenient method for the synthesis of certain methylchlorodisilanes\(^6\). Thus, one can obtain either 1,2-dichlorotetramethyldisilane or 1,1,2-trichlorotrimethylsilane in about 80 per cent yield from hexamethyldisilane depending upon the reaction conditions.

\[
(\text{CH}_3)_3SiSi(\text{CH}_3)_3 + HCl \xrightarrow{AlCl_3} \xrightarrow{50^\circ} Cl(CH_3)_2SiSi(CH_3)_2Cl
\]

\[
(\text{CH}_3)_3SiSi(\text{CH}_3)_3 \xrightarrow{HCl, AlCl_3} \xrightarrow{90^\circ} Cl(CH_3)_2SiSi(CH_3)_2Cl
\]

Silicon-functional organopolysilanes react with various reagents in normal ways with the silicon–silicon bond intact in many cases. Thus, ethoxy-pentamethyl-, 1,2-dioxytetramethyldisilane, 1,1,2-trioxytrimethyl- and even 1,1,2,2-tetraoxysilodimethylsilane are converted to the corresponding chloro- and/or fluorodisilanes under appropriate conditions, in good yields\(^2, 7\):

\[
C_2H_5O(CH_3)_2SiSi(CH_3)_3 + HClO_2 \xrightarrow{CH_3COCl} Cl(CH_3)_2SiSi(CH_3)_3
\]

\[
(\text{C}_2\text{H}_5\text{O})_2(\text{CH}_3)\text{SiSi(\text{CH}_3)_2(OC_2\text{H}_5)} \xrightarrow{\text{H}_2\text{SO}_4} \xrightarrow{\text{NH}_4\text{F-HF}} \text{F}_2(\text{CH}_3)\text{SiSi(CH}_3)_2\text{F}
\]

\[
(\text{C}_2\text{H}_5\text{O})_2(\text{CH}_3)\text{SiSi(\text{CH}_3)(OC}_2\text{H}_5)_2 \xrightarrow{\text{H}_2\text{SO}_4} \xrightarrow{\text{NH}_4\text{F-HF}} \text{F}_2(\text{CH}_3)\text{SiSi(\text{CH}_3)_2F}_2
\]

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Hydrolysis of mono- and 1,2-di-functional methylsilanes gives the disilanylene oxide \([\text{CH}_3\text{SiSi(CH}_3\text{)}_2\text{]}_2\text{O}\) and the cyclic compound \([-\text{O(CH}_3\text{)}_2\text{SiSi(CH}_3\text{)}_2\text{]}_2\), respectively:

\[
\begin{align*}
X(\text{CH}_3)_2\text{SiSi(CH}_3\text{)}_3 & \xrightarrow{\text{H}_2\text{O}} [(\text{CH}_3)_3\text{SiSi(CH}_3\text{)}_2\text{]}_2\text{O} \\
X_2(\text{CH}_3)_2\text{SiSi(CH}_3\text{)}_3 & \xrightarrow{\text{H}_2\text{O}} [(\text{CH}_3)_2\text{SiSi(Ch}_3\text{)]}_2\text{Si(Ch}_3\text{)}_2]
\end{align*}
\]

Hydrolysis of 1,1,2,2-tetraethoxydimethylsilane leads to the formation of the cubic dehydration tetrramer of 1,2-dimethylsilanetetraol:

\[
(\text{C}_2\text{H}_5\text{O})_2(\text{CH}_3)_2\text{SiSi(Ch}_3\text{)](OC}_2\text{H}_5)_2 \xrightarrow{\text{H}_2\text{O}}
\]

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

\[
\begin{align*}
[(\text{CH}_3)_3\text{SiSi(Ch}_3\text{)]}_2\text{O} \\
(\text{CH}_3)_2\text{SiSi(Ch}_3\text{)]}_2 \\
(\text{CH}_3)_2\text{SiSi(Ch}_3\text{)]}_2
\end{align*} \xrightarrow{\text{H}_2\text{SO}_4} \frac{\text{(Ch}_3\text{)}_3\text{SiSi(Ch}_3\text{)]_2[O(Ch}_3\text{)]_2\text{SiSi(Ch}_3\text{)]_nCh}_3}{n = 1,2,3,4}
\]

