# CARBOSILANES

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## I. Introduction

By carbosilanes we mean compounds with alternate carbon and silicon atoms in the molecule; these may be linear (e.g., $Cl_3Si{\cdot}CH_2{\cdot}SiCl_2{\cdot}CH_2{\cdot}SiCl_3$) or cyclic [e.g., $(SiCl_2{\cdot}CH_2)_3$], the latter being termed cyclocarbosilanes (*23*). Compounds which consist mainly of carbon atoms, between which a silicon atom is inserted as a "hetero-atom," are thus excluded from consideration here. So, too, are polymeric carbosilanes, which have recently been reviewed elsewhere (*59a*).

Carbon and silicon differ in atomic structure in that silicon has an empty 3*d* level available, and may attain a coordination number of six in its compounds; this is not possible for carbon. The electronegativities of the two elements are quite different (Si, 1.8; C, 2.5) and this gives rise to the polarity of the Si—C bond, and to the different character of compounds of the elements with the same atoms or groups (e.g., halogens, hydrogen). Bonds to hydrogen have polarity Si$^{(+)}$—H$^{(-)}$ but C$^{(-)}$—H$^{(+)}$. Generally speaking, polar character is greater in silicon compounds than in the corresponding carbon compounds (e.g., ⩾Si—Cl, ⩾C—Cl), and this, together with the difference in atomic and ionic radii (Si, 1.17; Si$^{4+}$, 0.41; C, 0.77; C$^{4+}$, 0.15 Å), is important in influencing chemical behavior. Bond energies in silicon and carbon compounds are notably different: Si—Si, 53; C—C, 83; Si—H, 75; C—H, 99; Si—Cl, 91; C—Cl, 81; Si—O, 108; C—O, 85 kcal/mole (*11*).

The Si—C bond is normally unreactive; its polarity is about 12% in the sense $Si^{(+)}$—$C^{(-)}$, and this opens up the possibility of influencing the reactivity of the bond by suitable substituents. Thus the Si—C bond in $Si(CH_3)_4$ is not cleaved in a definite way by alkali, whereas that in $(CH_3)Cl_2Si—CHCl_2$ is split quantitatively by 0.1 *N* NaOH with formation of 1 mole of $CH_2Cl_2$. The groupings Si-halogen, Si—OR, and Si—H are known as silicon functional groups, analogous to the functional groups in organic chemistry (*24*).

## II. Formation of Carbosilanes

### A. GAS PHASE PYROCHEMICAL SYNTHESIS

#### *1. By Thermal Decomposition of* $Si(CH_3)_4$

Studies of the reactions between $SiH_4$ and $C_2H_4$ (*25, 38*) or $SiH_4$ and $PH_3$ (*26, 27*) have shown that changes occur above the temperature required to break the Si—H bond, that are initiated by H atoms and silyl radicals and lead to compounds containing silicon and carbon or silicon and phosphorus. The reaction products may be isolated if they are removed sufficiently rapidly from the reaction zone and cooled. Thermal decomposition of compounds containing the Si—H bond may be detected quite readily in the gas phase reaction at about 400°C. The Si—C bond in simple alkyl silanes possesses a substantially greater thermal stability: decomposition of $Si(CH_3)_4$ and $Si(C_2H_5)_4$, for example, occurs above 650°C (*58*). If the experimental conditions are such that the alkyl silane is exposed to temperatures around 700°C for periods of hours, decomposition of the starting material is practically complete. Silicon, carbon, and silicon carbide are deposited, the gaseous products consisting of $H_2$ and a mixture of lower hydrocarbons in which $CH_4$ predominates. If, however, the pyrolysis mixture is removed rapidly from the hot zone and cooled, it is found that the radicals produced in the primary stages of the reaction undergo a series of subsequent reactions leading to compounds with molecular weights considerably greater than that of the starting material (*28*). $Si(CH_3)_4$ under such conditions gives mainly compounds containing the Si—C—Si skeleton, the molecular weight depending on the decomposition temperature and residence time. Higher temperatures and longer reaction times result in compounds of increasing molecular complexity, and insoluble solid deposits are formed (*29*) (Table I).

TABLE I

YIELDS OF HIGH-BOILING SILICON COMPOUNDS FROM $Si(CH_3)_4$ AT 720°C WITH VARIOUS RESIDENCE TIMES[a]

| No. | Residence time (min) | Product (b.p. 90°–180°C 760 mm Hg) (ml) | (vol%) | Product (b.p. 120°–180°C 100 mm Hg) (ml) | (vol%) | Product (b.p. 90°–300°C 1 mm Hg) (ml) | (vol%) | Product (insoluble solids) (ml) | (vol%) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 3 | 8 | 20.5 | 10.7 | 27 | 6 | 15.4 | 14.5 | 37.2 |
| 2 | 2 | 12.2 | 23.3 | 7.7 | 14.8 | 21.9 | 42 | 10.5 | 20.2 |
| 3[b] | 1 | 38.9 | 15.6 | 27.4 | 11 | 143.6 | 57 | 40 | 16 |

[a] Note that reduction in the residence time from 3 to 2 minutes increases the proportion of high-boiling (90°–300°C) products, and insoluble (yellow) solids are formed in smaller amounts.

[b] Experiment made with streaming gases.

*a. Study of the Pyrolysis of* $Si(CH_3)_4$. The apparatus shown in Fig. 1 is suitable for preparing useful quantities of pyrolysis products from $Si(CH_3)_4$. The furnace is heated to 720°C, this temperature being maintained constant to within ±5°C by a regulator. The reaction vessel *R* is a Rotosil tube (12-cm diameter, 80 cm long) and the vessel *K* contains $Si(CH_3)_4$ (b.p. 26°C). The circulating pump *P* draws $Si(CH_3)_4$ vapor through the previously evacuated apparatus in the direction of the arrow at a rate controlled to give a residence time in the heated zone of about 1 minute. Shortly after the reaction begins, white fumes appear at the exit

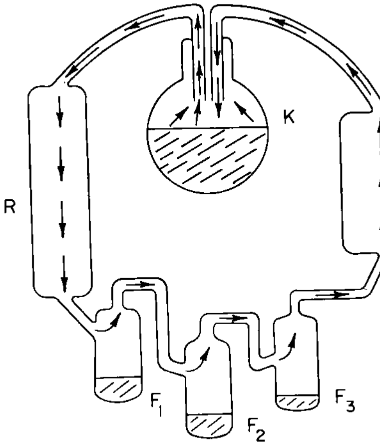


FIG. 1. Diagram of the apparatus used for pyrolysis.

of the tube and condense at room temperature in the receivers and connecting tubes. Later, molten yellow products run out of the tube and well-formed crystals separate on the glass walls below the furnace. Since the vapor pressure of $Si(CH_3)_4$ at 20°C is about 720 mm, excess pressure builds up in the apparatus after 2–3 hours. A mercury vent, which can also serve as a manometer, enables the pressure to be balanced. Since the pressure of $Si(CH_3)_4$ in the system remains constant as long as liquid $Si(CH_3)_4$ is present in *K*, steady conditions are very quickly established throughout the apparatus. A mixture of $Si(CH_3)_4$ and the higher boiling products, together with smaller quantities of $H_2$, $CH_4$, $C_2H_6$, $C_2H_4$, and alkyl silanes containing Si—H bonds, passes through, the proportions being dependent on the vapor pressures of the various liquids present in the system. The volatile materials which escape as the vent excess pressure builds up contain small amounts of $H_2$, lower hydrocarbons, and $Si(CH_3)_4$. The latter is condensed in cooled receivers and recovered, over-all losses of $Si(CH_3)_4$ being small. Deposition of elementary silicon is largely avoided under the conditions described.

*b. Pyrolysis Products from* $Si(CH_3)_4$. Table II shows the results of a distillation separation (rectification) of the total products of pyrolysis, with data indicating the percentage in each fraction.

Gas chromatographic studies (*30*) have shown fractions II to XXII to contain 45 different compounds, which separately make up between 0.001 and 10% of the total product. Only 12 of these substances are present in excess of 1% of the reaction mixture: 9 are between 0.5 and 1%, 11 between 0.5 and 0.1%, and 13 are below 0.1%. These 45 compounds (1590 ml) represent 52.9% of the total, 47.1% being made up of higher silicon compounds. The liquid fractions contain lower hydrocarbons up to hexane, but the actual percentage is very small. Benzene (0.9%) is in fact the most abundant liquid hydrocarbon. All higher fractions contain compounds of increasing molecular weight with several Si atoms. The mixture of gases produced during the pyrolysis contains the following compounds in the ratio shown:

$$H_2:CH_4:C_2H_4:C_2H_6:C_3H_6:C_3H_8 + SiH_4 + (CH_3)_2SiH_2:(CH_3)_3SiH$$
$$= 1:0.8:0.04:0.04:0.04:0.02:0.06$$

The more abundant products have been identified and their structures are shown in Table III (*24*). The analytical data and chemical properties of compounds (7) to (13) are consistent with structures containing condensed six-membered rings with alternating Si and C atoms, as in the formula shown for $Si_7C_{18}H_{46}$ (compound 10). This formulation is supported by the chemical behavior of the SiH group and also by steric con-

TABLE II
THE DISTILLATION OF THE DECOMPOSITION PRODUCTS OF $Si(CH_3)_4$

| Fraction number | B.p. range (°C) | Pressure (mm Hg) | Volume | | Properties |
|---|---|---|---|---|---|
| | | | (ml) | (%) | |
| II | 54–79.5 | 756 | 15 | 0.89 | Colorless liquid |
| III | 79.9 | 756 | 2 | 0.12 | Colorless liquid |
| IV | 79.5–119 | 756 | 40 | 2.4 | Colorless liquid |
| V | 119.2–119.9 | 756 | 20 | 1.18 | Colorless liquid |
| VI | 119.9–120.2 | 756 | 15 | 0.9 | Colorless liquid |
| VII | 120.3–132.6 | 756 | 90 | 5.32 | Colorless liquid |
| VIII | 132.7–133.0 | 756 | 35 | 2.1 | Colorless liquid |
| IX | 133.0–133.6 | 756 | 20 | 1.2 | Colorless liquid |
| X | 133.7–133.8 | 756 | 8 | 0.47 | Colorless liquid |
| XI | 133.8–164.0 | 756 | 50 | 2.96 | Colorless liquid |
| XII | 165.3–169.0 | 756 | 40 | 2.37 | Colorless liquid |
| XIII | 170.0–174.0 | 756 | 30 | 1.8 | Colorless liquid |
| XIV | 81–88 | 20 | 50 | 2.96 | Colorless liquid |
| XV | 88–92 | 20 | 50 | 2.96 | Colorless liquid |
| XVI | 92–98 | 20 | 50 | 2.96 | Colorless liquid |
| XVII | 98–111 | 20 | 50 | 2.96 | Colorless liquid |
| XVIII | 110–126 | 20 | 30 | 1.78 | Colorless liquid |
| XIX | 115–117 | 10 | 25 | 1.48 | Colorless liquid |
| XX | 70–72 | 1 (oil pump) | 30 | 1.78 | Colorless liquid |
| XXI | 72–73 | 1 (oil pump) | 43 | 2.54 | Colorless liquid |
| XXII | 100–110 | 2 | 160 | 9.47 | Colorless liquid |
| XXIII | 90–107 | 1 (oil pump) | 68 | 4.02 | Pale yellow, oily |
| XXIV | 87–*125* | 1 (oil pump) | 40 | 2.37 | Yellow, viscous |
| XXV | 130–*172* | 1 (oil pump) | 56 | 3.31 | Orange-yellow, viscous |
| XXVI | 178–*187* | Hg vac. | 44 | 2.6 | Orange-yellow, highly viscous |
| XXVII | 220–230 | Hg vac. | 68 | 4.0 | Orange solid |
| XXVIII | 270–280 | Hg vac. | 60 | 3.6 | Orange-red solid |
| Residue | | | 500 | 29.6 | Brown solid |

siderations concerning $Si_7C_{18}H_{30}Cl_{16}$, which is formed from it by photochlorination (*31*). In addition to the compounds listed in Table III, a number of cyclic carbosilanes, whose structures have not yet been fully elucidated, are formed in the pyrolysis.

Products with molecular weights between 515 and 800 change to substances of molecular weight about 2000 which are still soluble in benzene when they are heated subsequently (e.g., in the course of separation by distillation). When separate fractions are heated at 400°C for 30 hours, low molecular weight hydrocarbons tend to split off, leaving solid products of greater molecular complexity, some of which no longer dissolve in benzene

### TABLE III
### Compounds from the Pyrolysis of $Si(CH_3)_4$

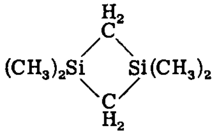
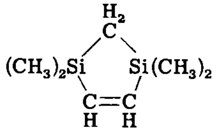
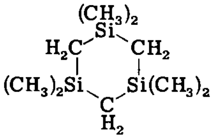
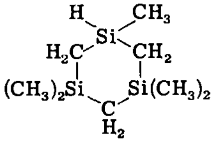
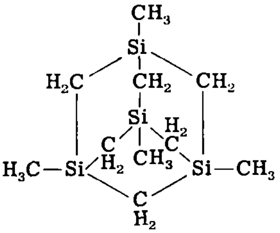
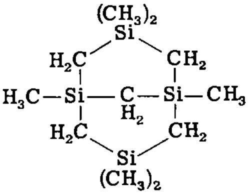
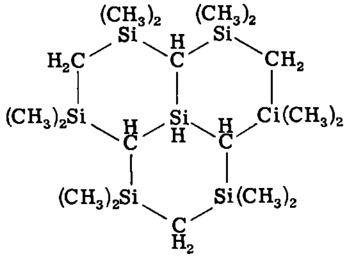
| | Compound | Vol % of product |
|---|---|---|
| 1. | $(CH_3)_3Si—CH_2—SiH(CH_3)_2$ | 2.4 |
| 2. |  | 3.2 |
| 3. | $(CH_3)_3Si—CH_2—Si(CH_3)_3$ | 6.9 |
| 4. |  (*54*) | 0.7 |
| 5. | $C_6H_5Si(CH_3)_3$ | 5.6 |
| 6. |  <br>and $[(CH_3)_3Si—CH_2]_2Si(CH_3)_2$ | 7.5 (together) |
| 7 |   | – |
| 8. | $Si_5C_{13}H_{34}$ (pale yellow oil) | – |
| 9. | $Si_6C_{14}H_{36}$ (yellow viscous oil) | – |

TABLE III (*Continued*)

| | | Compound | Volt% of product |
|---|---|---|---|
| 10. | $Si_7C_{18}H_{46}$ | <br>(yellow solid) | – |
| 11. | $Si_8C_{20}H_{50}$ | (yellow-brown solid) | – |
| 12. | $Si_8C_{24}H_{66}$ | (yellow-brown solid) | – |
| 13. | $Si_9C_{27}H_{74}$ | (red-brown solid) | – |

(*32*). Such compounds also separate in the course of the original pyrolysis experiments. Analysis gives a Si:C:H atomic ratio of about 1:2:3 and the substances contain the Si—C—Si grouping (*28*). Methods based on column and paper chromatography have been worked out for separating the high molecular weight pyrolysis products, which are distinguished by their strong fluorescence in ultraviolet light (*32*).

### 2. *By Thermal Decomposition of* $CH_3SiCl_3$, $(CH_3)_2SiCl_2$, *and* $(CH_3)_3SiCl$

Products formed by pyrolyzing $Si(CH_3)_4$, which are mostly Si-methyl carbosilanes, are not very reactive. In many investigations there is a need for compounds with the same basic structure but with more reactive groups attached to silicon (e.g., Si—Cl). Such compounds may be prepared by pyrolyzing the three methyl chlorosilanes (*24*). Thermal decomposition of these substances is sufficiently rapid at 700°C and a preparative study of the pyrolysis products can be made by the streaming method used for $Si(CH_3)_4$.

The separate methyl chlorosilanes behave similarly when they are decomposed thermally (*33*). As soon as decomposition begins, white vapors appear at the exit of the reaction tube as a result of suction by the circulating pump, and these condense in the receivers at room temperature. Gaseous products appear simultaneously, leading to a slow pressure rise in the apparatus. When the production of gases ($H_2$, $CH_4$) brings the pressure up to 1 atmosphere the decomposition proceeds less well, as is evident from the smaller amount of fume issuing from the reaction tube. After some days, colorless crystals and yellow and brown reaction products appear at the lower end of the reaction vessel. These melt in part when heated but also sublime to a certain extent. The molten material dissolves in the liquid products forming a yellowish red solution. The actual composition of the pyrolysis products depends on the experimental conditions. Table IV provides an example of the pyrolysis products of $(CH_3)_3SiCl$ separated by distillation.

TABLE IV

FRACTIONS ISOLATED FROM THE DECOMPOSITION PRODUCTS OF $(CH_3)_3SiCl$

| Compound | B.p. (°C) | Pressure (mm Hg) | Quantity (ml) | Vol% | Properties |
|---|---|---|---|---|---|
| 1 | 163–165 | 760 | 126 | 13.7 | Colorless liquid |
| 2 | 170–174 | 760 | 101 | 11.0 | Colorless liquid |
| 3 | 180–182 | 760 | 55 | 6.0 | Colorless liquid |
| 4 | 98–100 | 3 | 16 | 1.7 | (a) $\frac{2}{3}$ colorless, low viscosity<br>(b) $\frac{1}{3}$ colorless well-formed crystals |
| 5 | 97 | 1 | 5 | 0.5 | Colorless, low viscosity |
| 6 | 103–106 | 3 | 11 | 1.2 | (a) $\frac{1}{2}$ colorless, low viscosity<br>(b) $\frac{1}{2}$ well-formed white crystals |
| 7 | 106–110 | 3 | 6 | 0.7 | (a) $\frac{2}{3}$ colorless, low viscosity<br>(b) $\frac{1}{3}$ well-formed white crystals |
| 8 | 102–103 | 1 | 7 | 0.8 | Oily liquid with white crystals |
| 9 | 135 | 7 | 2–3 | 0.3 | Oily liquid with white crystals |
| 10 | 112 | 1 | 10 | 1.1 | Faintly yellow liquid with white crystals |
| 11 | 205–210 | 7 | 5 | 0.5 | Faintly yellow liquid with white crystals |
| 12 | 183 | Hg vac. | 11 | 1.2 | Yellow-green highly viscous oil with fine white crystals |
| 13 | 214 | Hg vac. | 11 | 1.2 | |
| 14 | 234 | Hg vac. | 11 | 1.2 | Deep yellow glassy solid |
| 15 | 278 | Hg vac. | 6 | 0.7 | Orange-yellow glassy solid |
| 16 | Residue | — | 190 | 20.6 | Brown, glassy, fusible, soluble |

Only the constant boiling fractions are given in Table IV. The values quoted for volume % are based on the total product (920 ml) (*33*). The residue from the distillation contained Si—Cl groups, was fusible, and was also soluble in organic solvents. Using 2.7 liters of $(CH_3)_3SiCl$, 920 ml of high-boiling and solid soluble compounds was obtained, 1.5 liters of methyl chlorosilanes (b.p. 55°–68°C) being recovered. The product contained 60 volume % (550 ml) of material of b.p. 163°–200°C at normal pressure and 40 volume % (370 ml) of oils and soluble solids. The total product was made up of 85% of colorless liquids and 15% of oils or solid, fusible, and colored substances.

All of the compounds formed in the pyrolysis of $(CH_3)_3SiCl$, $(CH_3)_2SiCl_2$, and $CH_3SiCl_3$ with boiling points up to about 250°C could be detected by gas chromatographic methods (*34*, *35*) and their relative amounts determined (*36*). The greatest number of compounds was produced from $(CH_3)_3SiCl$. Table V shows the carbosilanes obtained from the methyl chlorosilanes, with their structural formulas.

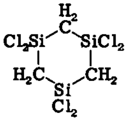
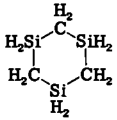
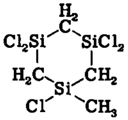
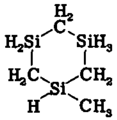
The structural formulas of compounds with two Si atoms (compounds 1–8) are based partly on the chemical properties and analytical data. The pairs of isomers (6 and 7, and 4 and 5) have closely similar chemical properties. Assignment of structure was achieved in these cases by dipole moment measurements using the principle that the dipole moment is smaller as the molecular symmetry increases (*36*).