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-tetraethoxydimethylsilane by lithium aluminium hydride gives the 1,2-dimethylsilane only in 47 and 35 per cent yield, respectively, whereas chloropentamethyl- and 1,2-dichlorotetramethylsilane are reduced to the corresponding hydrides in 94 and 85 per cent yield, respectively:

\[
\begin{align*}
\text{LiAlH}_4 \\
X_2(\text{CH}_3)_2\text{SiSi(Ch}_3\text{)]}_2 \xrightarrow{\text{H}_2\text{C(Ch}_3\text{)]}_2\text{SiSi(Ch}_3\text{)]}_2 + [\text{CH}_3\text{SiH}_3]} \\
X = \text{Cl (47% yield)} \\
X = \text{OC}_2\text{H}_5 (35% yield)
\end{align*}
\]
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\[
\text{Cl(\(\text{CH}_3\))}_2\text{SiSi(\(\text{CH}_3\))}_3 \xrightarrow{\text{LiAlH}_4} \text{H(\(\text{CH}_3\))}_2\text{SiSi(\(\text{CH}_3\))}_3 \\
\text{(94\% yield) }
\]

\[
\text{Cl(\(\text{CH}_3\))}_2\text{SiSi(\(\text{CH}_3\))}_2\text{Cl} \xrightarrow{} \text{H(\(\text{CH}_3\))}_2\text{SiSi(\(\text{CH}_3\))}_2\text{H} \\
\text{(85\% yield) }
\]

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 ethoxymethyl disilanes with ethanol in the presence of sodium ethoxide\textsuperscript{9}:

\[
\text{Si} \quad \text{Si} \quad + \quad 2 \quad \text{C}_2\text{H}_5\text{OH} \quad \xrightarrow{\text{C}_2\text{H}_5\text{O}^-} \quad 2 \quad \text{Si} \quad \text{OC}_2\text{H}_5 \quad + \quad \text{H}_2
\]

Table 1. Reaction of ethoxymethyl disilanes with sodium ethoxide-ethanol

<table>
<thead>
<tr>
<th>Compound</th>
<th>[Disilane] (mole/l)</th>
<th>[Sodium ethoxide] (mole/l)</th>
<th>Temp. (°C)</th>
<th>(k_2) (l/mole sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{CH}_3))\textsubscript{2}SiSi((\text{CH}_3))\textsubscript{3}</td>
<td>–</td>
<td>–</td>
<td>Reflux</td>
<td>No reaction</td>
</tr>
<tr>
<td>((\text{C}_2\text{H}_5))\textsubscript{2}SiSi((\text{CH}_3))\textsubscript{3}</td>
<td>–</td>
<td>High</td>
<td>Reflux</td>
<td>Very slow</td>
</tr>
<tr>
<td>((\text{C}_2\text{H}_5))\textsubscript{2}SiSi((\text{CH}_3))\textsubscript{3}</td>
<td>0.0910</td>
<td>11.0</td>
<td>30</td>
<td>1.20 \times 10^{-7}</td>
</tr>
<tr>
<td>((\text{C}_2\text{H}_5))\textsubscript{2}SiSi((\text{CH}_3))\textsubscript{3}</td>
<td>0.180</td>
<td>0.0105</td>
<td>30</td>
<td>4.20 \times 10^{-3}</td>
</tr>
<tr>
<td>((\text{C}_2\text{H}_5))\textsubscript{2}SiSi((\text{CH}_3))\textsubscript{3}</td>
<td>0.117</td>
<td>0.0060</td>
<td>30</td>
<td>1.07 \times 10^{-1}</td>
</tr>
</tbody>
</table>

PERMETHYLATED LINEAR POLYSILANES

Only a limited number of permethylated linear polysilanes of the formula (A) are known. Wilson and Smith\textsuperscript{10}, and Stolberg\textsuperscript{11} prepared the trisilane

\[
\begin{array}{c}
\text{CH}_3 \\
\text{Si} \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{(A)}
\end{array}
\]

and tetrasilane derivatives by condensation of chlorosilanes using sodium-potassium alloy as condensing agent. In our earlier work\textsuperscript{4}, 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-\textit{n}-heptane mixture\textsuperscript{12}. 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:

\[
(\text{CH}_3)\textsubscript{3}\text{SiSi(\(\text{CH}_3\))}_2\text{Cl} + \text{Cl(\(\text{CH}_3\))}_2\text{SiSi(\(\text{CH}_3\))}_2\text{Cl} \rightarrow \text{CH}_3[(\text{CH}_3)\textsubscript{2}\text{Si}]_n\text{CH}_3 \\
(\text{A}) \\
\quad n = 4, 6, 8, 10, 12
\]
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 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 methylpolysiloxanes\textsuperscript{13}. 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

$$\eta = A \exp\left(\frac{E_{vis}}{RT}\right)$$

while the latter values are those reported by Hurd\textsuperscript{14}. 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.
Figure 2. Viscosities of permethylated linear polysilanes and polysiloxanes at different temperatures [●, polysilanes; ○, polysiloxanes]

Figure 3. Relation between $E_{\text{rel}}$ 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$^8, 15$. 

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\[
(CH_3)_n Si_2 Cl_{6-n} + Cl_2 \xrightarrow{Cl_2 \text{u.v. light}} \xrightarrow{CH_3MgBr} ClCH_2(CH_3)_{n-1} Si_2 Cl_{6-n} \rightarrow (ClCH_2)(CH_3)_2 SiSi(CH_3)_3
\]

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.