Table V shows that all possible compounds with the basic structure —Si—$CH_2$—Si— which contain Cl and $CH_3$ groups have been isolated. In this table the relative quantities of 1,3-disilapropanes in the products from the three methyl chlorosilanes are compared, the quantity of $Cl_3Si—CH_2—SiCl_3$ being taken as 100 in each case. It will be seen that $(CH_3)_3SiCl$ forms $(CH_3)_3Si—CH_2—SiCl_3$, $Cl_3Si—CH_2—SiCl_3$, $(CH_3)_2ClSi—CH_2—SiCl_2(CH_3)$, $(CH_3)Cl_2Si—CH_2—SiCl_2(CH_3)$, and $(CH_3)_2ClSi—CH_2—SiCl(CH_3)_2$ preferentially whereas, for $(CH_3)_2SiCl_2$, the compounds $Cl_3Si—CH_2—SiCl_3$, $(CH_3)Cl_2Si—CH_2—SiCl_2(CH_3)$, and $(CH_3)_3Si—CH_2—SiCl_3$ are more abundant. The compound $Cl_3Si—CH_2—SiCl_3$ is the major product from $CH_3SiCl_3$. The proportion of 1,3-disilapropanes from the separate total pyrolysis products of the three compounds is: $(CH_3)_3SiCl$, 32%; $(CH_3)_2SiCl_2$, 43%; $CH_3SiCl_3$, 60%. Compounds containing the Si—H bond were also detected by infrared spectroscopy in the material from $(CH_3)_3SiCl$ which boiled in the range under discussion, but gas phase chromatography showed the proportion to be small.

Examination of higher molecular weight materials from the pyrolysis of the methyl chlorosilanes presupposes the separation of separate compounds from the mixture. Even with three Si atoms in the molecule, however, separation of the Si-chlorinated carbosilanes by distillation presents difficulties owing to the high boiling points. Gas chromatographic methods are also ruled out on the same grounds, although separation of single compounds is possible in especially favorable cases [e.g., for $(SiCl_2—CH_2)_3$ (*33*)]. Attempts were therefore made to replace the Cl atoms in SiCl groups by H by reaction with $LiAlH_4$. It was then possible to apply either distillation or gas chromatography to the lower boiling SiH compounds. The number of functional groups remained the same and this approach therefore

TABLE V

CARBOSILANES FROM THE PYROLYSIS OF $CH_3SiCl_3$, $(CH_3)_2SiCl_2$, AND $(CH_3)_3SiCl$; SiCl- AND DERIVED SiH-CONTAINING PRODUCTS[a]

| Compound number | SiCl compound in pyrolysis product | Derived SiH compound | B.p. (°C mm Hg) | Parts in hydrogenated mixture of [b] | | |
|---|---|---|---|---|---|---|
| | | | | $CH_3SiCl_3$ | $(CH_3)_2SiCl_2$ | $(CH_3)_3SiCl$ |
| 1 | $Cl_3Si-CH_2-SiCl_3$ | $H_3Si-CH_2-SiH_3$ | 17/757 | 100 | 100 | 100 |
| 2 | $(CH_3)_2SiCl-CH_2-SiCl_3$ | $(CH_3)_2SiH-CH_2-SiH_3$ | 70.5-71/768 | 2.5 | – | 0.8 |
| 3 | $(CH_3)_2ClSi-CH_2-SiCl_3$<br>$(CH_3)Cl_2Si-CH_2-SiCl_2(CH_3)$ | $(CH_3)_2HSi-CH_2-SiH_3$<br>$(CH_3)H_2Si-CH_2-SiH_2(CH_3)$(2:3) | –<br>71/768 | –<br>6.8 | –<br>33 | –<br>44.7 |
| 4 | $(CH_3)_3Si-CH_2-SiCl_3$ | $(CH_3)_3Si-CH_2-SiH_3$ | 91-92/768 | 0.5 | 23.7 | 141 |
| 5 | $(CH_3)_2ClSi-CH_2-SiCl_2(CH_3)$ | $(CH_3)_2HSi-CH_2-SiH_2(CH_3)$ | 88.5/768 | – | 10.7 | 71.4 |
| 6 | $(CH_3)_2ClSi-CH_2-SiCl(CH_3)_2$ | $(CH_3)_2HSi-CH_2-SiH(CH_3)_2$ | 107/768 | – | – | 41.9 |
| 7 | $(CH_3)_2ClSi-CH_2-SiCl(CH_3)_2$<br>$(CH_3)_3Si-CH_2-SiCl_2(CH_3)$ | $(CH_3)_2HSi-CH_2-SiH(CH_3)_2$<br>$(CH_3)_3Si-CH_2-SiH_2(CH_3)$(1:3) | –<br>103/768 | –<br>– | –<br>0.66 | –<br>13.9 |
| 8 | $(CH_3)_3Si-CH_2-SiCl(CH_3)_2$ | $(CH_3)_3Si-CH_2-SiH(CH_3)_2$ | 120/768 | – | – | 13.6 |
| 9 | $Cl_3Si-CH_2-SiCl_2-CH_2-SiCl_3$ | $H_3Si-CH_2-SiH_2-CH_2-SiH_3$ | 100/760 | 109 | 28 | 14 |
| 10 | $Cl_3Si-CH_2-SiCl_2-CH_2-SiCl_2(CH_3)$ | $H_3Si-CH_2-SiH_2-CH_2-SiH_2(CH_3)$ | 123/758 | 45 | – | 69 |
| 11 | $Cl_3Si-CH_2-SiCl_2-CH_2-SiCl(CH_3)_2$* | $H_3Si-CH_2-SiH_2-CH_2-SiH(CH_3)_2$*<br>$(CH_2)_3Si-CH_2-Si(CH_3)_3$ | 133/762<br>135/768 | –<br>– | –<br>– | 155<br>64 |
| 12 |  |  | 142/760 | 100 | 100 | 100 |
| 13 | $Cl_3Si-CH_2-SiCl_2-CH_2-Si(CH_3)_3$* | $H_3Si-CH_2-SiH_2-CH_2-Si(CH_3)_3$* | 154/756 | – | – | 69 |
| 14 |  |  | 159/766 | 25 | 50 | 960 |

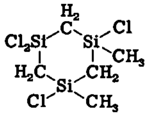
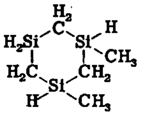
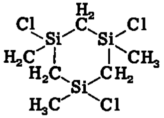
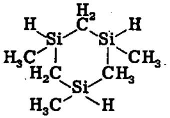
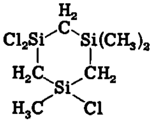
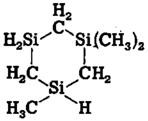
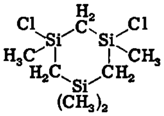
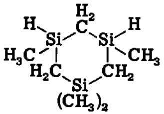
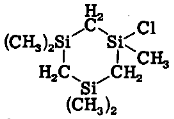
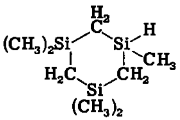
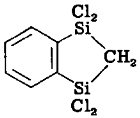
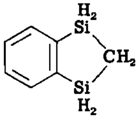
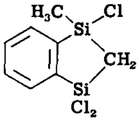
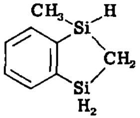
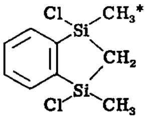
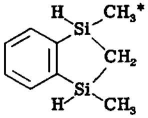
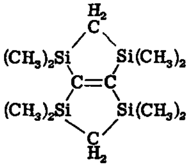
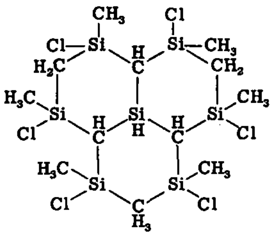
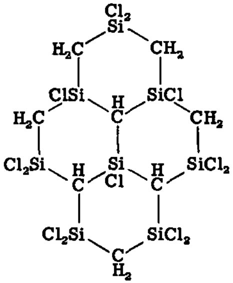
| | | | | | | |
|---|---|---|---|---|---|---|
| 15 |  |  | 166/764 | – | – | 1690 |
| 16 |  |  | 180/764 | – | – | 1000 |
| 17 |  |  | – | – | – | – |
| 18 |  |  | 190/764 | – | – | 168 |
| 19 |  |  | 201/767 | – | – | 65<br>(No. 11+12) |

TABLE V (*Continued*)

| Compound number | SiCl compound in pyrolysis product | Derived SiH compound | B.p. (°C mm Hg) | Parts in hydrogenated mixture of[b] | | |
|---|---|---|---|---|---|---|
| | | | | $CH_3SiCl_2$ | $(CH_3)_2SiCl_2$ | $(CH_3)_3SiCl$ |
| 20 |  |  | 204/746 | 4 | 9 | 65<br>(No. 11+12) |
| 21 |  |  | 210/767 | – | – | 59 |
| 22 |  |  | Not determined | – | – | 14 |
| 23 | SiCl - combining carbosilane with 4 Si atoms from $CH_3SiCl_3$<br>Methylation product → |  (46) | | | | |

| | | |
|---|---|---|
| 24 | $Si_4C_7H_{18}Cl_4$<br>$Si_4C_8H_{19}Cl_3$ | |
| 25 | $Si_7C_{12}H_{28}Cl_6$ |  |
| 26 | $Si_8C_8Cl_{16}H_{16}$ |  |

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[a] The asterisk indicates that isomeric composition is not yet estimated.

[b] Parts in hydrogenated mixture: compounds 1–8, relative to $(Cl_3Si)_2CH_2 = 100$, compounds 9–22, relative to $(SiCH_2—CH_2)_3 = 100$.

served the additional purpose of making available some hitherto little known carbosilanes with SiH groups (*37*).

Hydrogenation of SiCl-containing carbosilanes with $LiAlH_4$ proceeds without change in the Si—C—Si group. This is shown by work with Si-chlorinated 1,3-disilapropanes of known structures and with the crystalline cyclic trimer $(SiCl_2—CH_2)_3$. Table V shows the starting materials and the SiH-containing carbosilanes formed. The distribution of the SiCl groups in compounds 1–8 and 12 was determined before treatment with $LiAlH_4$ on the basis of dipole moment measurements. Subsequently the structural formulas of the SiH derivatives (Table V) were established by chemical analysis and by infrared, mass, and NMR spectrographic methods. NMR studies proved particularly useful for elucidation of structures of SiH compounds (*37*).

The investigation shows unambiguously that it is possible to deduce the structures of the original products containing SiCl groups from a study of the compounds formed on reduction with $LiAlH_4$. This principle was applied to higher boiling fractions of the pyrolysis products containing compounds with three Si atoms. The results are shown in Table V (compounds 9–22).

Comparison of the proportions of the various compounds in the hydrogenated pyrolysis mixture (Table V) shows that the tendency to form six-membered rings with alternating Si and C atoms increases with the number of Si—$CH_3$ groups in the starting material. The investigation of the higher pyrolysis products from the methyl chlorosilanes has not yet been completed, but it can be seen that the cyclic carbosilanes with SiCl groups which are produced are predominantly based on the same types of structure as are obtained from $Si(CH_3)_4$. The crystalline compounds with four Si atoms and variable numbers of SiCl and $SiCH_3$ groups produced from $(CH_3)_3SiCl$ and $(CH_3)_2SiCl_2$, for example, correspond in their basic structures with the adamantane-like structure of compound (7) in Table III derived from $Si(CH_3)_4$ (*33*). A crystalline compound $Si_4Cl_4C_6H_{12}$ of similar structure (1,3,5,7-tetrachloro-1,3,5,7-tetrasilaadamantane) is formed by interaction of $(CH_3)_3SiCl$ and $SiCl_4$ in the presence of $AlCl_3$ at high pressure and a temperature above 500°C (yield 0.1%) (*66*). A bright red compound was isolated from the colored higher silicon compounds from $CH_3SiCl_3$. This was a glassy solid at room temperature but was fusible and proved to be readily soluble (compound 26, Table V: distilled in high vacuum at 210°C). It had the empirical formula $Si_8C_8Cl_{13}H_{13}$ and this, together with its chemical properties, led to the formulation shown in Table V. The symmetrical arrangement shown is the most probable of the various possible ways in which four six-membered rings of alternating Si and C atoms might condense. A linear chain structure would imply an empirical formula $Si_8C_8Cl_{17}H_{17}$ (mol. wt. 941) whereas for a simple ring the formula would be $Si_8C_8Cl_{16}H_{16}$ (mol. wt. 904). Clearly both are excluded (*33*).

A further compound of this type, $Si_7C_{12}H_{28}Cl_6$ (compound 25, Table V), may be separated from the pyrolysis products of $(CH_3)_3SiCl$. It distills in high vacuum at 234°C and forms a brittle yellow glass at room temperature which dissolves in organic solvents to give a yellow solution. The infrared spectrum shows that an SiH group is present, although no hydrogen is evolved on treatment with hot alkali. The composition and chemical behavior are well represented by the structure shown (compound 25), with three condensed rings. This is a derivative of $Si_7C_{18}H_{46}$ (compound 10, Table III) obtained from $Si(CH_3)_4$. Investigation of the higher pyrolysis products is not yet completed.

In order to see how the different elements are distributed in the pyrolysis product from $CH_3SiCl_3$, the following three groups may be considered: (1) compounds with a single Si atom, (2) compounds with two Si atoms, and (3) higher products. The mixture of compounds with two Si atoms contains 71% Cl, 20% Si, and 6.2% C. In the mixture of higher compounds the chlorine content is lower (59.6%), whereas the Si and C contents are increased (26.4 and 12%, respectively). Chlorine from the SiCl groups of the methyl chlorosilanes appears in the products preferentially in the highly chlorinated 1,3-disilapropanes. This is clearly related to the fact that these are least suited for the synthesis of higher carbosilanes in pyrolysis (*36*). The reduction in the tendency to form higher compounds as the number of SiCl groups increases is also evident from a comparison of high molecular reaction products from the three methyl chlorosilanes.

### *3. Mechanism of the Pyrochemical Formation of Carbosilanes*

The carbosilanes described in Section II,A,1 and 2 are formed from $Si(CH_3)_4$ and the methyl chlorosilanes by gas phase thermal decomposition at 700°C. Under these conditions it is reasonable to assume that radical mechanisms are operative. Kinetic measurements of the thermal decomposition of $Si(CH_3)_4$ in a static system have shown (*58*) that, on heating to 700°C in the gas phase for several hours, hydrogen and methane are formed while Si and C are deposited. The primary step in the decomposition is assumed to be:

$$Si(CH_3)_4 \rightarrow (CH_3)_3Si\cdot + \cdot CH_3 \qquad (1)$$

In investigating the pyrochemical formation of carbosilanes from $Si(CH_3)_4$ with decomposition times of a few minutes, separation of silicon is almost completely suppressed. Instead, a mixture of substances based on the Si—C—Si structure is produced (*30*), as has been described. In order to explain the formation of these compounds, the reactions formulated below must be considered in addition to that in Eq. (1).

$$(CH_3)_3Si—CH_3 + \cdot CH_3 \rightarrow (CH_3)_3Si\dot{C}H_2 + CH_4$$

or

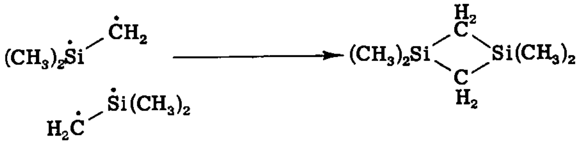
$$(CH_3)_3Si—CH_3 \rightarrow (CH_3)_3Si\dot{C}H_2 + \cdot H \qquad (2)$$

These processes give the radicals needed for the synthesis of the Si—C—Si unit, which should occur according to the equation:

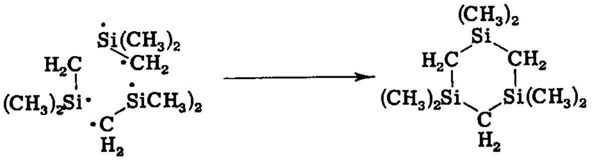
$$(CH_3)_3Si\dot{C}H_2 + \dot{S}i(CH_3)_3 \rightarrow (CH_3)_3Si—CH_2—Si(CH_3) \qquad (3)$$

This does not, however, explain the preferential formation of cyclic carbosilanes, such as Si-hexamethylcyclocarbosilane. The isolation of 1,3-disilacyclobutane (compound 2, Table III) appears to be especially significant in this connection. Its formation may be thought of as associated with Eq. (2):

$$(CH_3)_3Si-\dot{C}H_2 \longrightarrow (CH_3)_2\dot{S}i-\dot{C}H_2 + \dot{C}H_3$$

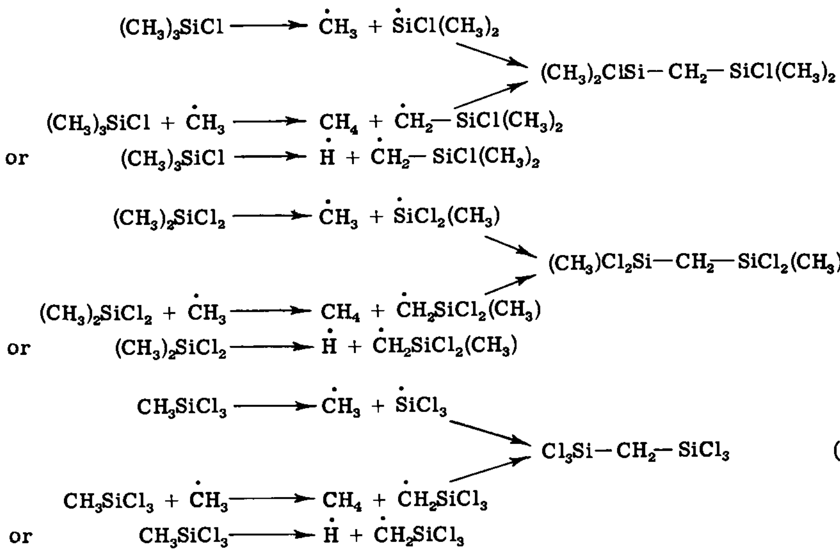


Formation of the six-membered ring may also be understood in terms of the $(CH_3)_2Si—\dot{C}H_2$ radical:



In order to understand the formation of the higher compounds shown in Table III it is necessary to postulate certain further steps. The existence of complicated radical reactions during the pyrolysis is shown by the appearance of benzene among the products. The formation of benzene and $C_6H_5Si(CH_3)_3$, starting from $Si(CH_3)_4$, may be understood in terms of the kinetics of the thermal decomposition of hydrocarbons.

Similar mechanistic considerations may be applied to the formation of SiCl-containing carbosilanes from the three methyl chlorosilanes in the gas phase at 700°C. The 1,3-disilapropanes containing SiCl groups, shown in Table V, are key substances in considering the mechanism of this reaction. As in the case of $Si(CH_3)_4$, cleavage of both the Si—C and the C—H bonds must be considered. It is possible to explain the formation of some of the compounds quite readily on this basis.



$$(CH_3)_3SiCl \longrightarrow \dot{C}H_3 + \dot{S}iCl(CH_3)_2 \searrow (CH_3)_2ClSi{-}CH_2{-}SiCl(CH_3)_2$$

$$(CH_3)_3SiCl + \dot{C}H_3 \longrightarrow CH_4 + \dot{C}H_2{-}SiCl(CH_3)_2 \nearrow$$

$$\text{or} \quad (CH_3)_3SiCl \longrightarrow \dot{H} + \dot{C}H_2{-}SiCl(CH_3)_2$$

$$(CH_3)_2SiCl_2 \longrightarrow \dot{C}H_3 + \dot{S}iCl_2(CH_3) \searrow (CH_3)Cl_2Si{-}CH_2{-}SiCl_2(CH_3)$$

$$(CH_3)_2SiCl_2 + \dot{C}H_3 \longrightarrow CH_4 + \dot{C}H_2SiCl_2(CH_3) \nearrow$$

$$\text{or} \quad (CH_3)_2SiCl_2 \longrightarrow \dot{H} + \dot{C}H_2SiCl_2(CH_3)$$

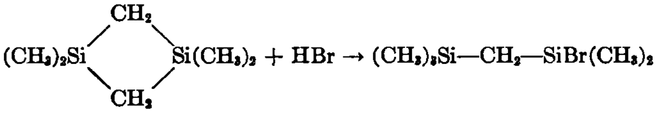
$$CH_3SiCl_3 \longrightarrow \dot{C}H_3 + \dot{S}iCl_3 \searrow Cl_3Si{-}CH_2{-}SiCl_3 \qquad (4)$$

$$CH_3SiCl_3 + \dot{C}H_3 \longrightarrow CH_4 + \dot{C}H_2SiCl_3 \nearrow$$

$$\text{or} \quad CH_3SiCl_3 \longrightarrow \dot{H} + \dot{C}H_2SiCl_3$$

From the nature of the compounds isolated (Table V) it is, however, evident that cleavage of the Si—Cl bond must also take place. Thus compounds are produced from $(CH_3)_3SiCl$ and $(CH_3)_2SiCl_2$ in which more Cl atoms are bonded to a Si atom than in the compound taken initially. Table V also shows that by no means all the possible 1,3-disilapropanes are produced in equal amounts from a methyl chlorosilane. The compounds which are most simply formed on the basis of Eq. (4) are also not the most abundant. Certain arrangements of groups seem to occur preferentially, e.g., $Cl_3Si{-}CH_2{-}SiCl_3$ and $(CH_3)_3Si{-}CH_2{-}SiCl_3$ from $(CH_3)_3SiCl$ or $(CH_3)_2SiCl_2$, and their formation involves considerable rearrangement.