(Cloromethyl)pentamethyldisilane undergoes three different types of nucleophilic reactions, depending upon the nature of the reagent used\(^\text{16}\). 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.

\[
(\text{ClCH}_2)(\text{CH}_3)_2 \text{SiSi(CH}_3)_3 + Y^- \xrightarrow{Y=I, C}_6 \text{H}_5 \text{S, C}_6 \text{H}_5 \text{S, (C}_2 \text{H}_5)_2 \text{N, C}_6 \text{H}_5 \text{NH}\]

\[
\rightarrow (\text{YCH}_2)(\text{CH}_3)_2 \text{SiSi(CH}_3)_3 + \text{Cl}^- \quad \text{Y}=\text{RO; R=CH}_3, \text{C}_2 \text{H}_5, \text{i-C}_3 \text{H}_7, \text{C}_6 \text{H}_5
\]

\[
\rightarrow \text{RO}(\text{CH}_3)_2 \text{SiSi(CH}_3)_3 + \text{CH}_3 \text{CN} + \text{Cl}^- \quad \text{Y}=\text{CN}
\]

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

\[
(CH_3)_3 \text{SiSi(CH}_3)_2 \text{CH}_2 \text{Cl} + \text{CH}_3 \text{CO}_2^- \xrightarrow{\text{CH}_3 \text{CO}_2^-} (\text{CH}_3)_3 \text{SiSi(CH}_3)_2 \text{CH}_2 \text{O}_2^- \xrightarrow{\text{CH}_3 \text{CO}_2^-} \text{CH}_3 \text{CO}_2 \rightarrow \text{CH}_3 \text{CO}_2 \text{(CH}_3)_2 \text{SiCH}_3 \text{Si(CH}_3)_3
\]

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

\[
\text{BF}_3 \cdot \text{O}(\text{C}_2 \text{H}_5)_2 \rightarrow (\text{CH}_3)_3 \text{SiSi(CH}_3)_2 \text{CH}_2 \text{MgCl} \rightarrow \text{H}_2 \text{O}_2 \rightarrow [(\text{CH}_3)_3 \text{SiSi(CH}_3)_2 \text{CH}_2]_3 \text{B} \rightarrow \text{OH}^- \rightarrow (\text{CH}_3)_2 \text{CO}_2 \rightarrow (\text{CH}_3)_3 \text{SiSi(CH}_3)_2 \text{CH}_2 \text{OH} \rightarrow (\text{CH}_3)_3 \text{SiSi(CH}_3)_2 \text{CH}_2 \text{O}_2 \text{CCH}_3
\]

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.

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$\text{(CH}_3\text{)}_3\text{SiSi(CH}_3\text{)}_2\text{Cl} + \text{ClCH}_2\text{OCH}_3 \xrightarrow{\text{Mg, THF}} \text{RO}^- \xrightarrow{\text{ROH}} \text{No reaction}$

$\xrightarrow{240^\circ} \text{No reaction}$

(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.

$\text{(CH}_3\text{)}_3\text{SiSi(CH}_3\text{)}_2\text{CH}_2\text{MgCl} + (\text{CN})_2 \xrightarrow{\text{C}_2\text{H}_5\text{OH}} \text{reflux} \xrightarrow{\text{C}_2\text{H}_5\text{OH}} \text{CN}^- \xrightarrow{\text{(CH}_3\text{)}_3\text{SiSi(CH}_3\text{)}_2\text{OC}_2\text{H}_5} + \text{CH}_3\text{CN}$

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

(Cloromethyl)pentamethyldisilane itself undergoes complete intramolecular rearrangement at $200^\circ$ within 8 h to give chloropentamethyldisilmethylene$^{17}$. Anhydrous aluminium chloride catalyzes the intramolecular rearrangement, making it proceed vigorously at or below room temperatures$^3$.

Table 2 lists the differences in the sum of bond energies between the rearrangement product SiCH$_2$SiX and the substitution product SiSiCH$_2$X. The relatively large difference in the sum of bond energies for X = OR

<table>
<thead>
<tr>
<th>X</th>
<th>Difference (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN</td>
<td>14-1</td>
</tr>
<tr>
<td>I</td>
<td>27-0</td>
</tr>
<tr>
<td>NR$_4$</td>
<td>28-0</td>
</tr>
<tr>
<td>SR</td>
<td>34-0</td>
</tr>
<tr>
<td>Cl</td>
<td>36-4</td>
</tr>
<tr>
<td>OR</td>
<td>49-1</td>
</tr>
</tbody>
</table>

Table 2. Differences in the sum of bond energies between SiCH$_2$SiX and SiSiCH$_2$X

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 yield\textsuperscript{15}. This reaction provides evidence for the structure of the disilane.

\[
\text{Cl}_2\text{CH} \text{CH}_2\text{SiSi(CH}_3\text{)}_3 \xrightarrow{\text{C}_2\text{H}_5\text{O}^- / \text{C}_2\text{H}_5\text{OH}} \text{C}_2\text{H}_5\text{O} \text{CH}_3\text{SiSi(CH}_3\text{)}_3 + \text{CH}_2\text{Cl}_2
\]