When cleavage of the SiCl group is postulated, it is then possible to account for the production of the various compounds in terms of the recombination of the corresponding radicals. It is not yet clear if exchange of chlorine occurs exclusively through free chlorine atoms. No HCl is detected in the gaseous pyrolysis products from $CH_3SiCl_3$. Its formation would be expected if free chlorine atoms were involved. It is also significant that no substance was isolated corresponding with the four-membered ring compound 1,3-disilacyclobutane, which is formed in the pyrolysis of $Si(CH_3)_4$. This strained ring is broken by HBr at relatively low temperatures:



$$+ HBr \rightarrow (CH_3)_3Si{-}CH_2{-}SiBr(CH_3)_2$$

so that a corresponding reaction might be expected with HCl under the conditions used in pyrolyzing the methyl chlorosilanes. This would explain both the absence of HCl in the pyrolysis products and the greater relative abundance of the unsymmetrical chlorinated silanes [Table V, compounds 1 and 4 from $(CH_3)_3SiCl$ and $(CH_3)_2SiCl_2$]. The conditions requisite for forming a four-membered ring must exist since all three methyl chlorosilanes give the six-membered ring (1,3,5-trisilacyclohexane) (Table V). The tendency to form ring compounds with alternating Si and C atoms is most marked with $(CH_3)_3SiCl$, and formation of compounds in which the substituents in the ring are as symetrically distributed as possible is favored (Table V).

The same types of radical reaction as are postulated to account for the SiCl-containing 1,3-disilapropanes will also explain the formation of these six-membered rings. This is illustrated by the two following examples (*37*).

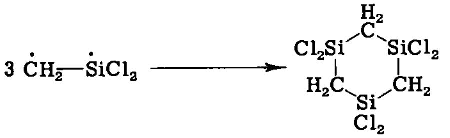
(*a*) Formation of $(SiCl_2—CH_2)_3$ from $(CH_3)_2SiCl_2$:

$$(CH_3)_2SiCl_2 \longrightarrow \dot{C}H_3 + \dot{S}iCl_2(CH_3)$$

$$(CH_3)_2SiCl_2 + \dot{C}H_3 \longrightarrow CH_4 + \dot{C}H_2—SiCl_2(CH_3)$$

$$(CH_3)_2SiCl_2 \longrightarrow \dot{H} + \dot{C}H_2—SiCl_2(CH_3)$$

$$\dot{C}H_2—SiCl_2(CH_3) \longrightarrow \dot{C}H_2—\dot{S}iCl_2 + \dot{C}H_3$$



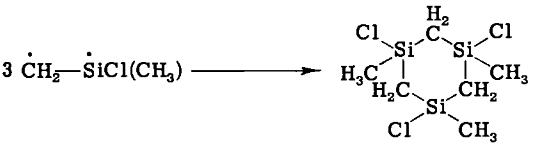
(*b*) Formation of $[SiCl(CH_3)—CH_2]_3$ from $(CH_3)_3SiCl$:

$$(CH_3)_3SiCl \longrightarrow \dot{C}H_3 + \dot{S}iCl(CH_3)_2$$

$$(CH_3)_3SiCl + \dot{C}H_3 \longrightarrow CH_4 + \dot{C}H_2—SiCl(CH_3)$$

$$(CH_3)_3SiCl \longrightarrow \dot{H} + \dot{C}H_2—SiCl(CH_3)_2$$

$$\dot{C}H_2—SiCl(CH_3)_2 \longrightarrow \dot{C}H_2—\dot{S}iCl(CH_3) + \dot{C}H_3$$



It should also be possible to use the radicals produced in the pyrolysis to form compounds containing Si—Si groups [e.g., $(CH_3)_2ClSi—SiCl(CH_3)_2$ from $\dot{S}iCl(CH_3)_2$]. Such compounds are not observed, but this is understandable as the Si—Si bond is less stable thermally. Consequently the grouping $Si—CH_2—Si$ is preferred. This is also evident from the rearrangement shown in the equation (*90*):

$$(CH_3)_3Si—Si(CH_3)_3 \xrightarrow{600°C} H(CH_3)_2Si—CH_2—Si(CH_3)_3$$

When comparison is made between the Si:C:H:Cl ratio of 1:1:3:3 of the starting material, $CH_3SiCl_3$, and of the total liquid and high molecular weight reaction product, the latter (ignoring the products boiling below room temperature, which contain no silicon compounds) is found to be 1:0.75:1.82:3.06. All the chlorine is bonded to silicon and may be split off readily by hydrolysis as Cl ions. The Si:Cl ratio in the pyrolysis product is practically the same as in the starting material, showing that no appreciable amounts of volatile compounds such as HCl can have been formed. On the other hand, both the C and H values in the product show a reduction and the gaseous products consist of compounds of these elements ($H_2$, hydrocarbons with $CH_4$ predominating) (*36*).

### *4. By the Electrical Discharge*

From the results on the pyrolytic decomposition of $Si(CH_3)_4$ and the various methyl chlorosilanes it may be inferred that the synthesis of carbosilanes could be effected by adding energy in other ways. One necessary condition is that the energy must suffice to produce radicals by breaking the Si—C bond. The possibility of forming Si—C bonds photochemically has already been considered (*26*). The possibility of introducing energy by a silent electrical discharge in an atmosphere of the gas was first examined in the case of the reaction between $SiCl_4$ and cyclohexane or benzene (*1*). When the vapor of $CH_3SiCl_3$ mixed with $H_2$ is passed through a discharge zone (27–28-kV ozone generator: discharge zone 30 cm), formation of $C_2H_2$ was observed (0.0003 mole per mole of $CH_3SiCl_3$ per hour), but $(CH_3)Cl_2Si—CH_2—SiCl_3$, $(CH_3)Cl_2Si—CH_2—CH_2—SiCl_3$, and considerable amounts of higher condensation products (b.p. 104°–200°C at 4–5 mm Hg) were also obtained. The composition of the latter showed them to be similar chain Si—C compounds with a greater number of Si units (*2*). After methylation of the SiCl groups in the condensation product, it was possible to isolate $(CH_3)_3Si—CH_2—Si(CH_3)_2—CH_2—Si(CH_3)_3$ and $(CH_3)_3Si—CH_2—CH_2—Si(CH_3)_2—CH_2—Si(CH_3)_3$ (*3*):

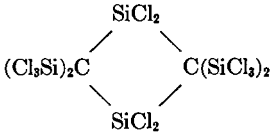
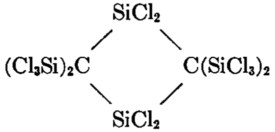
The corresponding decomposition of 2190 gm of $(CH_3)_2SiCl_2$ gave 305 gm of a mixture of condensation products from which the following com-

## TABLE VI
### CARBOSILANES FROM THE DIRECT SYNTHESIS

| Starting material | Copper catalyst (%) | Reaction temperature (°C) | Carbosilane | Proportion % | B.P. pressure (°C/mm) | $n_D$ | $d$ | Reference |
|---|---|---|---|---|---|---|---|---|
| $CH_2Cl_2$ | — | 320–350 | $Cl_2HSi—CH_2—SiCl_3$ | — | 163–163.2/748 | — | — | — |
| | | | $Cl_2HSi—CH_2—SiHCl_2$ | 40–52 | 151.2–152.5/772 | — | — | *(101)* |
| | | | $Cl_3Si—CH_2—SiCl_3$ | | 165/760 | — | — | *(100)* |
| $CH_2Cl_2$ | 10 | 300 | $Cl_3Si—CH_2—SiHCl_2$ | — | 51–52.5/10 | — | — | — |
| | | | $Cl_3Si—CH_2—SiCl_3$ | — | 63.7–65/10 | — | — | — |
| | | | $(Cl_2SiCH_2)_3$ | — | 130/10<br>(m.p. 81–82.5°C) | — | — | *(78)* |
| $CH_2Cl_2$ | 25 | 320–360 | $Cl_2HSi—CH_2—SiHCl_2$ | 40–52 | 151–152/772 | — | — | — |
| | | | $Cl_2HSi—CH_2—SiCl_3$ | | 163–163.5/748 | — | — | — |
| | | | $Cl_3Si—CH_2—SiCl_3$ | — | 182/762 | — | — | *(99)* |
| | | | $(Cl_2Si—CH_2)_3$ | — | 133–134/10 | — | — | — |
| $CH_2Cl_2$ | 10 | 310 | $Cl_3Si—CH_2—SiCl_3$ | 39 | 180–185 | — | — | *(77)* |
| $CH_2Cl_2$ | 10 | 350–400 | $(Cl_3Si)_2CH_2$ | 8 | 180 | $1.471^{22}$ | $1.545^{17}$ | — |
| | | | $Cl_2HSi—CH_2—SiCl_3$ | 3 | 167–168 | — | $1.464^{22.5}$ | *(21)* |
| $CH_2Cl_2$ | 10 | 280 | $Cl_3Si—CH_2—SiCl_3$ | — | — | — | — | *(53)* |
| | | | $Cl_3Si—CH_2—SiHCl_2$ | — | — | — | — | *(80)* |
| | | | $(Cl_2HSi)_2CH—CH_3$ | 6.5 | 165.5/750 | — | — | *(5)* |
| | | | $Cl_2HSi—CH(CH_3)—SiCl_3$ | 18.5 | 181/750 | — | — | — |
| | | | $(Cl_3Si)_2CH—CH_3$ | 18.5 | 197.5/750 | — | — | — |
| | | | $Cl_3Si—CH_2—CH_2—SiCl_3$ | — | — | — | — | — |
| | | | $(Cl_2Si—CH_2)_3$ | — | — | — | — | — |
| | | | $Cl_3Si—CH_2—SiCl_2—CH_2—SiHCl_2$ | — | — | — | — | — |
| | | | $Cl_3Si—CH_2—SiCl_2—CH_2—SiH_2Cl$ | — | — | — | — | — |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $CHCl_3$ | 10 | 300 | $Cl_3SiCH(SiHCl_2)_2$ | ca. 0.7 | 100–102/10 | — | — | — |
| | | | $Cl_3Si$—$CH_2$—$SiCl_3$ | ca. 7 | 183–184/750 | — | — | (*72*) |
| | | | $Cl_3Si$—$CH_2$—$SiHCl_2$ | ca. 1.5 | 160–167/760 | — | — | — |
| | | | $(Cl_3Si)_3CH$ | ca. 9 | 254.4–254.8/751<br>(m.p. 65.5°C) | — | — | — |
| | | | $(Cl_3Si)_2CHSiHCl_2$ | ca. 0.7 | 108.6–110.5/10 | — | — | — |
| $CCl_4$ | 10 | 310 | $C(SiCl_3)_4$ | — | 175–185/3<br>subl. (m.p. 420°C<br>decomp.) | — | — | (*73*) |
| $(H_3C)_2CCl_2$ | 20 | 360–380 | $Cl_2HSi$—$CMe_2$—$SiHCl_2$ | 14 | 175.8 | 1.4709 | 1.2635 | — |
| | | | $Cl_2HSi$—$CMe_2$—$SiCl_3$ | 11.5 | 195.5 | 1.4818 | 1.3808 | (*80*) |
| | | | $Me_2C(SiCl_3)_2$ | 8.5 | 214 | 1.4927 | 1.3733 | — |
| $H_3C$—$CHCl_2$ | 20 | 360–380 | $Cl_2HSi$—$CHMe$—$SiHCl_2$ | 6.5 | 165.5/750.5 | 1.4678 | 1.3343 | — |
| | | | $Cl_3Si$—$CHMe$—$SiHCl_2$ | 18.5 | 181/750.5 | 1.4740 | 1.4310 | — |
| | | | $Cl_3Si$—$CHMe$—$SiCl_3$ | 18.5 | 197.5/750.5 | 1.4820 | 1.5059 | (*80*) |
| $H_3C$—$CHCl_2$ | 10 | 350–400 | $Cl_3Si$—$CHMe$—$SiCl_3$ | 8 | 191 | $1.471^{23}$ | $1.454^{27.5}$ | (*21*) |
| $H_2C{=}CCl_2$ | 20 | 450 | $H_2C{=}C(SiCl_3)_2$ | — | 109/51 | 1.4861 | 1.4939 | (*81*) |
| $CH_2{=}CCl$—$CH_2Cl$ | 20 | 275–290 | $H_2C{=}C(SiCl_3)$—$SiHCl_2$ | — | 197/745 | 1.4846 | 1.3901 | (*82*) |
| | | | $H_2C{=}C(SiCl_3)_2$ | — | 211.2/745 | 1.4971 | 1.4659 | — |
| $Cl_3SiCH_2Cl$ | 20 | 360–370 | $Cl_3Si$—$CH_2$—$SiCl_3$ | 30 | — | — | — | (*87*) |
| | | | $Cl_3Si$—$CH_2$—$SiCl_2$—$CH_2$—$SiCl_3$ | 8.5 | 157–158/6 | 1.4970 | 1.5423 | (*83*) |
| $MeCl_2Si$—$CHCl_2$ | 20 | 360–370 | $MeCl_2Si$—$CH_2$—$SiCl_3$ | 10.5 | 182.5–183 | — | — | — |
| | | | $MeCl_2SiCH$—$(SiCl_3)_2$ | 14 | 124–125/10<br>(m.p. 49–50) | — | — | (*83*) |
| $MeCl_2SiCH_2Cl$ | 20 | 360–370 | $MeCl_2Si$—$CH_2$—$SiCl_3$ | 28.7 | 183.5–184.5/746 | 1.4692 | 1.4167 | (*87*) |
| | | | $MeCl_2Si$—$CH_2$—$SiCl_2$—$CH_2$—$SiCl_2Me$ | 16.7 | 123–124/3 | 1.4905 | 1.3782 | — |

TABLE VI (*Continued*)

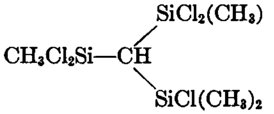
| Starting material | Copper catalyst (%) | Reaction Temperature (°C) | Carbosilane | Proportion (%) | B.P. pressure (°C/mm) | $n_D$ | $d$ | Reference |
|---|---|---|---|---|---|---|---|---|
| $CHCl(SiCl_3)_2$ | 20 | 360–370 | $Cl_3Si\text{—}CH_2\text{—}SiCl_3$ | 16.7 | 179.9 | — | — | — |
| | | | $HC(SiCl_3)_3$ | 29.8 | 168–169/3<br>(m.p. 57) | — | — | (*87*) |
| $Cl_3SiCHClMe$ | 20 | 360–370 | $Cl_3SiCHMeSiHCl_2$ | 5 | 180.4–181/730 | 1.4780 | 1.4373 | (*87*) |
| | | | $Cl_3SiCHMeSiCl_3$ | 25 | 197–197.3/730 | 1.4842 | 1.5121 | (*83*) |
| | | | $Cl_2Si(CHMeSiCl_3)_2$ | 6.6 | 272.5–275/736 | 1.4990 | 1.4736 | — |
| $Cl_3SiCHCl_2$ | 20 | 360–370 | $Cl_3Si\text{—}CH_2\text{—}SiCl_3$ | 22.4 | 58–59/8 | — | — | — |
| | | | $CH(SiCl_3)_3$ | 13 | 113–114.5/4 | — | — | (*87*) |
| $(Cl_3Si)_2CCl_2$ | — | 300 | $CH(SiCl_3)_3$ | ca. 7 | 124–126/10<br>(m.p. 65–66) | — | — | (*74*) |
| | | | $CCl(SiCl_3)_3$ | ca. 0.7 | — | — | — | — |
| | | | $C(SiCl_3)_4$ | ca. 34 | subl. | — | — | — |
| | | |  | — | (m.p. 275–278) | — | — | — |
| $(Cl_3Si)_3CCl$ | 25 | 380 | $CH(SiCl_3)_3$ | ca. 30 | 124–126/10 | — | — | (*74*) |
| | | | $C(SiCl_3)_4$ | ca. 25 | (m.p. 65–66)<br>subl.<br>(420 decomp.) | — | — | — |
| | | |  | ca. 40 | (m.p. 275–278) | — | — | (*75*) |
| $Cl_2SiEtCHClMe$ | 20 | 370–380 | $Cl_2SiEt\text{—}CHMe\text{—}SiHCl_2$ | — | 205/750 | 1.4765 | 1.2966 | — |
| | | | $Cl_2SiEt\text{—}CHMe\text{—}SiCl_3$ | 11 | 67/1 | 1.4810 | 1.3590 | — |
| | | | $Cl_2Si(CHMe\text{—}SiEtCl_2)_2$ | 7.5 | 146–148/2 | 1.4995 | 1.3012 | (*88*) |

pounds were isolated (*4*). (The values in % represent proportions of the condensation product.)

$$\mathrm{(CH_3)_2ClSi{-}CH_2{-}SiCl_2(CH_3)} \qquad \text{(10\%) b.p. 184°–186°C}$$

$$\left.\begin{array}{l}\mathrm{(CH_3)_2Cl{-}CH_2{-}CH_2{-}SiCl_2(CH_3)}\\ \mathrm{(CH_3)Cl_2Si{-}CH_2{-}CH_2{-}SiCl_2(CH_3)}\end{array}\right\} \quad \text{(14\%) b.p. 86°–87°C (9 mm)}$$

$$\left.\begin{array}{l}\mathrm{(CH_3)Cl_2Si{-}CH_2{-}CH_2{-}SiCl(CH_3){-}CH_2{-}SiCl_2(CH_3)}\\ \mathrm{(CH_3)Cl_2Si{-}CH_2{-}CH_2{-}SiCl_2{-}CH_2{-}SiCl(CH_3)_2}\end{array}\right\} \quad \begin{array}{l}\text{(5.6\%) b.p. 115°–125°C}\\ \text{(9 mm)}\end{array}$$



$$\mathrm{CH_3Cl_2Si{-}CH[SiCl_2(CH_3)][SiCl(CH_3)_2]}$$

(3%) b.p. 135°–145°C (9 mm)

In the decomposition of $(CH_3)_3Si(C_2H_5)$ (41% of condensation products) the compounds obtained were $(CH_3)_3Si—CH_2—CH_2—Si(CH_3)_3$, $C_2H_5(CH_3)_2Si—CH_2—Si(CH_3)_3$, $C_2H_5(CH_3)_2Si—CH(CH_3)—Si(CH_3)_3$ and unidentified isomers of the compositions $Si_2C_9H_{24}$ and $Si_3C_{12}H_{32}$, together with a mixture of polymers $(SiC_{3.8}H_9)_x$ (b.p. 220°C at 5 mm Hg) (*5*). Decomposition of $(CH_3)_2Si(C_2H_5)_2$ also gave condensation products, the composition of which was not given. A reaction mechanism involving a chain reaction in which H atoms and $CH_3$ radicals participate has been discussed.

## B. By Direct Synthesis from Silicon and Alkyl Chlorides

The reaction of $CH_3Cl$ with silicon in the presence of catalysts leads to various methyl chlorosilanes (Direct Synthesis) (*86, 71, 72*). When higher chlorinated hydrocarbons [$CH_2Cl_2$, $CHCl_3$, $CCl_4$, $(H_3C)_2CCl_2$, $H_3C—CHCl_2$, $H_2C{=}CCl_2$, $H_2C{=}CCl—CH_2Cl$] or alkyl chlorosilanes with C—Cl groups are used in place of $CH_3Cl$, products containing the carbosilane group Si—C—Si are obtained in addition to simple organochlorosilanes. Table VI shows the carbosilanes formed in such reactions and the conditions used.

The mechanism involved in the formation of these compounds is discussed in the references quoted. It has been established that three main types of reaction are involved:

(1) *Direct synthesis*, in which C-halogens are replaced by $—SiCl_3$, $—SiHCl_2$, and $—SiRCl_2$.

(2) *Dehalogenation*, resulting in condensation of the products which have been produced directly to compounds of higher molecular weight.

(3) *Pyrolysis*, the effect of which depends on the nature of the alkyl or aryl halides used and of the products formed.