Interestingly, (dichloromethyl)pentamethyldisilane undergoes two successive and discrete intramolecular rearrangements with anhydrous aluminium chloride\textsuperscript{15}. 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.

\[
\begin{array}{cc}
\text{(CH}_3\text{)}_3\text{Si} & \text{Cl} \\
\text{CH}_3\text{Si} - \text{CHCl}_2 & \xrightarrow{\text{AlCl}_3 / 70-80^\circ} \text{CH}_3\text{Si} - \text{CHSi} - \text{CH}_3 \\
& \text{CH}_3 \\
& \text{Cl} \\
& \text{Cl} \\
& \xrightarrow{\text{AlCl}_3 / 140-50^\circ} \text{CH}_3\text{Si} - \text{CHSi} - \text{CH}_3 \\
& \text{CH}_3 \\
& \text{CH}_3 \\
& \text{CH}_3
\end{array}
\]

Thermal rearrangement of (dichloromethyl)pentamethyldisilane is effected by heating at 200\degree for 8 h to give (trimethylsilyl)(chlorodimethylsilyl)-chloromethane as a single product\textsuperscript{17}.

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(CH\textsubscript{3})\textsubscript{2}Si grouping as a framework of the molecule in good yields\textsuperscript{18}.

\[
\begin{array}{cc}
\text{CH}_3 & \text{CH}_3 \\
\text{CH}_2=\text{C} - \text{Si} - \text{Si} - \text{CH}_3 & \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_3 - \text{Si} - \text{C} - \text{Si} - \text{F} \\
\text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\
\text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\
\text{NH}_4\text{F-HF} & \text{NH}_4\text{F-HF} & \text{NH}_4\text{F-HF}
\end{array}
\]
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 hexamethylidisilane\(^1\), which produces pentamethyldisilimethylene together with a small amount of trimethylsilane when passed in quartz tube heated to 600\(^\circ\).

\[
\text{(CH}_3\text{)}_3\text{SiSi(\text{CH}_3)_3} \xrightarrow{600^\circ} \text{(CH}_3\text{)}_3\text{SiCH}_2\text{Si(\text{CH}_3)_2H} + \text{(CH}_3\text{)}_3\text{SiH}
\]

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

\[
\text{(CH}_3\text{)}_3\text{SiSi(\text{CH}_3)_3} \xrightarrow{600^\circ} 2(\text{CH}_3\text{)}_3\text{Si}.
\]

\[
(\text{CH}_3\text{)}_3\text{Si} + (\text{CH}_3\text{)}_3\text{SiSi(\text{CH}_3)_3} \rightarrow (\text{CH}_3\text{)}_3\text{SiH} + (\text{CH}_3\text{)}_3\text{SiSi(\text{CH}_3)_2CH}_2\cdot
\]

\[
(\text{CH}_3\text{)}_3\text{SiSi(\text{CH}_3)_2CH}_2\cdot \rightarrow (\text{CH}_3\text{)}_3\text{SiCH}_{2}\text{Si(\text{CH}_3)_2}\cdot
\]

\[
(\text{CH}_3\text{)}_3\text{SiCH}_{2}\text{Si(\text{CH}_3)_2}\cdot + (\text{CH}_3\text{)}_3\text{SiSi(\text{CH}_3)_3} \rightarrow (\text{CH}_3\text{)}_3\text{SiCH}_{2}\text{Si(\text{CH}_3)_2H} + (\text{CH}_3\text{)}_3\text{SiSi(\text{CH}_3)_2CH}_2\cdot
\]

In connection with intramolecular rearrangement by free radical mechanisms, it was of interest to know whether the addition of bromotrichloromethane to vinylpentamethylsilane in the presence of peroxide will be accompanied by intramolecular rearrangement or not. Experiments showed
that only normal addition occurs to give γ, γ-trichloro-γ-bromopropylpentamethyldisilane in 85 per cent yield\(^2\).

\[(\text{CH}_3)_3\text{SiSi(CH}_3)_2\text{CH} = \text{CH}_2 + \text{BrCCl}_3 \xrightarrow{85^\circ} \frac{(\text{C}_6\text{H}_5\text{COO})_2}{\text{(CH}_3)_3\text{SiSi(CH}_3)_2\text{CHBrCH}_2\text{CCl}_3}\]

This result is analogous to that reported by Nesmeyanov and co-workers\(^2\) for the addition of bromotrichloromethane to compounds \(R(\text{C}_6\text{H}_5)_2\text{ECH} = \text{CH}_2\), where \(R = \text{C}_6\text{H}_5\), \(\text{CH}_3\) and \(E = \text{Sn}, \text{Si}, \text{C}\).

**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:

\[
\text{Si—Si} + \text{X—Y} \rightarrow \text{Si—X} + \text{Y—Si} \\
\text{X} \quad \text{Y} \\
\text{C}=\text{C} + \text{X—Y} \rightarrow \text{C—C}
\]

Hexaalkyldisilanes and alkylchlorodisilanes of lower chlorine content are cleaved by halogens\(^2\)\(^2\). 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 \(\text{Cl}_2 > \text{Br}_2 > \text{I}_2\). A study of kinetics of the cleavage of several alkylsilanes by iodine and by bromine indicates that the reaction is of the first order both in disilane and iodine (or bromine)\(^2\)\(^3\). 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>
<thead>
<tr>
<th>Compound</th>
<th>Halogen</th>
<th>(k_b(30^\circ) \times 10^4) (1/mole sec)</th>
<th>(E_{exp}) (kcal/mole)</th>
<th>(\Delta S^\ddagger(30^\circ)) (e.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{CH}_3)_3\text{SiSi(CH}_3)_3)</td>
<td>(\text{I}_2)</td>
<td>6.35</td>
<td>10.5 ± 0.8</td>
<td>−39 ± 3</td>
</tr>
<tr>
<td>((\text{C}_6\text{H}_5)_2\text{CH}_2\text{SiSiCH}_3(\text{CH}_3)_2)</td>
<td>(\text{I}_2)</td>
<td>4.93</td>
<td>11.7 ± 0.5</td>
<td>−35 ± 2</td>
</tr>
<tr>
<td>((\mu-\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{SiSi(CH}_3)_3)</td>
<td>(\text{I}_2)</td>
<td>6.93</td>
<td>7.9 ± 1.8</td>
<td>−47 ± 6</td>
</tr>
<tr>
<td>(\text{Cl}(\text{CH}_3)_2\text{SiSi(CH}_3)_3)</td>
<td>(\text{I}_2)</td>
<td>0.7</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>(\text{Cl}(\text{CH}_3)_3\text{SiSi(CH}_3)_2\text{Cl})</td>
<td>(\text{I}_2)</td>
<td>Very slow</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>((\text{C}_6\text{H}_5)_2\text{CH}_3\text{SiSiCH}_3(\text{CH}_3)_2)</td>
<td>(\text{Br}_2)</td>
<td>3880(25°)</td>
<td>5.2 ± 0.1</td>
<td>−43 ± 1</td>
</tr>
<tr>
<td>(\text{Cl}(\text{CH}_3)_2\text{SiSi(CH}_3)_3)</td>
<td>(\text{Br}_2)</td>
<td>970</td>
<td>9.2 ± 0.2</td>
<td>−33 ± 1</td>
</tr>
<tr>
<td>(\text{Cl}(\text{CH}_3)_3\text{SiSi(CH}_3)_2\text{Cl})</td>
<td>(\text{Br}_2)</td>
<td>59</td>
<td>11.9 ± 0.2</td>
<td>−29 ± 1</td>
</tr>
</tbody>
</table>

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 study\(^8\).

\[
\text{Br}_2 \quad \text{CH}_3[\text{(CH}_3)_2\text{Si}]_n\text{CH}_3 \rightarrow 2\text{(CH}_3)_2\text{SiBr} + \text{Br}(\text{CH}_3)_2\text{SiSi(CH}_3)_2\text{Br}
\]

N-Bromosuccinimide attacks hexamethyldisilane with the formation of trimethylbromosilane and N-(trimethylsilyl)succinimide\(^{24}\).

\[
\begin{align*}
\text{CO–CH}_2 & \quad \text{CHCl}_3 \\
(\text{CH}_3)_3\text{SiSi(CH}_3)_3 + \text{BrN} & \quad \rightarrow (\text{CH}_3)_3\text{SiBr} \\
\text{CO–CH}_2 & \\
\text{CO–CH}_2 & \quad + (\text{CH}_3)_3\text{SiN}
\end{align*}
\]

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 difluoroocymethyltetrasilanes (in nearly the equimolar ratio)\(^{25}\).

\[
\text{CH}_3[\text{(CH}_3)_2\text{Si}]_4\text{CH}_3 \underset{\text{H}_2\text{SO}_4}{\text{NH}_4\text{F-HF}} \rightarrow (\text{CH}_3)_3\text{SiF}
\]

\[
\begin{align*}
\text{F(}\text{CH}_3)_2\text{SiSi(} \times \text{CH}_3)_2\text{F}, \\
\text{F(}\text{CH}_3)_2\text{SiSi(} \times \text{CH}_3)_2\text{Si(} \times \text{CH}_3)_2\text{F}, \\
\text{F[}(\text{CH}_3)_2\text{Si}]_4\text{F}, \\
\text{F(}\text{CH}_3)_2\text{SiSi(} \times \text{CH}_3)_2\text{Si(}\times \text{CH}_3)_3(\times \text{F})\text{Si(} \times \text{CH}_3)_3
\end{align*}
\]