### C. BY REARRANGEMENT OF THE Si—Si—C GROUP TO Si—C—Si

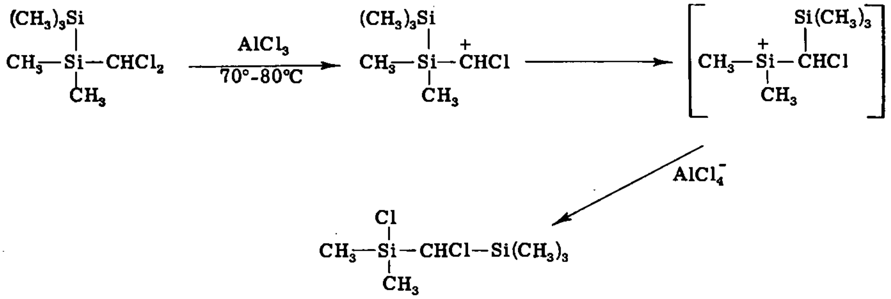
Because of the higher bond energy of Si—C (76 kcal) compared with that of Si—Si (53 kcal), the structure —Si—C—Si— is more favorable on energetic grounds than —Si—Si—C— (*11*). Rearrangements in this sense may be brought about either catalytically, under the action of aluminum chloride, or thermally. The following equations show the examples of this sort of rearrangement which have been found so far (*63, 64*):

$$\mathrm{ClCH_2Me_2Si{-}SiMe_3 \xrightarrow{AlCl_3} ClMe_2Si{-}CH_2{-}SiMe_3}$$

$$\mathrm{ClCH_2Me_2Si{-}SiMe_2Cl \xrightarrow{AlCl_3} ClMe_2Si{-}CH_2{-}SiMe_2Cl}$$

$$\mathrm{Me_3Si{-}SiMe_2CHCl_2 \xrightarrow[70^\circ\text{-}80^\circ C]{AlCl_3} (83\%)\ Me_3Si{-}CHCl{-}SiMe_2Cl}$$

These rearrangements are formulated as taking place through formation of an intermediate carbonium or siliconium ion:

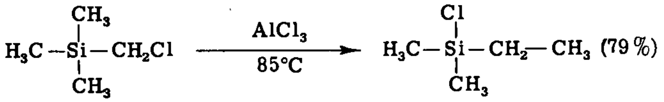


For carbosilanes containing a CHCl bridge a further rearrangement involving methyl group migration from the Si atom to the carbonium carbon is observed at higher temperatures. This is demonstrated by the following examples:

$$\mathrm{Me_3Si{-}CHCl{-}SiMe_3 \xrightarrow{AlCl_3} Me_3Si{-}CHMe{-}SiMe_2Cl}$$

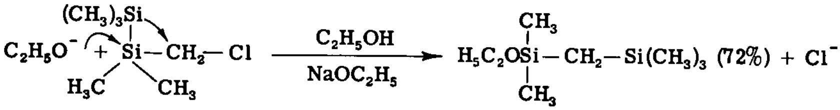
$$\mathrm{Me_3Si{-}CHCl{-}SiMe_2Cl \xrightarrow[140^\circ\text{-}150^\circ C]{AlCl_3} ClMe_2Si{-}CHMe{-}SiMe_2Cl}$$

The same reaction is known for simple α-chloro organosilanes (*104*):



$$\mathrm{H_3C{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}CH_2Cl \xrightarrow[85^\circ C]{AlCl_3} H_3C{-}\overset{Cl}{\underset{CH_3}{Si}}{-}CH_2{-}CH_3}\ (79\%)$$

The first example of a nucleophilic rearrangement leading to the formation of the Si—C—Si structure is shown in the following equation (*63*):



The course of this reaction is analogous to that of the corresponding reactions with simple silanes such as (chloromethyl)aryl dimethylsilanes (*16*) and (chloro- or iodomethyl) dimethylsilanes (*93*), although in these it is aryl or hydride migration that leads to rearrangement.

Thermal rearrangement of Si—Si—C to Si—C—Si occurs at temperatures above 500°C: instances of this type of reaction are given in the following equations (*10, 90*), where the yields at the given temperature are recorded in parentheses:

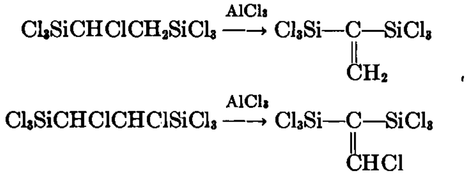
$$(CH_3)_3Si{-}Si(CH_3)_3 \xrightarrow{600°C} (CH_3)_3Si{-}CH_2{-}Si(CH_3)_2H$$

$$(CH_3)_3Si{-}Si(CH_3)_3 \xrightarrow{C_6H_5Cl} (CH_3)_3Si{-}CH_2{-}Si(CH_3)_2Cl$$
$$(500°C,\ 18\%;\ 550°C,\ 51\%;\ 600°C,\ 54\%)$$

$$(CH_3)_3Si{-}Si(CH_3)_2Cl \xrightarrow[500°\text{–}600°C]{C_6H_5Cl} Cl(CH_3)_2Si{-}CH_2{-}Si(CH_3)_2Cl$$
$$(500°C,\ 25\%;\ 550°C,\ 21.6\%;\ 600°C,\ 13\%)$$

$$(CH_3)_4Si_2Cl_2 \xrightarrow[600°C]{C_6H_5Cl} Cl(CH_3)_2Si{-}CH_2{-}Si(CH_3)_2Cl\ (22\%)$$

Simple cleavage products from the Si—Si system such as $Me_3SiCl$ and $Me_2SiCl_2$ are also formed, together with benzene and biphenyl. In these thermal rearrangements it seems certain that radical reactions must be operative. The Si—C—C—Si group is also capable of undergoing rearrangement to Si—C—Si, as shown by the following examples (*67, 68*):



$$Cl_3SiCHClCH_2SiCl_3 \xrightarrow{AlCl_3} Cl_3Si{-}\underset{\underset{CH_2}{\|}}{C}{-}SiCl_3\ ,$$

$$Cl_3SiCHClCHClSiCl_3 \xrightarrow{AlCl_3} Cl_3Si{-}\underset{\underset{CHCl}{\|}}{C}{-}SiCl_3$$

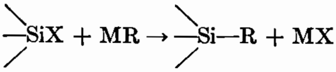
These rearrangements are brought about through catalytic cleavage of HCl in presence of anhydrous $AlCl_3$. The corresponding cleavage of HCl with the aid of nitrogenous bases (e.g., piperidine) occurs without rearrangement. The reverse reaction, i.e., formation of Si—C—C—Si from Si—C—Si, has also been observed, e.g.,

$$ClCH_2{-}CCl(SiCl_3)_2 \xrightarrow{AlCl_3} \begin{array}{ll} ClCH{=}C(SiCl_3)_2 & (\alpha) \\ Cl_3Si{-}CCl{=}CH{-}SiCl_3 & (\beta) \end{array}$$

Reaction occurs to the extent of 66% with 10% of α and 90% of β in the product.

## D. SYNTHESIS WITH THE AID OF ORGANOMETALLIC COMPOUNDS

The synthesis of organosilicon compounds (i.e., formation of the Si—C bond) starting from a silicon halide and an organometallic compound (RMgX, LiR) (*9, 14, 60*) is well known:



(where X = halogen or OR and M = MgCl, Li, Na). This approach has been made use of in synthesizing fully methylated carbosilanes. The following compounds (*96*):

$$(CH_3)_3Si—CH_2—Si(CH_3)_3$$

$$(CH_3)_3Si—CH_2—Si(CH_3)_2—CH_2—Si(CH_3)_3$$

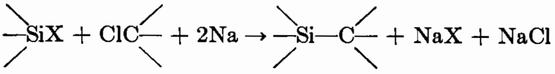
$$(CH_3)_3Si—CH_2—Si(CH_3)_2—CH_2—Si(CH_3)_2—CH_2—Si(CH_3)_3$$

may be formed by the type of reaction shown in Eq. (5):

$$(CH_3)_3Si—CH_2M + Cl—Si(CH_3)_2—CH_2Cl \rightarrow (CH_3)_3Si—CH_2—Si(CH_3)_2CH_2Cl + MCl \quad (5)$$

In such cases side reactions are largely excluded because of the limited number of functional groups. This approach is restricted to the synthesis of unbranched chains. Interaction of $SiHCl_3$ with $(CH_3)_3Si—CH_2MgBr$ gives $(CH_3)_3Si—CH_2—SiHCl_2$, $[(CH_3)_3Si—CH_2]_2SiHCl$, and $[(CH_3)_3Si—CH_2]_3SiH$ (*12*).

Formation of a metallic salt is also responsible for the production of Si—C bonds in the type of reaction:



where X = halogen or OR). The reaction of $ClCH_2(CH_3)_2SiCl$ (143 gm) with $(CH_3)_2SiCl_2$ (268 gm) in the presence of Mg, Zn, or an alkali metal in THF (500 ml) with a reaction time of 15 hours gave (*56*):

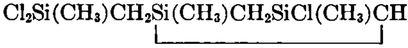
$$Cl(CH_3)_2Si—CH_2—Si(CH_3)_2Cl \quad (41\ gm)$$

$$Cl(CH_3)_2Si—CH_2—Si(CH_3)_2—CH_2—Si(CH_3)_2Cl \quad (21\ gm)$$

$$Cl(CH_3)_2Si—CH_2—Si(CH_3)_2—CH_2—Si(CH_3)_2—Si(CH_3)_2Cl \quad (12.9\ gm)$$

$$Cl(CH_3)_2Si—CH_2—Si(CH_3)_2—CH_2—Si(CH_3)_2—CH_2—Si(CH_3)_2—CH_2—Si(CH_3)_2Cl \quad (8.4\ gm)$$

Derivatives of these compounds were made by further reaction with $LiAlH_4$, and vinyl- or allyl-MgBr (*57*). Besides these linear carbosilanes, 1,1,3,3-tetramethyl-1,3-disilacyclobutane was prepared by the reaction of $Cl(CH_3)_2SiCH_2Si(CH_3)_2CH_2Cl$ with Mg in THF (*56*). A very similar procedure starting from $Cl(CH_3)_2SiCH_2Cl$ and Mg also yields small amounts of the four-membered ring system, the main products being polymeric (*55*, *69*). The reaction leads to higher yields of compounds of low molecular weights if the Mg turnings, in contrast to the normal way, are slowly added to the solution of $ClSi(CH_3)_2CH_2Cl$ in THF (*62*). Thus $[(CH_3)_2SiCH_2]_2$, $[(CH_3)_2SiCH_2]_3$, and $[(CH_3)_2SiCH_2]_4$ can be obtained. This procedure was then extended to prepare cyclocarbosilanes with functional groups from $Cl_2Si(CH_3)CH_2Cl$, but only small amounts of



$$Cl_2Si(CH_3)CH_2Si(CH_3)CH_2SiCl(CH_3)CH_2$$

and $[Cl(CH_3)SiCH_2]_3$ have been isolated. Replacing one Si—Cl group in the starting compound by the less reactive Si —$OC_2H_5$ group led to $[(H_5C_2O)CH_3SiCH_2]_2$ (35.3% yield) and small amounts of $[(H_5C_2O)CH_3SiCH_2]_3$. The trimer was formed in 40.4% yield from the reaction of $(CH_3)(H_5C_2O)_2SiCH_2Cl$ with Mg, besides 12.4% of the dimer. Steric factors are considered to be responsible for the preferred formation of the six-membered ring. The ethoxyl compounds were converted into the corresponding chloro derivatives which were reacted with $LiAlH_4$, $CH_3MgX$, and $C_6H_5MgX$ to yield the hydride, methyl, and phenyl derivatives (see Table VIII) (*62*).

Stepwise synthesis of cyclic and complicated linear carbosilanes requires organosilanes with reactive groups attached both to Si and to C atoms from which carbosilanes can be built up containing several Si atoms having functional groups on selected atoms. It depends on first synthesizing pure compounds of the types $(CH_3)_2XSi—CH_2M$ and $(CH_3)X_2Si—CH_2M$ (M = Li; X = halogen or OR). Synthesis of the Si—C—Si skeleton (with functional groups) by interaction of such an organometallic compound with a chlorosilane carrying functional groups may then be attempted. Difficulties arise, however, both in the synthesis of the required Si compounds and in avoiding unwanted side reactions of the functional groups in the course of the condensation designed to give the Si—C—Si structure. This is illustrated by the following examples.

(*a*) In the interaction of equimolar quantities of $(CH_3)_3SiCH_2Li$ and $Cl_2Si(CH_3)CH_2Cl$ the unwanted product $[(CH_3)_3SiCH_2]_2Si(CH_3)CH_2Cl$ is obtained to a considerable extent instead of $(CH_3)_3Si—CH_2—SiCl(CH_3)CH_2Cl$, which would have functional groups on Si and C (*41*).

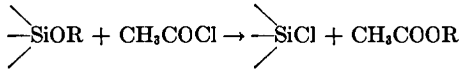
(*b*) Whereas $(CH_3)_3SiCH_2Cl$ can be converted in good yield into the corresponding Grignard compound (*94*), neither $(CH_3)_2(C_2H_5O)SiCH_2Cl$ nor $CH_3(C_2H_5O)_2SiCH_2Cl$ will react even when warmed for up to 10 hours with activated magnesium in ether, dibutyl ether, or tetrahydrofuran (*41*).

(*c*) Reaction occurs between lithium and either of the two alkoxy silanes in (*b*). When $(CH_3)_2(C_2H_5O)SiCH_2Cl$ reacts with Li in pentane, $(CH_3)_2(C_2H_5O)SiCH_2Si(CH_3)_2CH_2Cl$ is formed by condensation of the Li compound formed in the first place with unreacted starting material:

$$(CH_3)_2(C_2H_5O)SiCH_2Cl + 2Li \rightarrow (CH_3)_2(C_2H_5O)SiCH_2Li + LiCl \qquad (6)$$

$$(CH_3)_2(C_2H_5O)SiCH_2Li + (C_2H_5O)Si(CH_3)_2CH_2Cl \rightarrow$$
$$(CH_3)_2(C_2H_5O)Si{-}CH_2{-}Si(CH_3)_2CH_2Cl + C_2H_5OLi \qquad (7)$$

Because of these reactions only 1 mole of Li reacts instead of two, corresponding with the complete conversion of the ethoxy silane to its lithium derivative. Because of the thermal lability of the ethoxy group, the product was treated with acetyl chloride and $(CH_3)_2ClSi{-}CH_2{-}Si(CH_3)_2CH_2Cl$ isolated (*17*, *22*):



$$\rangle SiOR + CH_3COCl \rightarrow \rangle SiCl + CH_3COOR$$

Synthesis of the Li compound is thus prevented because of its high reactivity toward the $SiOC_2H_5$ group, and for this reason it proved impossible to prepare functional trisilylmethylene derivatives according to the equation

$$2(CH_3)_2(C_2H_5O)SiCH_2Li + Cl_2Si(R)CH_2Cl \rightarrow$$
$$(CH_3)_2(C_2H_5O)Si{-}CH_2{-}SiR(CH_2Cl){-}CH_2{-}Si(OC_2H_5)(CH_3)_2$$

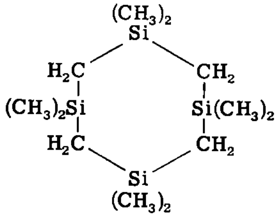
Conditions are more favorable when $(CH_3)(OC_2H_5)_2SiCH_2Cl$ is treated with Li and solutions of $CH_3(C_2H_5O)_2SiCH_2Li$ may be obtained. At 20°C in pentane, diethyl ether, or THF, condensation of the Li compound with the starting material $CH_3(C_2H_5O)_2SiCH_2Cl$ is still slow so that orange-red solutions of $CH_3(C_2H_5O)_2SiCH_2Li$ result. If higher temperatures are used, however, the condensation reaction (Eq. 7) again becomes significant (*41*).

### E. SYNTHESIS OF FUNCTIONAL CARBOSILANES BY SYNTHESIS AND CLEAVAGE OF PHENYL CHLOROMETHYL CARBOSILANES

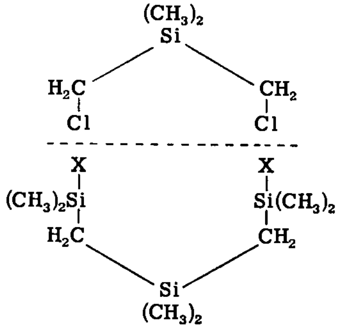
In forming Si-functional Mg and Li compounds difficulties arise because of secondary reaction between the products and unused starting material. For the synthesis of the organometallic intermediates and their subsequent condensation reactions, therefore, compounds were considered in which the Si atoms carry protective groups. These must hinder attack of the metal and condensation reactions at unwanted positions and must also be capable of subsequent cleavage to form reactive Si functional groups. The $SiC_6H_5$ group is well suited to this purpose. The way in which the possibilities of cleavage for this group by halogens and hydrogen halides depend on the remaining substituents on the silicon atom is well known (*39, 98*), and the formation of $(CH_3)_2C_6H_5SiCH_2MgCl$ has been described (*95*). Moreover, it was easy to establish that the $SiCH_2Cl$ group is not attacked when a phenyl group is split off according to the equation:

$$(CH_3)_2C_6H_5SiCH_2Cl + Br_2 = (CH_3)_2BrSiCH_2Cl + C_6H_5Br$$

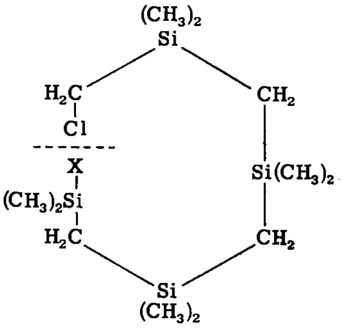
Synthesis of compound (I) (below), based on a final stage involving the condensations shown in (II) or (III), is therefore conceivable.



(I)

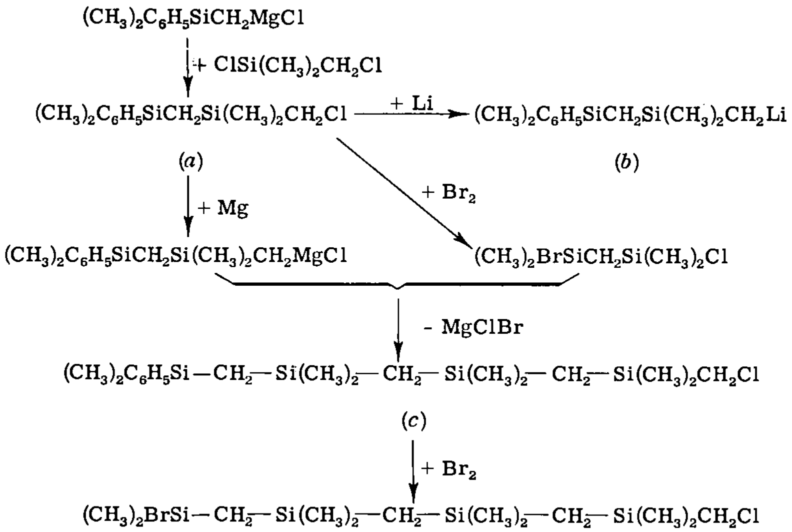


(II)

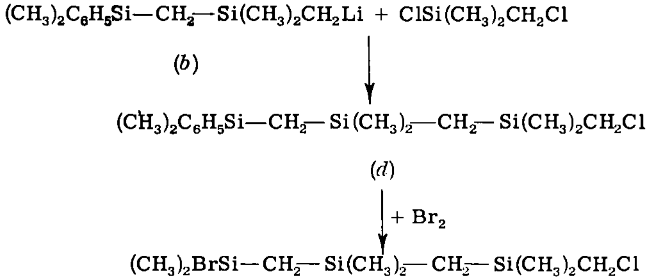


(III)

Compound (III) is made in the following way (*41*):



(III)



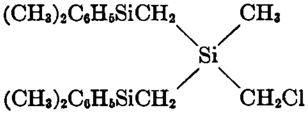
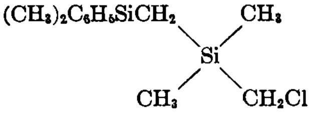
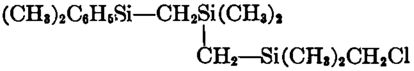
In order to form (*a*), stoichiometric quantities of the two starting materials are allowed to react for 49 hours in boiling ether and subsequently heated for an additional 8 hours at 100°C after distilling off the ether. The yields of $(CH_3)_2C_6H_5SiCH_2Si(CH_3)_2CH_2Cl$ were 15–30%, depending on the reaction time. Compound (*a*) is a colorless liquid which reacts practically quantitatively with Mg in ether to form the Grignard compound. No reaction occurs between (*a*) and Li in pentane, but the Li compound (*b*) is formed in ether (dark brown solution). Only some 50% of the calculated quantity of Li reacts, however. Reaction of the Li compound (*b*) with $ClSi(CH_3)_2CH_2Cl$ yields (*d*): $(CH_3)_2C_6H_5—Si—CH_2—Si(CH_3)_2—CH_2—Si(CH_3)_2CH_2Cl$ as a colorless liquid of low viscosity. It reacts in ether with both Li and Mg to form the organometallic compound and gives $(CH_3)_2BrSi{-}CH_2{-}Si(CH_3)_2{-}CH_2{-}Si(CH_3)_2CH_2Cl$ quantitatively with $Br_2$. Synthesis of (*c*) may be brought about through the metallated trisilmethylene (*d*) or by reaction of the metal derivative of (*a*) with $(CH_3)_2BrSiCH_2Si(CH_3)_2CH_2Cl$. The latter route gives the higher yield because of the smaller number of intermediate steps. The Li compound has the higher reactivity but is formed in only 50% yield. The Mg compound is formed almost quantitatively and is therefore preferable for further reactions.