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.

\[
(\text{CH}_3)_2\text{Si} \quad \text{Si(} \times \text{CH}_3)_2 \underset{\text{H}_2\text{SO}_4}{\text{NH}_4\text{F-HF}} \quad \text{F(} \times \text{CH}_3)_2\text{SiSi(} \times \text{CH}_3)_n\text{Si(} \times \text{CH}_3)_2\text{F}
\]

\[
\begin{align*}
\text{F(} \times \text{CH}_3)_2\text{SiSi(} \times \text{CH}_3)_n\text{Si(} \times \text{CH}_3)_2\text{F} \\
n = 3,4
\end{align*}
\]

The reaction with 1,2-disilacycloheptane, however, proceeds in a lesser degree of cleavage of the silicon–silicon bond, giving the expected fluorode-
methylation product in about 20 per cent yields as well as a few ring-opening products.

\[
\begin{align*}
(\text{CH}_3)_2\text{Si} & \xrightarrow{\text{H}_2\text{SO}_4, \text{NH}_4\text{F-HF}} \text{Si(\text{CH}_3)_2} \\
| & (\text{CH}_2)_6 \\
(i) \quad \text{F(\text{CH}_3)Si} & \xrightarrow{} \text{Si(\text{CH}_3)F} \\
| & (\text{CH}_2)_6 \\
(ii) \quad \text{F(\text{CH}_3)_2SiSi(\text{CH}_3)_2F} & (21\%) \\
(iii) \quad \text{F(\text{CH}_3)_2Si(\text{CH}_2)_5Si(\text{CH}_3)_2F} & (24\%) \\
(iv) \quad \text{F(\text{CH}_3)_2SiSi(\text{CH}_3)(n-C_6\text{H}_{11})F} & (16\%) \\
\end{align*}
\]

1,2-Dimethyl-1,2-bis(tetramethylene)disilane, in which the silicon–silicon linkage does not participate in the construction of the ring, undergoes almost exclusively ring-opening, but only slight cleavage of the silicon–silicon bond by sulphuric acid.\(^{26}\)

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_2-\text{CH}_2 & \quad \text{CH}_2-\text{CH}_2 \\
| & \quad | \\
\text{Si} & \quad \text{Si} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_2-\text{CH}_2 & \quad \text{CH}_2-\text{CH}_2 \\
| & \quad | \\
\text{Si} & \quad \text{Si} \\
\text{n-C}_4\text{H}_9 & \quad \text{n-C}_4\text{H}_9 \\
\text{F} & \quad \text{F} \\
(95\% \text{ yield}) \\
\end{align*}
\]

All the disilanes and polysilanes mentioned above are quite stable to the cleavage of the silicon–silicon bond by hydrogen chloride under moderate conditions. Only at higher temperatures, some of them undergo the cleavage.\(^{27}\) Thus, hexamethylsilisilane is cleaved by an equimolar amount of dry hydrogen chloride to give a 1 : 1 mixture of trimethylsilane and trimethylchlorosilane in 15 per cent yield at 350\(^{\circ}\), but 54 per cent yield at 450\(^{\circ}\).

\[
(\text{CH}_3)_3\text{SiSi(\text{CH}_3)_3} + \text{HCl} \rightarrow (\text{CH}_3)_3\text{SiCl} + (\text{CH}_3)_3\text{SiH}
\]

Chloropentamethylsilisilane is much more resistant to the cleavage, and did not undergo appreciable change when passed together with hydrogen chloride through a tube heated to 450\(^{\circ}\). At 500\(^{\circ}\), however, its cleavage occurred with the formation of dimethylchlorosilane (36 per cent yield) and trimethylchlorosilane (53 per cent yield).

\[
(\text{CH}_3)_3\text{SiSi(\text{CH}_3)_2Cl} + \text{HCl} \rightarrow (\text{CH}_3)_3\text{SiCl} + (\text{CH}_3)_2\text{SiHCl}
\]

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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 chloride\(^{28}\). Thus, \(1,1'\)-bis(pentamethyldisilanylferrrocene is cleaved to give two compounds, ferrocene and \(1,3-(1,1'\)-ferrocenylenetetramethyl-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 formation of the ferrocenylendisiloxane, i.e. the selective cleavage of the silicon–silicon bond. If the bis-disilanyferrocene is allowed to stand in \(10^{-3}\) M-hydrochloric acid-ethanol solution at room temperatures for two days, the ferrocenylendisiloxane is obtained in substantially the theoretical yield.

\[
\text{Fe} \quad \text{Si(CH}_3\text{)}_2 \cdot \text{Si(CH}_3\text{)_3} \\
\text{Si(CH}_3\text{)_2} \cdot \text{Si(CH}_3\text{)_3} \quad \xrightarrow{\text{ROH, } H^+} \\
\text{Fe} \quad \text{Si(CH}_3\text{)}_2 \\
\text{Si(CH}_3\text{)_2} \\
\text{Si(CH}_3\text{)}_2 \\
\text{Fe}
\]

1,2-(\(1,1'\)-Ferrocenylenetetramethyl-disilane seems to be more sensitive to acid-catalyzed cleavage, and gives the same two compounds as above under similar conditions\(^{29}\).

\[
\text{Fe} \quad \text{Si(CH}_3\text{)}_2 \\
\text{Si(CH}_3\text{)}_2
\]

Pentamethyldisilanylferrocene and \(1,1'\)-bis(heptamethyltrisilylferrrocene also undergo a similar type of cleavage to that mentioned above under the same conditions. From the reaction with pentamethyldisilanylferrocene in
ethanol we were able to detect ferrocene, ethoxydimethylsilylferrocene, trimethylthioxysilane and hexamethyldisiloxane by gas chromatography.

\[
\begin{align*}
\text{Si(CH}_3\text{)}_2\cdot\text{Si(CH}_3\text{)}_3 &\xrightarrow{\text{H}^+_{\text{C}_2\text{H}_5\text{OH}}} \text{Si(CH}_3\text{)}_2\cdot\text{Si(CH}_3\text{)}_2\cdot\text{Si(CH}_3\text{)}_2\cdot\text{Si(CH}_3\text{)}_3 \\
\text{Fe} &\quad \text{Fe} &\quad \text{Fe} \\
\end{align*}
\]

\[+ (\text{C}_2\text{H}_5\text{)}_3\text{SiOC}_2\text{H}_5 + (\text{CH}_3\text{)}_3\text{SiOSi(CH}_3\text{)}_3\]

1,1'-Bis(heptamethyltrisilyl)ferrocene gave 1,3-(1,1'-ferrocenylenetetramethyl)disiloxane, ethoxypentamethyldisiloxane and diethyl ether.

\[
\begin{align*}
\text{Si(CH}_3\text{)}_2\cdot\text{Si(CH}_3\text{)}_2\cdot\text{Si(CH}_3\text{)}_2\cdot\text{Si(CH}_3\text{)}_3 &\xrightarrow{\text{H}^+_{\text{C}_2\text{H}_5\text{OH}}} \\
\text{Fe} &\quad \text{Fe} &\quad \text{Fe} \\
\end{align*}
\]

\[+ (\text{CH}_3\text{)}_2\text{SiSi(CH}_3\text{)}_2\cdot\text{OC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OC}_2\text{H}_5\]

These ferrocenes containing the silicon–silicon bond are very stable to the action of basic reagents. For example, 1,1'-bis(pentamethyldisilanylferrrocene gave no appreciable reaction when refluxed with 0.012–0.14 M sodium methoxide in methanol for several hours. Cyclopentadienylpentamethyldisiloxane 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 case 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.

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\[
\text{ROH} \quad \text{Si(CH}_2\text{OR)}_2 \quad \text{Fe} \\
+ \text{ROSi(CH}_3\text{)}_2\text{R} + \text{H}_2
\]

\( R = \text{CH}_3, \ (\text{CH}_3)\text{Si} \) \\
\( R = \text{CH}_3, \ \text{C}_2\text{H}_5 \)

Stabilization of carbonium ions adjacent to a ferrocenyl group in a similar way has been proposed by Richard and Hill\textsuperscript{30}, and supported by many other authors\textsuperscript{31}:

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 bond\textsuperscript{32}:

\[
\text{R(}\text{CH}_3\text{)}_2\text{SiSi(}\text{CH}_3\text{)}_3 + \text{C}_6\text{H}_5\text{CO}_3\text{H} \rightarrow \\
\text{R(}\text{CH}_3\text{)}_2\text{SiOSi(}\text{CH}_3\text{)}_3 + \text{C}_6\text{H}_5\text{CO}_2\text{H}
\]

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 \( \sigma^+ \) for the reaction of phenylpentamethyldisilane with perbenzoic acid in benzene at 45-0°](image-url)
MAKOTO KUMADA

constants against values of $\sigma^+$ of Brown and Okamoto$^{33}$ 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 $p_s-d_s$ 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