The reaction scheme described above is a specific example of a method of synthesizing complicated carbosilanes which is of general applicability. With appropriate modifications, which will be dealt with in the following paragraphs, it has been used successfully in preparing such compounds.

Systematic studies (*41, 95*) have shown that Mg compounds of the type $R_2C_6H_5SiCH_2MgX$ (R = alkyl) are readily obtained. They react slowly with chlorosilanes, however, and give unsatisfactory yields of product. It is frequently possible to obtain better results by replacing the Mg compound by that of Li. Reaction of chloromethyl silanes with Li is greatly dependent on the substituents that are attached to Si. In some cases it was not possible to obtain the Li compound by direct synthesis, in spite of variations in the solvent, temperature, and reaction time. Table VII summarizes qualitatively the behavior of chloromethyl silane derivatives with magnesium and lithium.

TABLE VII

REACTION OF THE $SiCH_2Cl$ GROUP WITH Li AND Mg

| | Reaction with | |
|---|---|---|
| Compound | Mg | Li |
| 1. $(CH_3)(C_2H_5O)_2SiCH_2Cl$ | None | Good |
| 2. $(CH_3)_2(C_2H_5O)SiCH_2Cl$ | None | Good |
| 3. $(CH_3)_3SiCH_2Cl$ | Good | Good |
| 4. $(CH_3)_2C_6H_5SiCH_2Cl$ | Good | None |
| 5.  | None | None |
| 6.  | Good | Good |
| 7.  $(CH_3)_2C_6H_5Si{-}CH_2\underset{\substack{\vert \\ CH_2-Si(CH_3)_2CH_2Cl}}{Si}(CH_3)_2$ | Good | Good |

Ethoxy and phenyl groups produce an opposite effect in the simple chloromethyl silanes. The ethoxy group hinders the formation of the Mg compound, whereas the phenyl group hinders that of the Li compound. Examples 5, 6, and 7 (Table VII) also show the effect of the Si-phenyl group. When the Si atom next to the CCl group carries two $(CH_3)_2C_6H_5Si—CH_2$ groups, metallic compounds are not formed; with only one such group reaction occurs with both metals.

In spite of these difficulties the lithium compounds, which are often essential for the synthesis of carbosilanes, may be obtained by an indirect route involving organomercury compounds (*41*, *97*). The readily accessible Mg compound is treated in ether with the stoichiometric amount of $HgCl_2$. With a reaction time of about 3 days the mercurial is formed in high yield and can then be purified by distillation:

$$2(CH_3)_2C_6H_5SiCH_2MgCl + HgCl_2 \rightarrow [(CH_3)_2C_6H_5SiCH_2]_2Hg\ (71\%) + 2MgCl_2 \quad (8)$$

When the mercurial is treated with an excess of lithium, the derivative of the latter is produced in an equilibrium reaction (orange-red solution):

$$[(CH_3)_2C_6H_5SiCH_2]_2Hg + 2Li \rightleftharpoons 2(CH_3)_2C_6H_5SiCH_2Li\ (86\%) + Hg \quad (9)$$

Mercury compounds prepared in this way (Table VIII) are strongly refractive liquids which crystallize in favorable cases. They dissolve readily in organic solvents and are stable to water. Since the mercury compounds can be obtained in a pure form (by distillation, recrystallization) they are actually isolated as an intermediate step in carbosilane synthesis. This results in the removal of all the impurities arising from the various steps in the synthesis, a factor which is particularly important in making carbosilanes of higher molecular weights, where purification becomes more difficult as the molecular weight increases and by-products tend to have an unfavorable effect on the synthesis.

Synthesis of the eight-membered ring (I) is carried out by the method shown earlier in subsection E (condensation reaction II) (*41*).

$$2(CH_3)_2C_6H_5SiCH_2Li + Cl_2Si(CH_3)_2 \rightarrow [(CH_3)_2C_6H_5SiCH_2]_2Si(CH_3)_2 + 2LiCl$$

$$\downarrow + Br_2$$

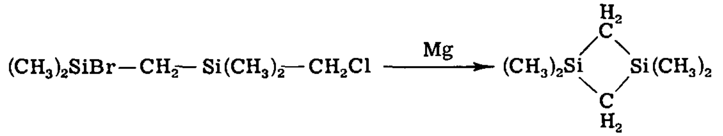
$$[(CH_3)_2BrSiCH_2]_2Si(CH_3)_2$$

$$(CH_3)_2BrSiCH_2]_2Si(CH_3)_2 + (CH_3)_2Si(CH_2Cl)_2 \xrightarrow[113°C]{Na,\ toluene} [Si(CH_3)_2—CH_2]_4\ (ca.\ 3\%)$$

When the red ethereal solution of the Li compound is added to the chlorosilane the quantitative progress of the reaction may be followed by the color change from red to colorless, much as in an ordinary titration.

$[Si(CH_3)_2—CH_2]_4$ may be sublimed at 90°–100°C as colorless needles from the product of the last stage of the synthesis.

Closely related to this synthesis of the eight-membered ring is a route to the four-membered ring compound 1,1,3,3-tetramethyl-1,3-disilacyclobutane (*40*). The final step is shown in Eq. (10); ring closure is brought about with Mg in diethyl ether with a yield of 70%:



(10)

The last step of this reaction shows some similarity to the old synthesis of the compound (*61*), where ring closure is effected on $(CH_3)_2SiF—CH_2—Si(CH_2)_2CH_2Cl$, the latter being obtained from $(CH_3)_3SiOSi(CH_3)_2CH_2Si(CH_3)_2CH_2Cl$ by cleavage with $BF_3$.

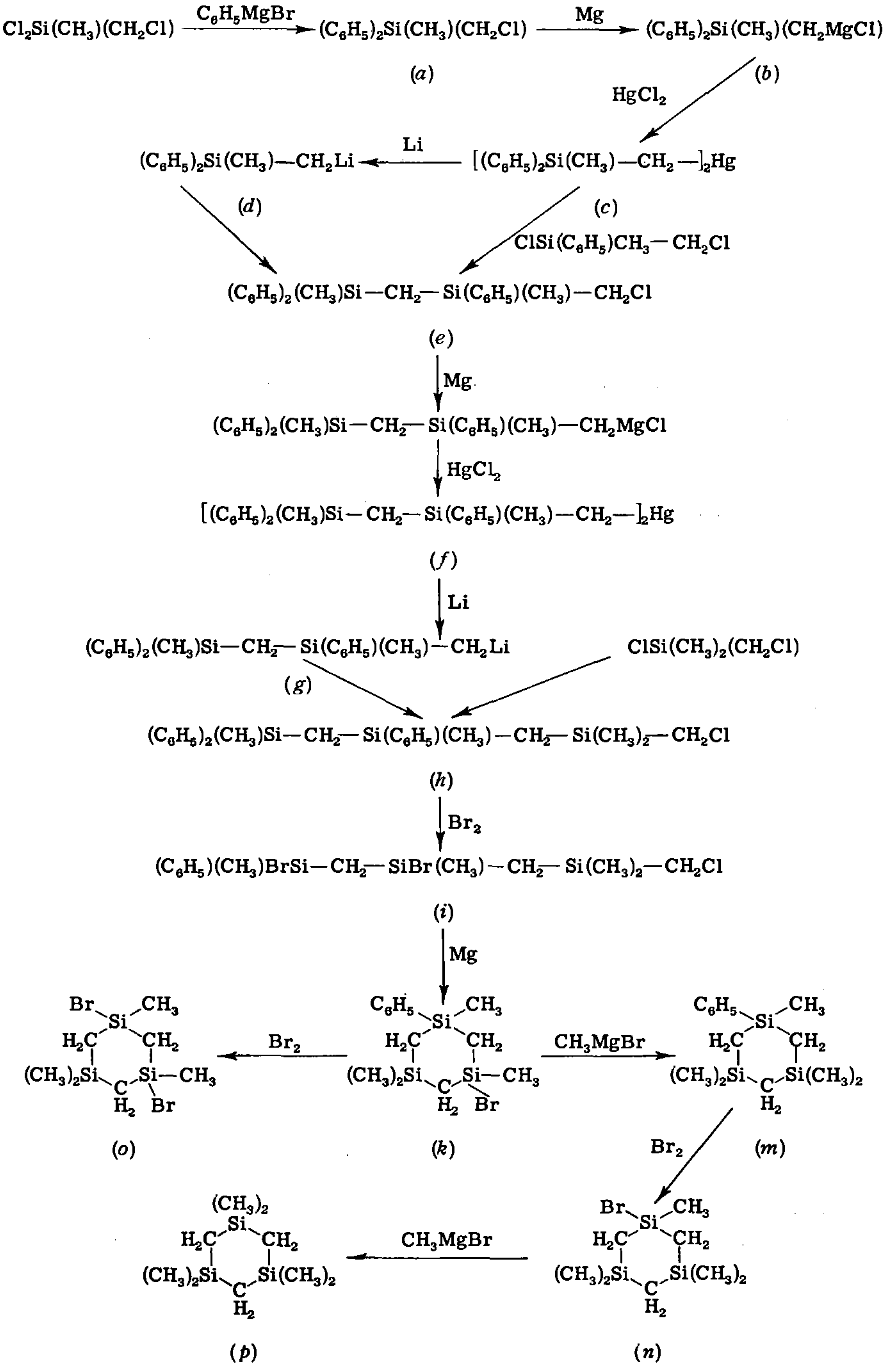
A prerequisite for building up cyclic carbosilanes with functional groups is the preparation of linear carbosilanes with more than two functional groups distributed in the desired way on different Si atoms. A trisilacyclohexane with two Si functional groups has been prepared according to the scheme on page 382 (*42*).

Since cleavage of the $Si—C_6H_5$ groups becomes more difficult as the remaining substituents on this silicon atom become more negative (*39*), only one of the two phenyl groups on the same silicon atom is split off by careful bromination of compound (*h*). Reaction of the resulting

$$(C_6H_5)(CH_3)BrSi—CH_2—SiBr(CH_3)—CH_2—Si(CH_3)_2CH_2Cl \quad (i)$$

with Mg in ether leads to ring closure in which the six-membered ring (*k*) or the four-membered ring (1,3-disilacyclobutane) with a side chain might result. In fact the six-membered ring is less strained and is the only species produced. Various derivatives may be made from (*k*) by making use of the Si functional groups. Some reactions which have been investigated are included in the reaction scheme (*42*).

The cyclic carbosilanes (*k*), (*m*), and (*o*), which are liquid at room temperature, may be separated by distillation; (*o*) crystallizes at −20°C as long transparent needles, (*m*) is transformed to (*n*) by reaction with $Br_2$, and from (*n*) the fully methylated ring (*p*) is made with $CH_3MgBr$. Ring (*p*) is identical with the six-membered ring compound $Si_3C_9H_{24}$ produced by pyrolyzing $Si(CH_3)_4$, a fact which provides further confirmation of the structure proposed. Table VIII summarizes the functional carbosilanes made by the organometallic route.


Cl2Si(CH3)(CH2Cl)
C6H5MgBr
(C6H5)2Si(CH3)(CH2Cl)
(a)
Mg
(C6H5)2Si(CH3)(CH2MgCl)
(b)
HgCl2
Li
(C6H5)2Si(CH3)—CH2Li
(d)
[(C6H5)2Si(CH3)—CH2—]2Hg
(c)
ClSi(C6H5)CH3—CH2Cl
(C6H5)2(CH3)Si—CH2—Si(C6H5)(CH3)—CH2Cl
(e)
Mg
(C6H5)2(CH3)Si—CH2—Si(C6H5)(CH3)—CH2MgCl
HgCl2
[(C6H5)2(CH3)Si—CH2—Si(C6H5)(CH3)—CH2—]2Hg
(f)
Li
(C6H5)2(CH3)Si—CH2—Si(C6H5)(CH3)—CH2Li
(g)
ClSi(CH3)2(CH2Cl)
(C6H5)2(CH3)Si—CH2—Si(C6H5)(CH3)—CH2—Si(CH3)2—CH2Cl
(h)
Br2
(C6H5)(CH3)BrSi—CH2—SiBr(CH3)—CH2—Si(CH3)2—CH2Cl
(i)
Mg
Br2
(o)
(k)
CH3MgBr
(m)
Br2
CH3MgBr
(p)
(n)

## TABLE VIII
### SYNTHETIC FUNCTIONAL CARBOSILANES

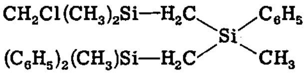
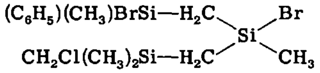
| Substance | B.p. (°C) | Pressure (mm Hg) | Ref. |
|---|---|---|---|
| $(CH_3)_2ClSi-CH_2-Si(CH_3)_2CH_2Cl$ | 88-90 | 12 | *(41)* |
| $(CH_3)(C_2H_5O)_2Si-CH_2-Si(CH_3)_2CH_2Cl$ | 90 | 1 | *(41)* |
| $CH_3(C_2H_5O)_2Si-CH_2-SiCH_3(OC_2H_5)CH_2Cl$ | 106 | 1 | *(41)* |
| $(CH_3)_2C_6H_5Si-CH_2-Si(CH_3)_2CH_2Cl$ | 156-159 | 18 | *(41)* |
| $(CH_3)_2BrSi-CH_2-Si(CH_3)_2CH_2Cl$ | 75-78 | 20 | *(41)* |
| $Cl(CH_3)_2Si-CH_2-Si(CH_3)_2Cl$ | 58 | 11 | *(56)* |
| $H(CH_3)_2Si-CH_2-Si(CH_3)_2H$ | 103-4 | 729 | *(57)* |
| $[(CH_3)_2C_6H_5Si-CH_2]_2Hg$ | 180-182 | 1 | *(41)* |
| $[(C_6H_5)_2CH_3)Si-CH_2]_2Hg$ | (m.p. 32-34)<br>(m.p. 63-65) | – | *(42)* |
| $[(C_6H_5)_2(CH_3)Si-CH_2-Si(C_6H_5)(CH_3)-CH_2]_2Hg$ | Syrup | – | *(42)* |
| $(CH_3)_2C_6H_5SiCH_2Li$ | – | – | *(41)* |
| $(C_6H_5)_2(CH_3)Si-CH_2Li$ | – | – | *(42)* |
| $(C_6H_5)_2(CH_3)Si-CH_2-Si(C_6H_5)(CH_3)-CH_2Li$ | – | – | *(42)* |
| $(C_6H_5)(CH_3)SiCl(CH_2Cl)$ | 105-106 | – | *(42)* |
| $(C_6H_5)_2(CH_3)Si-CH_2-Si(C_6H_5)(CH_3)(CH_2Cl)$ | 185 | 1 | *(42)* |
| $(CH_3)_2C_6H_5Si-CH_2-Si(CH_3)_2-CH_2-Si(CH_3)_2CH_2Cl$ | 160-161 | 1 | *(41)* |
| $(CH_3)_2BrSi-CH_2-Si(CH_3)_2-CH_2-Si(CH_3)_2CH_2Cl$ | 120-122 | 20 | *(41)* |
| $[(CH_3)_2C_6H_5Si-CH_2]_2Si(CH_3)CH_2Cl$ | 188-193 | 1 | *(41)* |
| $[(CH_3)_2BrSi-CH_2]_2Si(CH_3)CH_2Cl$ | 87-90 | 1 | *(41)* |
| $[(CH_3)_2C_6H_5Si-CH_2]_2Si(CH_3)_2$ | 150-151 | 1 | *(41)* |
| $[(CH_3)_2BrSi-CH_2]_2Si(CH_3)_2$ | 78-79 | 1 | *(41)* |
|  $\begin{matrix} CH_2Cl(CH_3)_2Si-H_2C & & C_6H_5 \\ & Si & \\ (C_6H_5)_2(CH_3)Si-H_2C & & CH_3 \end{matrix}$ | – | – | *(41)* |
|  $\begin{matrix} (C_6H_5)(CH_3)BrSi-H_2C & & Br \\ & Si & \\ CH_2Cl(CH_3)_2Si-H_2C & & CH_3 \end{matrix}$ | – | – | *(41)* |
| $Cl(CH_3)_2SiCH_2Si(CH_3)_2CH_2Si(CH_3)_2Cl$ | 114-116 | 12 | *(56)* |
| $Cl(CH_3)_2SiCH_2[Si(CH_3)_2CH_2]_2Si(CH_3)_2Cl$ | 90-92 | 1.8 | *(56)* |
| $Cl(CH_3)_2SiCH_2[Si(CH_3)_2CH_2]_3Si(CH_3)_2Cl$ | 117-118 | 0.08 | *(56)* |
| $H(CH_3)_2SiCH_2Si(CH_3)_2CH_2Si(CH_3)_2H$ | 186 | – | *(57)* |
| $H(CH_3)_2SiCH_2[Si(CH_3)_2CH_2]_2Si(CH_3)_2H$ | 96 | 0.2 | *(57)* |
| $(CH_3)_2BrSiCH_2[Si(CH_3)_2CH_2]_2Si(CH_3)_2CH_2Cl$ | 131-132 | 1 | *(41)* |
| $(CH_3)_2HOSi-C(CH_3)_2-Si(CH_3)_3$ | 90 | 23 | *(64a)* |
| $(CH_3)_2FSi-C(CH_3)_2-Si(CH_3)_3$ | 160 | – | *(64a)* |

TABLE VIII (*Continued*)

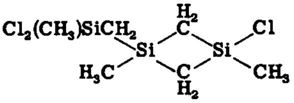
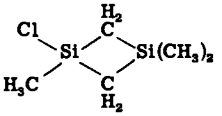
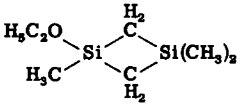
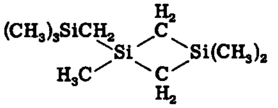
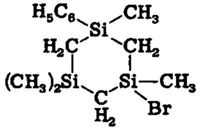
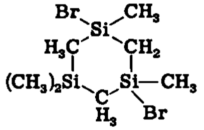
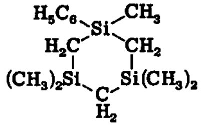
| Substance | B.p. (°C) | Pressure (mm Hg) | Ref. |
|---|---|---|---|
| $(CH_3)_2FSi-C(CH_3)_2-SiF(CH_3)_2$ | 151 | – | (*64a*) |
| $(CH_3)_2FSi-C(CH_3)_2-SiF(CH_3)-C(CH_3)_3$ | 99 | 30 | (*64a*) |
| $(CH_3)_3Si-C(CH_3)_2-SiF(CH_3)-C(CH_3)_3$ | 91 | 13 | (*64a*) |
| $(CH_3)_3Si-C(CH_3)_2-Si(CH_3)_2-C(CH_3)_3$ | 118 | 21 | (*64a*) |
| $(CH_3)_2HSi-C(CH_3)_2-SiH(CH_3)-C(CH_3)_3$ | 100 | 32 | (*64a*) |
| $(CH_3)_2FSi-C(CH_3)_2-Si(CH_3)_2-C(CH_3)_2-SiF(CH_3)_2$ | 125 | 13 | (*64a*) |
| $(CH_3)_3Si-C(CH_3)_2-Si(CH_3)_2-C(CH_3)_2-Si(CH_3)_3$ | 149 | 13 | (*64a*) |
| $(CH_3)_2FSi-C(CH_3)_2-SiF(CH_3)-C(CH_3)_2-SiF(CH_3)_2$ | 115.5 | 13 | (*64a*) |
| $[Cl(CH_3)SiCH_2]_2$ | 59<br>(m.p. - 7 to - 6.5) | 20 | (*62*) |
| $[(C_2H_5O)CH_3SiCH_2]_2$ | 78-79 | 16 | (*62*) |
| $[H(CH_3)SiCH_2]_2$ | 96 | – | (*62*) |
| $[C_6H_5(CH_3)SiCH_2]_2$ | 99 | 1.1 | (*62*) |
|  | 131 | 20 | (*62*) |
|  | 67.5-68 | 59 | (*62*) |
|  | 71 | 40 | (*62*) |
|  | 112.5-113<br>75 | 50<br>10 | (*62*)<br>(*62*) |
| $[Cl(CH_3)SiCH_2]_3$ | 117-118<br>93-94<br>(m.p. 59) | 5<br>2 | (*62*)<br>(*62*) |
| $[(H_5C_2O)(CH_3)SiCH_2]_3$ | 68-69<br>97 | 0.20-0.25<br>1.7 | (*62*)<br>(*62*) |
| $[H(CH_3)SiCH_2]_3$ | 68-71 | 19 | (*62*) |
| $[(C_6H_5)CH_3SiCH_2]_3$ | – | – | (*62*) |

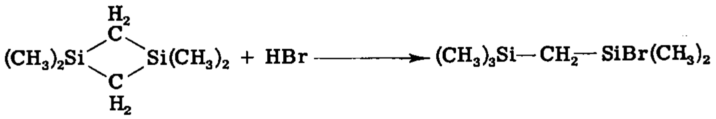
TABLE VIII (*Continued*)

| Substance | B.p. (°C) | Pressure (mmHg) | Ref. |
|---|---|---|---|
|  | 93-95 | 1 | (*42*) |
|  | 90-91 | 1 | (*42*) |
|  | 108-112 | 1 | (*42*) |

## F. REACTIONS OF CARBOSILANES

### 1. *Chemical Properties*

The chemical properties of the Si—C—Si unit in carbosilanes are influenced by the nature of the groups attached to the two silicons and the bridge carbon atom. Complete methylation of the silicon atoms leads in general to compounds which are rather inert. Reactions take place only under extreme conditions (at high temperatures, with strong bases and acids, or on photochlorination) or for strained ring systems. Thus 1,1,3,3-tetramethyl-1,3-disilacyclobutane undergoes ring cleavage with HBr:



$$[(CH_3)_2Si\text{—}CH_2]_2 + HBr \longrightarrow (CH_3)_3Si\text{—}CH_2\text{—}SiBr(CH_3)_2$$

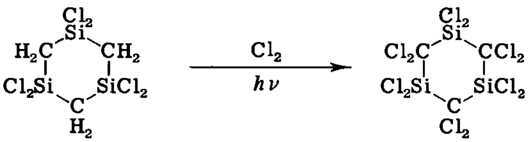
The corresponding six-membered ring (Si-hexamethyl-1,3,5-trisilacyclohexane) does not show this reaction. The compound $[(CH_3)_2Si\text{—}CH_2]_2$ reacts with $AgNO_3$ with separation of metallic silver (*40*, *61*, *69*) and polymerizes when heated to 300°C (1.5 hour, 400 lb/sq. in.) to give $[(CH_3)_2Si\text{—}CH_2]_x$ ($x \sim 200$) (*61*).