<table>
<thead>
<tr>
<th>Disilane</th>
<th>$k_2 \times 10^4 (45^\circ)$ (1/mole sec)</th>
<th>$\Delta H^\ddagger$ (kcal/mole)</th>
<th>$-\Delta S^\ddagger$ (e.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH$_3$)$_2$SiSi(CH$_3$)$_3$</td>
<td>11.7</td>
<td>13.7</td>
<td>27.8</td>
</tr>
<tr>
<td>p-CH$_3$OC$_6$H$_5$Si(CH$_3$)$_2$Si(CH$_3$)$_3$</td>
<td>11.9</td>
<td>14.2</td>
<td>27.4</td>
</tr>
<tr>
<td>p-CH$_3$Cy$_2$Si(CH$_3$)$_2$Si(CH$_3$)$_3$</td>
<td>8.79</td>
<td>14.0</td>
<td>28.7</td>
</tr>
<tr>
<td>m-CH$_3$Cy$_2$Si(CH$_3$)$_2$Si(CH$_3$)$_3$</td>
<td>7.44</td>
<td>13.8</td>
<td>29.6</td>
</tr>
<tr>
<td>Cy$_2$Si(Si(CH$_3$)$_2$Si(CH$_3$)$_3$</td>
<td>6.93</td>
<td>13.4</td>
<td>31.1</td>
</tr>
<tr>
<td>p-ClCy$_2$Si(Si(CH$_3$)$_2$Si(CH$_3$)$_3$</td>
<td>6.46</td>
<td>13.2</td>
<td>31.6</td>
</tr>
<tr>
<td>m-ClCy$_2$Si(Si(CH$_3$)$_2$Si(CH$_3$)$_3$</td>
<td>6.55</td>
<td>14.2</td>
<td>29.6</td>
</tr>
<tr>
<td>Cy$_2$Si(CH$_3$)$_2$Si(CH$_3$)$_2$CyH$_5$</td>
<td>3.89</td>
<td>17.7</td>
<td>18.6</td>
</tr>
</tbody>
</table>

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 ethylenes.$^{34}$

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 peracid.$^{35}$ (Analogous molecular mechanism involving electrophilic attack by a cyclic hydrogen-bonded form of peracid was first suggested by P. D. Bartlett.$^{35}$)

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 Prince$^{36}$ first observed that hexaphenylsiladisilane 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, Cy$_2$H$_5$[Si(CH$_3$)$_2$]$\_n$Cy$_2$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 studied$^{38}$ 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. Hexamethyl-disilane, 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 \(p_\pi\)–\(d_\pi\) 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

<table>
<thead>
<tr>
<th>Polysilane</th>
<th>(\lambda_{\text{max}}) (m(\mu))</th>
<th>(\epsilon_{\text{max}} \times 10^{-4})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}_x\text{H}_y\text{Si}(\text{CH}_3)_3)</td>
<td>231-0</td>
<td>1-09</td>
</tr>
<tr>
<td>(\text{C}_x\text{H}_y\text{Si}(\text{CH}_3)_2\text{Si}(\text{CH}_3)_2)</td>
<td>238-0</td>
<td>1-85</td>
</tr>
<tr>
<td>(\text{C}_x\text{H}_y\text{Si}(\text{CH}_3)_2\text{Si}(\text{CH}_3)_2)</td>
<td>240-0</td>
<td>2-59</td>
</tr>
<tr>
<td>(\text{C}_x\text{H}_y\text{Si}(\text{CH}_3)_2\text{Si}(\text{CH}_3)_2)</td>
<td>223-5</td>
<td>0-52</td>
</tr>
<tr>
<td>(\text{C}_x\text{H}_y\text{Si}(\text{CH}_3)_2\text{Si}(\text{CH}_3)_2)</td>
<td>227-5</td>
<td>0-97</td>
</tr>
<tr>
<td>(\text{C}_x\text{H}_y\text{Si}(\text{CH}_3)_2\text{Si}(\text{CH}_3)_2)</td>
<td>221-3</td>
<td>1-30</td>
</tr>
<tr>
<td>(\text{C}_x\text{H}_y\text{Si}(\text{CH}_3)_2\text{Si}(\text{CH}_3)_2)</td>
<td>243-0</td>
<td>1-3</td>
</tr>
</tbody>
</table>

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

![Diagram of 1,2-diphenyltetramethyldisilanes]

<table>
<thead>
<tr>
<th>Substituents</th>
<th>(\lambda_{\text{max}}) (m(\mu))</th>
<th>(\epsilon_{\text{max}} \times 10^{-4})</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>238-0</td>
<td>1-85</td>
</tr>
<tr>
<td>(p)-CH(_3)</td>
<td>238-5</td>
<td>2-11</td>
</tr>
<tr>
<td>(p)-CH(_3)</td>
<td>239-0</td>
<td>2-49</td>
</tr>
<tr>
<td>(p)-CH(_3)</td>
<td>242-0</td>
<td>3-26</td>
</tr>
<tr>
<td>(p)-CH(_3)</td>
<td>241-0</td>
<td>2-58</td>
</tr>
<tr>
<td>(p)-CH(_3)</td>
<td>241-5</td>
<td>2-82</td>
</tr>
<tr>
<td>(p)-Cl</td>
<td>242-5</td>
<td>2-80</td>
</tr>
<tr>
<td>(p)-Cl</td>
<td>244-5</td>
<td>2-46</td>
</tr>
</tbody>
</table>

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)tetramethylsilanes (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](image)

**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; stereochernistry 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-Shibaura Electric Co. Ltd., and Nitto Electric Industrial Co. Ltd.
References