### 2. *Photochlorination*

Photochlorination leads to attack of CH groups in the carbosilane and, under carefully controlled conditions, it is possible to restrict radical attack to this group. Degradation of the Si—C—Si structure is thus largely avoided (*48, 49, 50, 70*). As in the case of the alkyl monosilanes, chlorination proceeds as far as steric considerations will allow. Intermediate chlorinated products can be isolated only in a few cases. Thus the following reactions are observed:

$$Cl_3Si{-}CH_2{-}SiCl_3 \xrightarrow[h\nu]{Cl_2} Cl_3Si{-}CCl_2{-}SiCl_3$$

$$Cl_3Si{-}CH_2{-}SiCl_2{-}CH_2{-}SiCl_3 \xrightarrow[h\nu]{Cl_2} Cl_3Si{-}CCl_2{-}SiCl_2{-}CCl_2{-}SiCl_3$$



The partially chlorinated compound $(Cl_3Si{-}CHCl)_2SiCl_2$ has been isolated from the product of photochlorination of $(Cl_3SiCH_2)_2SiCl_2$ without a solvent (*49*). Compounds which are chlorinated on carbon are less stable than the parent substance with C—H bonds. Thus the Si—C bond is relatively easily cleaved by hydrolysis: for example, $(Cl_3Si)_2CCl_2$ gives $CH_2Cl_2$ quantitatively in neutral aqueous solution (*50*). Reaction of $(SiCl_2{-}CCl_2)_3$ with a 3% solution of NaOH in a water-propanol mixture at the boiling point is also quantitative within 2 hours:

$$(SiCl_2{-}CCl_2)_3 + 6NaOH + 6H_2O \rightarrow 3Si(OH)_4 + 6NaCl + 3CH_2Cl_2$$

This degradation has been used as evidence for the ring structure (*48*). In concentrated alkali solutions the C—Cl bond is also cleaved to yield $Cl^-$ ions.

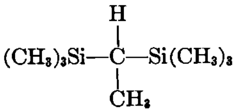
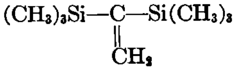
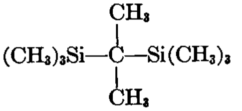
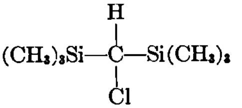
### 3. *Reactions of Perchlorinated Carbosilanes with* $CH_3MgCl$ *and* $LiCH_3$

Methylation of the SiCl group in C-chlorinated chloromethyl monosilanes with $CH_3MgCl$ or $LiCH_3$ gives the corresponding methyl derivatives in high yield, as is shown by the methylation of $(CH_3)_2ClSiCHCl_2$ to $(CH_3)_3SiCHCl_2$ by $CH_3MgCl$. Side reactions of the C-chlorinated group are of very minor importance in such cases but, with C-chlorinated carbosilanes, reaction no longer follows this relatively simple course. Instead, a number of reactions occur, leading to various products.

When $(Cl_3Si)_2CCl_2$ is methylated with $CH_3M$ (M = MgCl or Li), the Si-methylated compound $[(CH_3)_3Si]_2CCl_2$ cannot be isolated from the reaction mixture, even in small amounts (*51*). Instead, the compounds shown in Table IX are obtained.

TABLE IX

REACTION OF $(Cl_3Si)_2CCl_2$ WITH $CH_3MgCl$ AND $LiCH_3$

| Reaction product | Reaction with | |
|---|---|---|
| | $CH_3MgCl$ | $LiCH_3$ |
| $(CH_3)_3Si—CH_2—Si(CH_3)_3$ | 2.5[a] | 5[a] |
|  $(CH_3)_3Si—\overset{H}{\underset{CH_3}{C}}—Si(CH_3)_3$ | 2.1 | 23 |
|  $(CH_3)_3Si—\underset{CH_2}{\underset{\Vert}{C}}—Si(CH_3)_3$ | 84.6 | 3 |
|  $(CH_3)_3Si—\overset{CH_3}{\underset{CH_3}{C}}—Si(CH_3)_3$ | 2.3 | 25 |
|  $(CH_3)_3Si—\overset{H}{\underset{Cl}{C}}—Si(CH_3)_3$ | 2.2 | 28 |

[a] Mole% of reaction product.

Formation of these products may be explained in terms of the reaction scheme shown in Table X. Stepwise methylation of the SiCl group in $(SiCl_3)_2CCl_2$ first occurs, reaction (1). Product (I) is, however, never isolated as the CCl group reacts with the organometallic compound either during the methylation of the SiCl groups or after (I) has been formed. This reaction (2) gives (II) and $MgCl_2$. (III) is formed from (II) by splitting off HCl under the conditions used for the reaction with $CH_3MgCl$. This HCl reacts with $CH_3MgCl$ to give $CH_4$. A side reaction (4) between (II) and $CH_3MgCl$ yields (IV) and $MgCl_2$.

Formation of $[(CH_3)_3Si]_2CHCH_3$, $[(CH_3)_3Si]_2CH_2$, and $[(CH_3)_3Si]_2CHCl$ is less readily understood. The occurrence of the $[(CH_3)_3Si]_2CH$ group is not attributable to metallation followed by hydrolysis.

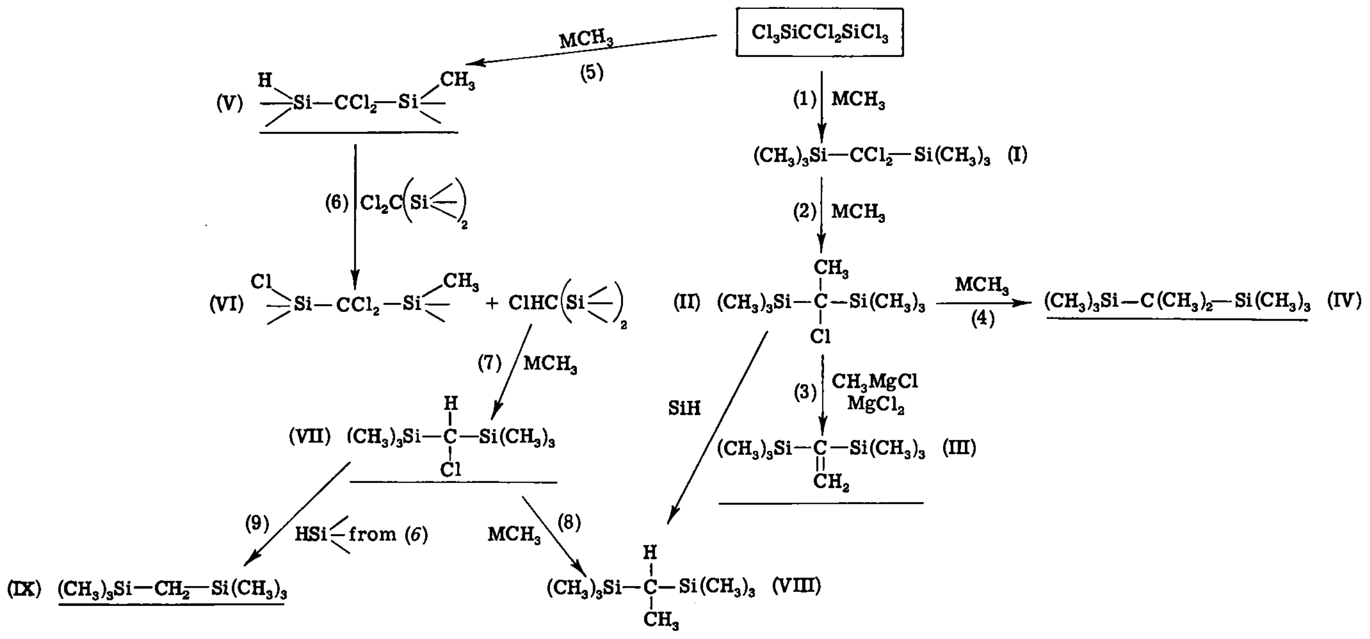
$$[(CH_3)_3Si]_2CCl_2 + CH_3MgCl \rightarrow [(CH_3)_3Si]_2CCl—MgCl + CH_3Cl$$

The results may be interpreted in two ways:

(a) By supposing that interaction of $(Cl_3Si)_2CCl_2$ with the organometallic compound involves not only methylation of the SiCl group (reac-

## TABLE X

REACTION OF $(Cl_3Si)_2CCl_2$ WITH $MCH_3$[a,b]



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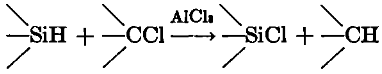
[a] M = MgCl, Li.

[b] The compounds isolated are underlined.

tion 1) but also conversion to the SiH group (reaction 5). The observed formation of ethylene is accounted for in this way. Since SiH groups are known to react with CCl groups according to the equation (*103*):



$$\equiv\text{SiH} + \equiv\text{CCl} \xrightarrow{\text{AlCl}_3} \equiv\text{SiCl} + \equiv\text{CH}$$

a similar reaction (6) may occur in the presence of Mg salts leading to compounds of type (VI). These will then react with $CH_3MgCl$ to give (VII). Compounds (VIII) and (IX) may be explained similarly.

(b) Compounds with the CH group between the two Si atoms (VII–IX) may also be formed by direct reactions between the $CCl_2$ group in $(Cl_3Si)_2CCl_2$ with the organometallic compound. Polyhalogeno compounds of carbon react similarly with organometallic compound. The changes which occur are complicated, but hydrocarbons result (e.g., $CCl_4$ with $C_2H_5MgBr$ gives $CH_4$ and $C_2H_4$) (*8*).

In the reactions between $(Cl_3Si)_2CCl_2$ and $CH_3MgCl$ or $LiCH_3$, the same products are produced in different amounts (Table IX). This is attributable to differences in behavior of (II) with the two reagents. Formation of methane in the reaction with $CH_3MgCl$ may be explained if formation of (III) from (II) occurs in the presence of Mg salts, HCl being split off. This reaction is suppressed when $LiCH_3$ is used in favor of the side reactions 4, 7, and 8 and, as a result, little methane is then formed. The product from $(Cl_3Si)_2CCl_2$ with $n$-$C_3H_7MgCl$ is $[(C_3H_7)_3Si]_2CH_2$ (88%).

In the reaction between $CH_3MgCl$ and $(Cl_3Si{-}CCl_2)_2SiCl_2$ under similar conditions nine compounds are formed, none of which contains chlorine or ethylenic groups. The main product is $(CH_3)_3Si{-}CH_2{-}Si(CH_3)_2{-}CH_2{-}Si(CH_3)_3$. The cyclic compound $(SiCl_2{-}CCl_2)_3$ also yields nine compounds with $CH_3MgCl$, among them being $[Si(CH_3)_2{-}CH_2]_3$. The main product, however, is $Si_3C_{12}H_{24}$, the structure of which is unknown, although it contains an ethylenic group (*49*).

### *4. Rearrangement Reactions*

Methylation of the SiCl group in simple alkyl chlorosilanes with organolithium compounds or $CH_3MgCl$ occurs without effect on the Si—C bonds in the molecule. When, however, $(Cl_3Si)_2CH{-}CH_3$ is treated with $CH_3MgCl$ (100% excess) (*44*), the product is $[(CH_3)_3Si]_2CH{-}CH_3$ together with 18% of the isomer $(CH_3)_3Si{-}CH_2{-}CH_2{-}Si(CH_3)_3$. Formation of the 1,2 isomer seems to be directly associated with the methylation of the SiCl groups. Thus when the chlorosilane has been added to the Grignard solution the ratio of the two isomers remains constant even after warming to 100°–120°C for 72 hours. It is also found that, when pure $[(CH_3)_3Si]_2CH{-}CH_3$

is warmed under the same conditions with the reaction components, no formation of the 1,2 isomer can be detected. Interaction of $(Cl_3Si)_2CH—CH_3$ with $LiCH_3$ (30% excess) also gives the two isomers $[(CH_3)_3Si]_2CH—CH_3$ and $(CH_3)_3Si—CH_2—CH_2—Si(CH_3)_3$ in a total yield of 40%. Four other compounds are also formed which have not been identified. Methylation of $Cl_3Si—CH_2—CH_2—SiCl_3$ likewise gives a mixture of isomers (*91*):

$$Cl_3Si—CH_2—CH_2—SiCl_3 + CH_3MgX \rightarrow [(CH_3)_3Si]_2CH—CH_3 + (CH_3)_3Si—CH_2—CH_2—Si(CH_3)_3$$

### 5. *Reactions of the Si Functional Groups*

Si functional groups in carbosilanes (e.g., SiH, SiOR, $SiC_6H_5$, and SiHal) show the same characteristic reactions as in the monosilanes (*17a*). The reaction with bases has been examined in several cases (*30, 31*). Thus $(CH_3)_2HSiCH_2Si(CH_3)_3$ yields hydrogen quantitatively, whereas the highly condensed cyclic carbosilane $Si_7C_{18}H_{46}$ is hardly attacked, presumably because of steric effects. Halogens yield the corresponding halogen derivatives. In the absence of steric effects this reaction may be used in the quantitative determination of Si—H bonds (*41b*).

The SiOR group reacts with acetyl chloride to form the corresponding SiCl carbosilane (*41*), but treatment with hydriodic acid results in cleavage of alkyl iodide. This is quantitative and may be used in determining SiOR groups (*41a*). $Si—C_6H_5$ groups are cleaved by hydrogen halides and halogens in the normal way (*39, 41, 98*), and in many cases it is possible to modify the reaction with $Br_2$ so that it can be used to determine Si-phenyl groups quantitatively (*41b*). The importance of this reaction for synthetic purposes is discussed elsewhere (subsection D).

The Si-halogen carbosilanes are the most important group of Si-functional compounds because of their reactivity. With organo compounds of Mg or Li they readily undergo alkylation or arylation, and are also converted to alkoxy or aryloxy carbosilanes by alcoholysis or treatment with alcoholates. This has yielded a large number of derivatives, particularly of the simpler carbosilanes such as 1,3-disilapropane or 1,3,5-trisilacyclohexane. Hydrolysis of the Si-halogenated carbosilanes is quantitative in most cases, hydrogen halide being split off to leave a residue of silanol or siloxane. In some instances the sensitivity to hydrolysis is much reduced, presumably because of steric effects (*33, 66*). It is not possible to discuss the reactions mentioned in this section in greater detail within the scope of this article.

When the Si-halogenated carbosilanes are treated with $LiAlH_4$ the corresponding SiH compounds are formed. This route has yielded $H_3Si—CH_2—SiH_3$, $H_3Si—CH_2—SiH_2—CH_2—SiH_3$, and $(SiH_2—CH_2)_3$, which may be regarded as the parent substances of the family of carbosilanes. In the cases studied, reduction takes place without change in the basic structure of the molecule (*21*, *37*, *83a*). The molecular dimensions of $(SiH_2—CH_2)_3$ have been determined by electron diffraction (Si—H, 1.42 Å; Si—C, 1.86 Å; C—Si—C and Si—C—Si, 109.5°) (*15*).

Perchlorinated carbosilanes are also reduced by $LiAlH_4$, only the SiCl groups being converted to SiH. Thus, for example, $(Cl_3Si)_2CCl_2$ gives $(H_3Si)_2CCl_2$ (*47*), which is not spontaneously inflammable in air, although it decomposes explosively when warmed gently even in absence of air. This compound is considerably less stable than $(H_3Si)_2CH_2$ and $(Cl_3Si)_2CH_2$, which is in keeping with the bond energy values (Si—H, 75; Si—Cl, 91; C—H, 99; C—Cl, 81 kcal/mole) (*11*).

### 6. *Influence of Double Bonds on Bridge Carbon Atoms of the Si—C—Si Skeleton*

The compounds $[(CH_3)_3Si]_2C{=}CH_2$ and $R_3Si—CH{=}CH_2$ differ in the reactions with halogens and hydrogen halides (*43*). Compounds such as $R_3SiCH{=}CH_2$ or $Cl_3SiCH_2{=}CH_2$ add halogen to the double bond (*96*):

$$(CH_3)_3SiCH{=}CH_2 + X_2 \rightarrow (CH_3)_3SiCHX—CH_2X$$

On the other hand, treatment of $[(CH_3)_2Si]_2C{=}CH_2$ with $Cl_2$ at −20°C or with $Br_2$ at −60°C in a 1:1 molar ratio results in cleavage of the molecule. The products are $(CH_3)_3SiCl$ and $(CH_3)_3SiCCl{=}CH_2$ or $(CH_3)_3SiBr$ and $(CH_3)_3SiCBr{=}CH_2$ (*43*). Cleavage by halogen occurs so readily that the addition reaction is not observed.

Reaction with hydrogen halides follows a similar course. Compounds such as $(CH_3)_3SiCH{=}CH_2$ or $(CH_3)_3SiCH{=}C(CH_3)_2$ add HBr across the double bond (*79*, *96*), e.g.

$$(CH_3)_3SiCH{=}C(CH_3)_2 \xrightarrow{HBr} (CH_3)_3SiCH_2—CBr(CH_3)_2$$

whereas $[(CH_3)_3Si]_2C{=}CH_2$ at −70°C undergoes the reaction (*43*):

$$[(CH_3)_3Si]_2CCH_2 + HBr \rightarrow (CH_3)_3SiBr + (CH_3)_3SiCHCH_2$$

Reaction with HI is appreciably slower, but here also cleavage occurs under these reaction conditions and there is no addition at the double bond (*43*).

## III. Spectroscopic Investigation of Carbosilanes

### A. MASS SPECTRA

Mass spectra of various groups of carbosilanes have been investigated to supplement the information gained from chemical studies (*52*). The first

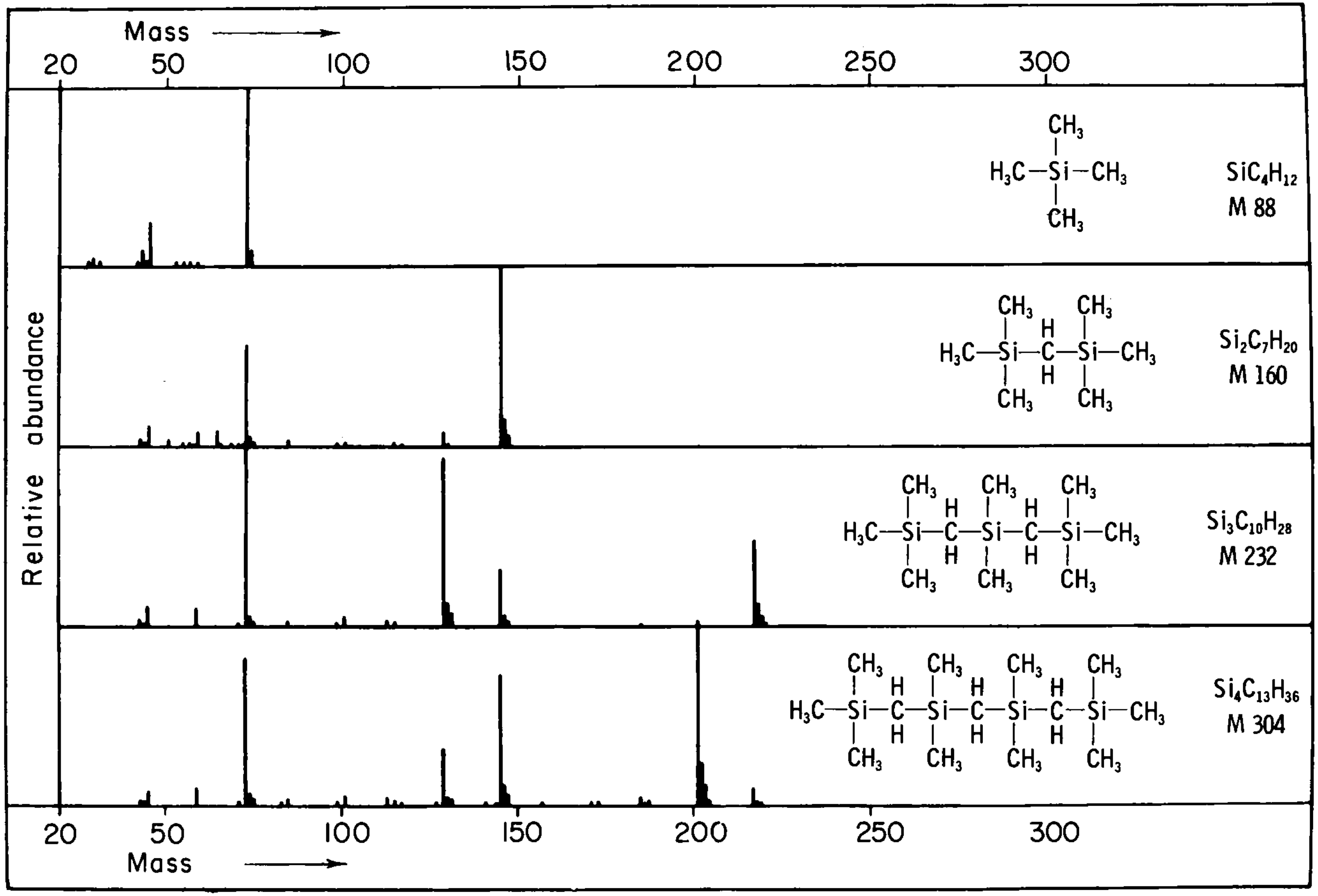


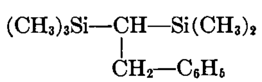
FIG. 2. Mass spectra of $Si(CH_3)_4$, $[(CH_3)_3Si]_2CH_2$, $[(CH_3)_3Si—CH_2—]_2Si(CH_3)_2$, and $[(CH_3)_3Si—CH_2—Si(CH_3)_2]_2CH_2$.

such group comprised $Si(CH_3)_4$ and related linear compounds with two, three, and four fully methylated silicon atoms. These were compared with the simple cyclocarbosilanes with two, three, and four Si atoms (4-, 6-, and 8-membered rings). The third group of mass spectra relates to linear SiH-containing carbosilanes, the fourth to SiH-containing cyclic carbosilanes, and the fifth to compounds with two Si atoms, which are derived from $[(CH_3)_3Si]_2CH_2$ by substitution for the H atoms in the $CH_2$ group between the two Si atoms. In addition, the spectra of

$$(CH_3)_3SiCH_2CH_2Si(CH_3)_3$$

$$[(C_2H_5)_3Si]_2CH_2$$

$$[(C_2H_5)_3Si]_2CH \cdot C_2H_5$$



$$\begin{array}{c}(CH_3)_3Si\text{—}\underset{\displaystyle CH_2\text{—}C_6H_5}{\underset{|}{CH}}\text{—}Si(CH_3)_2\end{array}$$

are recorded.

Figures 2 and 4–7 show the percentage abundance of the masses referred to the most abundant species observed. This is, for example, 73 in the case of $Si(CH_3)_4$ and $[(CH_3)_3Si\text{—}CH_2]_2Si(CH_3)_2$, 145 (molecular mass − 15) for $[(CH_3)_3Si]_2CH_2$, and 201 (molecular mass − 103) for the Si-methylated compound $[(CH_3)_3Si\text{—}CH_2\text{—}Si(CH_3)_2]_2CH_2$. The mass numbers and percentage abundances of the ions from the linear compounds are summarized in Fig. 2. The ions which occur result, as a rule, from cleavage of the Si—C bond. Both $CH_2Si(CH_3)_3$ and $CH_3$ groups are split off and this will account for the greater part of the observed masses. For the mass spectra from carbosilanes of the general formula $Si_nC_{3n+1}H_{8n+4}$, the most abundant masses of the ions formed may be represented by:

$$(A) \qquad P - Si_mC_{3m+1}H_{8m+3} \qquad (m = 0, 1, 2 \ldots n - 1)$$

$$(B) \qquad P - Si_mC_{3m+2}H_{8m+7}$$

(where $P$ = the mass of the molecule ion). The remaining masses are made up predominantly of the rearrangement ions SiH, $SiH_3$, $H_2SiCH_3$, and $HSi(CH_3)_2$, which give masses of 29, 31, 45, and 59. More than 96% of all the observed ions are accounted for in this way. The mass spectrum of $Si(CH_3)_4$ has already been described (*13*). The reported results agree with later measurements, although ions of mass 45 are more abundant than those of mass 43.

Figure 3 shows the abundances of the fragments formed from $Si(CH_3)_4$ and from the linear compounds when the same group is split off. It is seen that the abundances of masses $P - 15$, $P - 87$, and $P - 159$ (where $P$ = mass of the molecule ion) decrease steadily from $Si(CH_3)_4$ ($M = 88$)

to $[(CH_3)_3SiCH_2—Si(CH_3)_2]_2CH_2$ ($M$ = 304). Loss of mass 15 (= $CH_3$) or 87 [= $CH_2Si(CH_3)_3$] from series of breakdown products corresponds with degradation series *A* (above). The change in abundance of the most important masses 73, 145, 217, 289 (degradation series *A*) in the spectrum of the homologous series of compounds may be seen in Fig. 3.

Figure 4 shows the mass spectra of the cyclic compounds (*52*). In the case of the 6-membered ring, loss of the $CH_3$ ion first occurs, leaving the fragment ($P$ − 15) with the ring intact as the most abundant species (*6*). All the other masses of high abundance can be explained in terms of

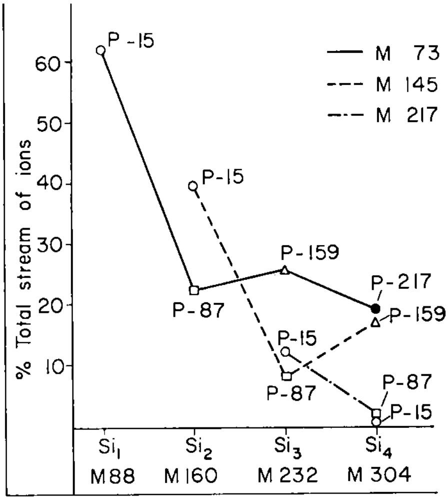


FIG. 3. Comparison of the abundance of masses with molecular mass − $x$ = ($P$ − $x$) in the compounds $Si(CH_3)_4$, $[(CH_3)_3Si]_2CH_2$, $[(CH_3)_3Si—CH_2—]Si(CH_3)_2$, and $[(CH_3)_3Si—CH_2—Si(CH_3)_2]_2CH_2$, as well as the abundance of masses 73, 145, 217, and 289 in these compounds. The abundance is related to the total stream of ions.

fragmentation of the ring. Spectra of the cyclic compounds differ characteristically from those of linear molecules with the same number of Si atoms. The cyclic compounds are more stable under electron impact than are the linear structures, and this is shown by the relatively greater abundance of masses associated with the intact 4-, 6-, or 8-membered ring. Thus the proportion of ions in the total ion stream with an intact 8-membered ring structure (27.5%) is considerably larger than for the intact chain from 1,1,1,3,3,5,5,7,7,7-decamethyl-1,3,5,7-tetrasilaheptane (0.6%). In the case of the 6-membered ring, ions with the complete basic structure account for 58% of the total ion current, whereas the value is about 18% for the corresponding chain (1,1,1,3,3,5,5,5-octamethyl-1,3,5-trisilapentane (*7*, *24*).

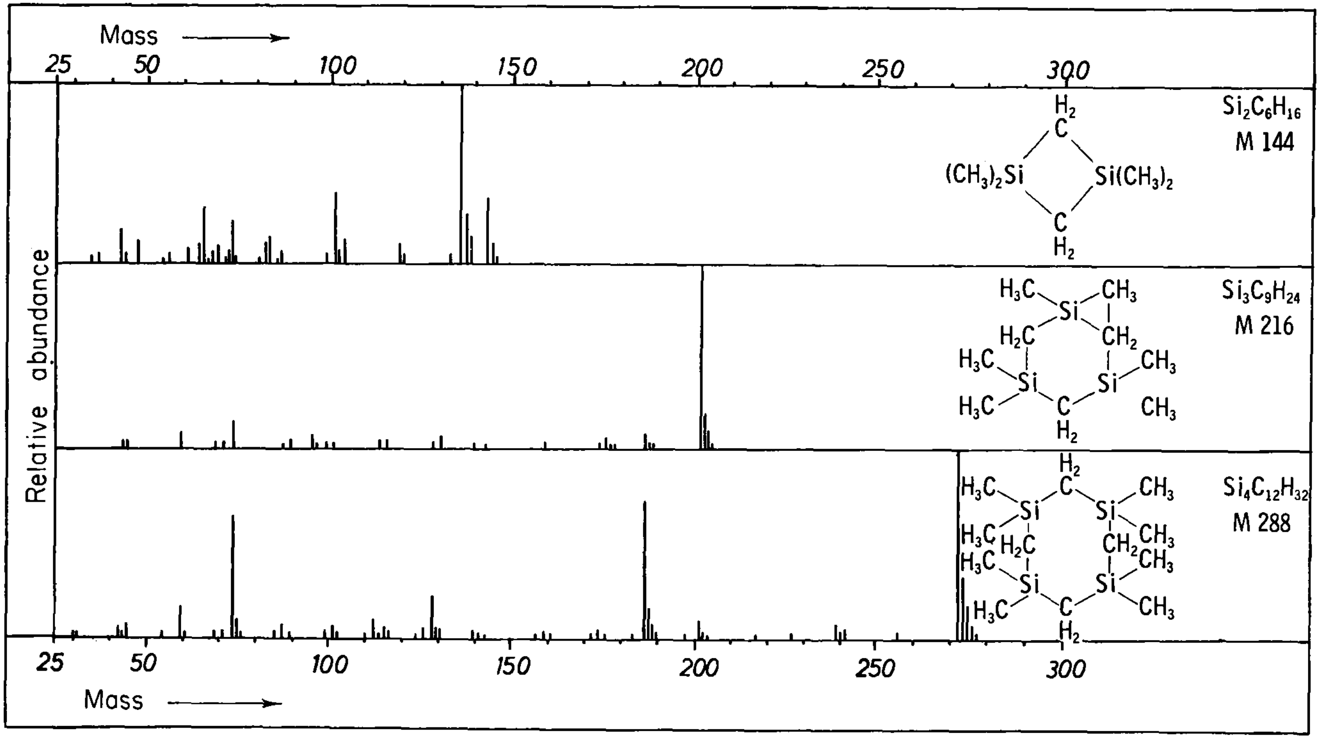


Fig. 4. Mass spectra of Si-methyl cyclocarbosilanes $[Si(CH_3)_2—CH_2]_2$, $[Si(CH_3)_2—CH_2]_3$, and $[Si(CH_3)_2—CH_2]_4$.

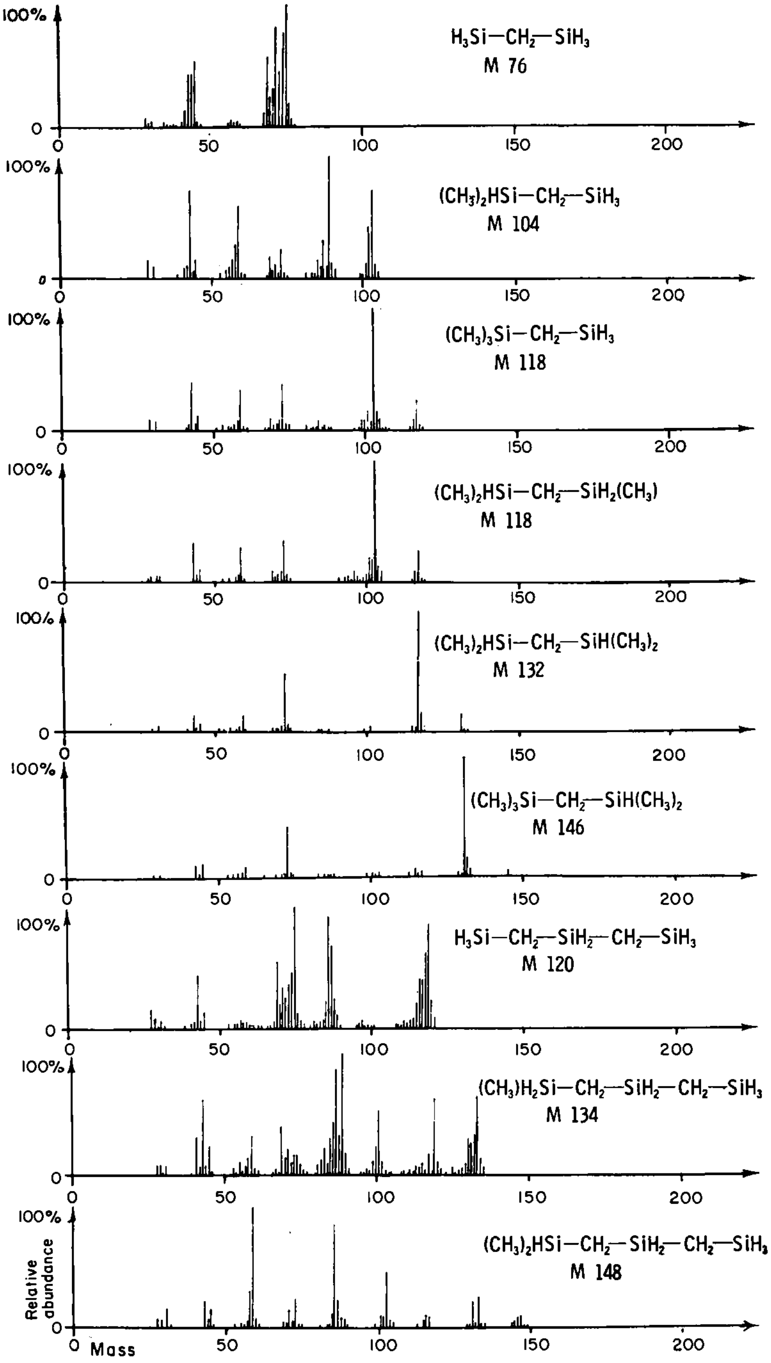


FIG. 5. Mass spectra of SiH-containing carbosilanes.

Figures 5 and 6 show the mass spectra of linear and cyclic carbosilanes containing SiH groups. The most striking difference between carbosilanes with SiH and $SiCH_3$ groups is that, as the hydride content increases, the mass spectrum becomes richer in lines. With methylated compounds, ions are formed almost exclusively by cleavage of Si—C bonds (mass lines single, apart from isotope effects, with a minimum separation of 14 mass units). On the other hand, ions are formed from molecules with Si—H bonds by

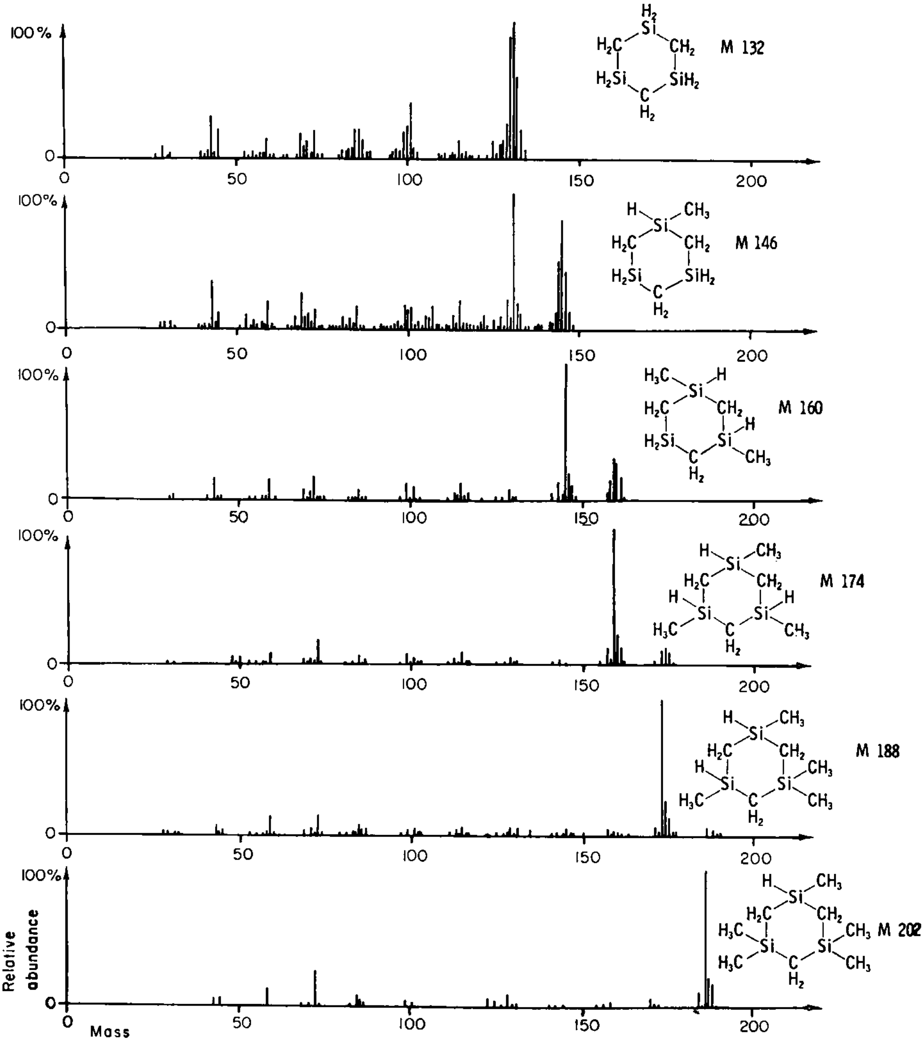


Fig. 6. Mass spectra of SiH-containing cyclocarbosilanes.

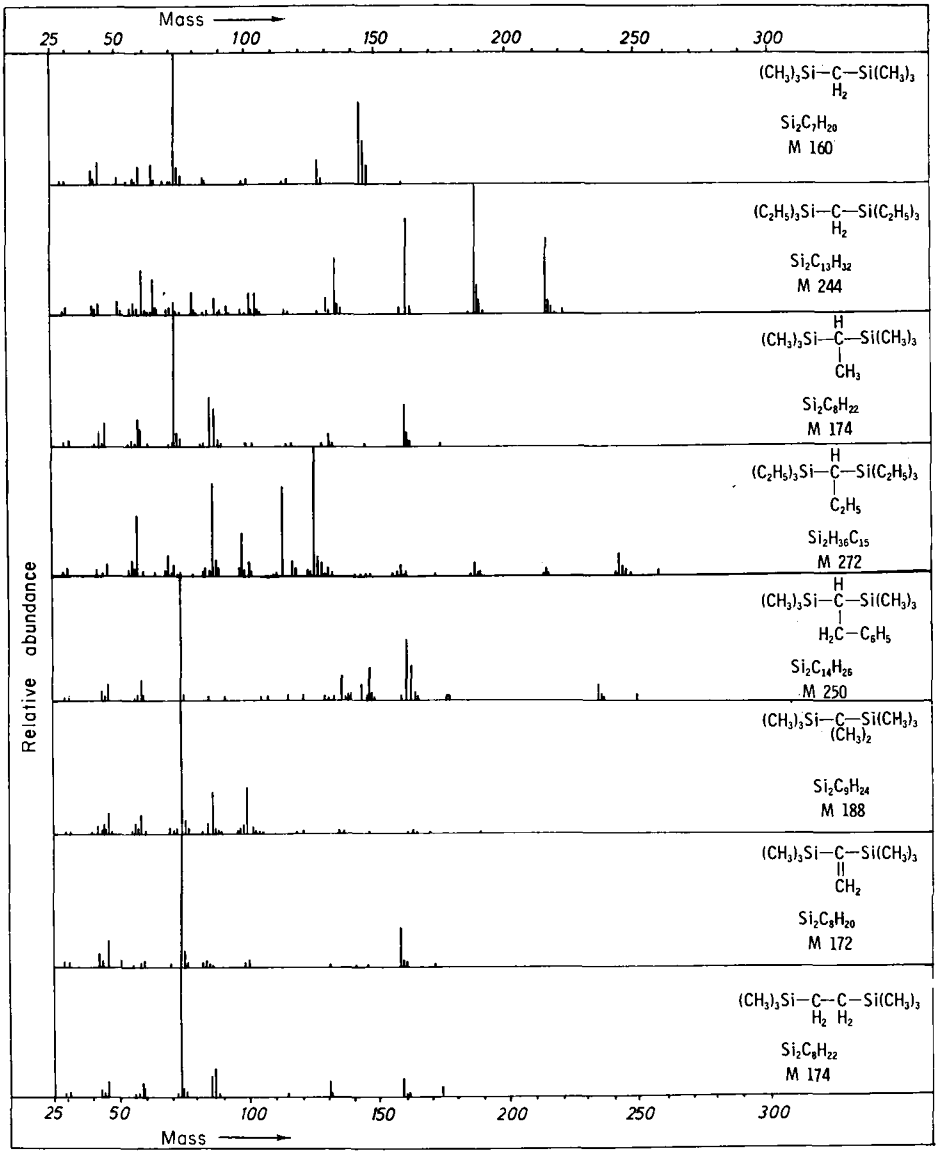


FIG. 7. Mass spectra of carbosilanes with two Si atoms.

cleavage of one or more Si—H bonds as well. Thus the fully hydrogenated chain $H_3SiCH_2SiH_3$ will give all the ions from $Si_2CH_7^+$ to $Si_2C^+$ with an appreciable intensity, and it is clear that the hydrogen atoms attached to carbon are also split off.

The ion of mass 73, $Si(CH_3)_3^+$, which is characteristic for Si-methylated compounds, carries a decreasing proportion of the total ion current as the hydride content of the molecule is increased. In the full hydrogenated chain an ion of this mass does indeed occur, but it has the composition $Si_2CH_5^+$. With decrease in the number of Si-methyl groups in the molecule there is a systematic change in the relative intensities of the ions of mass $(P - 15)$ and $(P - 1)$ ($P$ = mass of molecule), formed by splitting off $CH_3$ or H. Whereas no $(P - 1)$ ions are detected for a fully *Si*-methylated chain, the $(P - 15)$ peak is missing in the mass spectrum of the fully Si-hydrogenated compound. The transition between these two extremes is continuous, the probability of formation of the $(P - 15)$ and $(P - 1)$ ions being in roughly the ratio 5:1. This means that the occurrence of these two species will be about the same for a compound with five Si—H groups and one $Si—CH_3$ group. The same results are obtained from a study of the mass spectra of ring compounds, differences and similarities between the ring with various SiH contents corresponding with those for the chain compounds.

The observed difference between the spectra of fully methylated chains and rings with respect to the relative frequencies of ions with a complete basic structure (the complete structure being more abundant in ions from the cyclic compounds) seems at first sight not to apply as the number of SiH groups is increased. If, however, the proportion of ions of this type in the total ion current is considered for these various compounds, it is seen that the stability of the basic structure is not appreciably altered by replacing $Si—CH_3$ by Si—H groups.

Figure 7 shows the mass numbers of ions in the mass spectra of $[(CH_3)_3Si]_2CH_2$, $[(CH_3)_3Si]_2CH(CH_3)$, $[(CH_3)_3Si]_2CH—CH_2—C_6H_5$, $[(CH_3)_3Si]_2C(CH_3)_2$, $[(C_2H_5)_3Si]_2CH_2$, $[(C_2H_5)_3Si]_2CH(C_2H_5)$, $[(CH_3)_3Si]_2C{=}CH_2$ and $(CH_3)_3Si—CH_2—CH_2—Si(CH_3)_3$ with their percentage abundance (52). Here also the nature of the ions produced is determined primarily by cleavage of the Si—C bond. The influence of substituents on the C atom between the two Si atoms on the stability of the Si—C—Si group may be recognized in the spectra. In the case of $[(CH_3)_3Si]_2CH_2$ the most abundant mass results from cleavage of a $CH_3$ group from the parent molecule, whereas in $[(CH_3)_3Si]_2CHCH_3$, $[(CH_3)_3Si]_2{\cdot}CH{\cdot}CH_2{\cdot}C_6H_5$, and $[(CH_3)_3Si]_2C(CH_3)_2$ it stems from breakup of the main structure to form $Si(CH_3)_3$ ions. Considering the ions which are left after cleavage of a $CH_3$ group from the parent molecule, the abundance ratio for the various compounds is:

$$[(CH_3)_3Si]_2CH_2:[(CH_3)_3Si]_2CH{\cdot}CH_3:[(CH_3)_3Si]_2CHCH_2C_6H_5:[(CH_3)_3Si]_2C(CH_3)_2 = 85.7:16.4:7.2:1$$

(referred to mass 73 as 100).

The abundance of all masses with the unchanged basic structure of the parent molecule decreases in a similar manner. The same picture is obtained for the two ethylated compounds. From this it follows that the stability of the basic skeleton decreases with substitution on the C atom between the two Si atoms. On comparing the spectra of $[(C_2H_5)_3Si]_2CH_2$ and $[(CH_3)_3Si]_2CH_2$, it is found that ions with the complete skeleton are more abundant for the ethyl than for the methyl compound in a ratio of 1.3:1. The ethyl compound is thus more stable than the methyl compound, which is also the case for ethyl and methyl chlorosilanes (*92*). It is notable that the most abundant masses in the spectrum of the ethyl compound are formed by addition of H atoms following cleavage of ethyl groups ("rearrangement ions"). Comparison of the mass spectra of the isomers $[(CH_3)_3Si]_2CH{\cdot}CH_3$ and $(CH_3)_3SiCH_2{\cdot}CH_2{\cdot}Si(CH_3)_3$ shows that these two molecules may be differentiated in this way. When the spectra of $[(CH_3)_3Si]_2CH_2$ and $(CH_3)_3Si{-}CH_2{-}CH_2{-}Si(CH_3)_3$ are compared, one can also see the difference in stability of compounds in which two Si atoms are linked either by one or by two $CH_2$ groups. Masses associated with the intact skeleton are most abundant for $[(CH_3)_3Si]_2CH_2$, the value relative to that for the corresponding products from $(CH_3)_3Si{-}CH_2{-}CH_2{-}Si(CH_3)_3$ being in the ratio 1:0.5. Thus the stability decreases when the two $Si(CH_3)_3$ groups are separated by two $CH_2$ groups rather than one.

The spectrum of $[(CH_3)_3Si]_2C{=}CH_2$ differs from the others in that the molecule ion gives the most abundant mass, showing the greater stability of compounds with a double bond. This effect is also found in the spectra of $(CH_3)_3SiCH{=}CH_2$ and $C_6H_5Si(CH_3)_3$. It is seen from the above that the different types of compound studied have characteristic mass spectra, which also reveal the influence of substituents on the stability of the structure. Mass spectrographic investigations offer a route to the analysis of mixtures of such compounds and yield valuable information relating to other questions.

## B. NMR Spectra

Nuclear magnetic resonance (NMR) investigations on carbosilanes have so far been limited in scope. They have dealt exclusively with the study of proton magnetic resonance (PMR) and no direct measurements of the $C^{13}$ and $Si^{29}$ resonances of these compounds have been made, except in the case of $Me_3SiCH_2SiMe_3$ (*59*). The work done so far on $H^1$ resonance spectra shows that this approach is valuable in elucidating the structures of carbosilanes. Systematic investigations, which were first conducted on compounds of known structure to provide basic data and then used to determine the structure of unknown carbosilanes, have also demonstrated that interesting information may be obtained on bonding in these compounds.

Proton magnetic resonance spectra of SiH-free carbosilanes are very simple (*18*, *40*) and correspond with predictions for compounds of known structure. If there is no C—C bond in the substituents of the Si—C structure, equivalent CH groups give only one sharp resonance signal. It has proved impossible so far to detect splitting of the main resonances by $H^1 - H^1$ coupling between CH groups which are linked through an Si atom, even with a resolving power of <0.5 cycle/sec. Maxima are, however, somewhat broadened in some cases relative to cyclohexane or tetramethyl silane. On both sides of the main absorption lines, resonance lines occur as satellites due to spin-spin coupling between the protons and both the magnetic isotope $Si^{29}$ (spin $\frac{1}{2}$) in the $Si^{29}CH$ group and the magnetic isotope $C^{13}$ (spin $\frac{1}{2}$) in the $C^{13}H$ group. Their areas relative to the main signal correspond with the natural abundances of the two isotopes ($Si^{29} \sim 4.7\%$, $C^{13} \sim 1.1\%$) (*84*, p. 480). In some cases the position of these satellites could not be measured as they were hidden by other resonance signals. Unlike the main resonances, the satellites under high resolution (<0.5 cycle/sec) do not always consist of a single line but show either structure or line broadening relative to the main signal. The significance of these satellite lines for the analysis of PMR spectra and for elucidating the structure of unknown carbosilanes will be more fully discussed later. Chemical shifts and coupling constants for the SiH-free carbosilanes which have been examined so far are collected in Table XI. The assignments may be made without difficulty on the basis of the relative positions of the signals and their integrated areas. The latter show good agreement in all cases with expected values.

A number of regularities are apparent from the spectra. Thus $SiCH_2Si$ groups may be distinguished quite readily from SiMe groups. Substitution of a proton of the $SiCH_3$ group by a further silyl group displaces the proton resonance of the bridge $CH_2$ group to higher field relative to the SiMe group. This is true only for halogen-free carbosilanes. If the two silyl groups bonded to the $CH_2$ bridge are substituted with halogen, the influence of the electronegative substituent is greater on the $CH_2$ group (two Si-halogen neighbors) than on the methyl group (one Si-halogen neighbor) and the resonance of the $CH_2$ protons appears at lower field relative to the $CH_3$ protons (*65*). Since halogen-carbosilanes have been little studied so far, further discussion will relate only to halogen-free compounds.

The $Si^{29}C\mathit{H}$ and $C^{13}H$ coupling constants for $SiCH_3$ and $SiCH_2Si$ groups in chain-like alkyl carbosilanes show a characteristic difference, thus providing another criterion for the presence of the two groups. The value of $|J(Si^{29}C\mathit{H})|$ for $SiCH_3$ groups in all compounds studied so far, is about 2–3 cps smaller and $|J(C^{13}H)|$ about 10 cps greater than for the $SiCH_2Si$ group.

Another interesting relationship exists for the cyclic carbosilanes between the ring size and $J(Si^{29}C\mathit{H})$ and $J(C^{13}H)$ in the ring methylene

TABLE XI

NMR PARAMETERS OF SiH-FREE CARBOSILANES (*18*, *40*)[a]

| Compound | $\tau(CH_3)$ (ppm ± 0.01) | $\tau(CH_2)$ (ppm ± 0.01) | $J(C^{13}H_3)$ (cps ± 0.3) | $J(C^{13}H_2)$ (cps ± 0.3) | $J(Si^{29}CH_3)$ (cps ± 0.2) | $J(SiCH_2)$ (cps ± 0.3) |
|---|---|---|---|---|---|---|
| $(CH_3)_3SiCH_2Si(CH_3)_3$ | 9.98 | 10.26 | 118.2 | 108.4 | 6.7 | 8.8 |
| $Me_3{}^aSiCH_2{}^cSiMe_2{}^bCH_2SiMe_3$ | $9.98^a$ | 10.26 | $118.3^a$ | 108.5 | $6.5^a$ | 8.8 |
|  | $9.95^b$ | — | $118.4^b$ | — | $6.4^b$ | — |
| $Me_3{}^aSiCH_2{}^cSiMe_2{}^bCH_2{}^dSiMe_2CH_2SiMe_3$ | $9.98^a$ | $10.26^c$ | $118.4^a$ | $108.4^c$ | $6.4^a$ | $8.7^c$ |
|  | $9.95^b$ | $10.25^d$ | $118.4^b$ | $108.4^b$ | $6.4^b$ | $8.7^d$ |
| $Me_3SiCHMeSiMe_3$ | 10.00 | — | 118.6 | — | 6.4 | — |
|  | $CCH_3$ | 8.98 }[I] | 124 ± 1 | — | $Si^{29}CCH_3$ 6.7 | — |
|  | CH | 10.24 } | — | — | — | — |
| $Me_3SiCMe_2SiMe_3$ | 10.2 | — | — | — | 6.4 | — |
|  | $CCH_3$ | 9.05 | — | — | 6.5 | — |
| $(Me_3Si)_2C{=}CH_2$ | 9.90 | — | 118.9 | — | 6.5 | — |
|  | $C{=}CH_2$ | 3.72 | — | 154.8 | 11.8; 17.6[II] | $J_{HH} = 5.2$ |
| $(Me_2SiCH_2)_2$ | 9.76 | 10.01 | 119.3 | 122.4[III] | 7.0 | 6.2 |
| $(Me_2SiCH_2)_3$ | 9.95 | 10.31 | 119.0 | 111.5 | 6.7 | 8.0 |
| $(Me_2SiCH_2)_4$ | 9.96 | 10.19 | 118.6 | 109.5 | 6.3 | 8.5 |
| $Si_4C_{10}H_{24}$ [Table XII (a)] | 9.91 | 10.28 | 118.9 | 113 | 6.8 | 7.3 |
| $Si_4C_{12}H_{28}$ [Table XII (c)] | 9.86 | 10.27 | 119.4 | — | 6.5 | 6.3 |
| $(Cl_2SiCH_2)_3$ | — | 8.55 | — | 120 ± 2 | — | 10.6[III] |
| $Si_2C_7H_{16}$ [Table XII (b)] | 9.87 | 10.38 | 119.3 | 118.4 | 6.8 | 6.8 |
|  | =CH | 3.02 | — | — | — | — |

[a] All compounds were measured in dilute $CCl_4$ solution with $SiMe_4$. ($\tau$ = 10.00) as internal standard.

[I] Analysis of the $A_3B$ $CH_3CH$ spectrum gave $J_{HH}$ = 7.6 ± 0.3 cps.

[II] Analyzed as ABX spectrum; $\delta_{AB} = 0$.

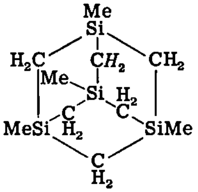
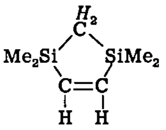
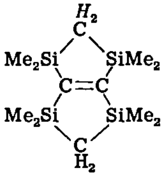
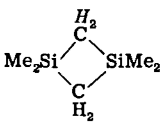
[III] These satellites show fine structure.

groups, $|J(C^{13}H)|$ increasing and $|Si^{29}CH|$ decreasing as the ring gets smaller (Table XII). A similar change has been observed for the $C^{13}H$ coupling constants in small aliphatic rings relative to chains (*76*). The relationship may be rationalized in terms of increasing *s* character in the C—H bonds and decreasing *s* character in the Si—C bonds as the rings contract. Although more compounds must be studied before the correlation is regarded as established, it nevertheless represents a valuable aid in determining the ring size of unknown alkyl silanes.

It is possible by investigating the fine structure of the $Si^{29}CH$ and

TABLE XII

COUPLING CONSTANTS FOR THE $CH_2$ GROUP IN CARBOSILANES (*18*)

| Compound | Ring size | $J(Si^{29}CH_2)$ | $J(C^{13}H)$ |
|---|---|---|---|
| $(Me_3Si)_2CH_2$ | Straight chain | 8.6 ± 0.3 | 108.4 ± 0.3 |
| $(Me_3SiCH_2)_2SiMe_2$ | Straight chain | 8.7 ± 0.2 | 108.6 ± 0.5 |
| $(Me_3SiCH_2^bSiMe_2)_2CH_2^a$ | Straight chain | 8.7 ± 0.2[a,b] | 108.4 ± 0.5[a,b] |
| $(Me_2SiCH_2)_4$ | 8 | 8.5 ± 0.2 | 109.8 ± 1 |
| $(Me_2SiCH_2)_3$ | 6 | 8.1 ± 0.2 | 111.5 ± 0.6 |
|  (a) | 6 | 7.3 ± 0.2 | 113.0 ± 0.6 |
|  (b) | 5 (one double bond) | 6.8 ± 0.5 | 118.4 ±1.5 |
|  (c) | 5 (one double bond) | 6.3 ± 0.2 | – |
|  | 4 | 6.2 ± 0.3 | 122.4 ± 0.3 |

$C^{13}H$ satellites to arrive at conclusions about $H^1$—$H^1$ coupling between CH groups which are separated by a Si atom. As was mentioned earlier, each of the different possible CH groups gives rise to a single sharp resonance with no resolvable fine structure, e.g., it is not possible to detect $H^1$—$H^1$ coupling between nonequivalent groups separated by Si (as, for example, in $H_3CSiCH_2$) in the compounds so far studied.

While this may be due to unfavorable chemical shifts and magnitudes and relative signs of the coupling constants, no conclusions at all can be drawn as to the $H^1$—$H^1$ coupling between equivalent CH groups (e.g., $RH_2CSiCH_2R$ or $CH_3SiCH_3R_2$). The situation becomes more favorable for both cases when the $C^{13}H$ and $Si^{29}CH$ satellites are studied in detail; in the first case, the presence of an effective chemical shift which is much larger in most cases than the actual shift between the CH groups, especially for the $C^{13}H$ satellites, may result in a more pronounced splitting pattern. In the case of equivalent CH groups, the presence of $C^{13}$ in one of these groups renders the protons of $C^{13}H$ no longer magnetically equivalent to the $C^{12}H$ group protons. Because of the small natural abundance of $C^{13}$ ($\sim$1%) it is unlikely, moreover, that more than one $C^{13}$ atom will be present in a molecule. $H^1$—$H^1$ coupling between these groups should therefore be observed, in principle, in the $C^{13}H$ satellites. Such coupling between protons separated by four or more bonds would certainly be small. Similar considerations apply to equivalent CH groups if one is bonded to a $Si^{29}$ atom. Magnetic equivalence of protons in groups bonded to $Si^{29}$ and $Si^{28}$ no longer exists and coupling should appear in the $Si^{29}CH$ satellites.

Investigation of the fine structure of the $Si^{29}CH$ satellites of the compounds, for which the corresponding coupling constants are given in Table XIV, shows (*65*) that the satellites for the linear peralkyl carbosilanes are sharp lines without fine structure when examined with a resolution of $\sim$0.3 cps. For $Si^{29}CH$ satellites of CH groups which are linked directly to the bridge carbon atom of the Si—C—Si group, $J(Si^{29}CCH)$ is not appreciably different from $J(Si^{29}CH)$, in spite of the separation by an additional bond (*18*). It is therefore conceivable that, in the carbosilanes, $Si^{29}$—$H^1$ coupling with about the same strength is possible over the system $Si^{29}$—C—Si—C$H$, or CH groups which are still further removed. On this basis the compound $Me_3SiCH_2SiMe_2CH_2SiMe_3$ should show a maximum of three $Si^{29}CH_2$ and five $Si^{29}CH_3$ couplings with about the same $J$ values. In spite of these various coupling possibilities each main signal appears with only one pair of satellites. It seems that such long-range coupling is beyond the limits of observation. A final decision as to whether it exists can be reached only when the ratio of the areas of the main and satellite resonances has been determined exactly for the separate compounds. Little is known about the $Si^{29}CH$ satellites for the cyclic compounds. In the case of the chlorinated six-membered ring $(Cl_2Si—CH_2)_3$, a triplet pattern has been found for the $Si^{29}CH_2$ satellites with a line separation of about 0.45 cycle/sec (*65*). It is not yet known if this splitting is due to $H^1—H^1$ coupling of the $CH_2$ groups or to the various possible $Si^{29}CH$ couplings of the compound, $J(Si^{29}CH)$ and $J(Si^{29}CSiCH_2)$, which, as has been shown, may be of about the same magnitude. Splitting by $H^1—H^1$ coupling, however, seems more probable.

The value of $J(Si^{29}C{=}CH_2)$ for the system $Si^{29}C{=}CH_2$ is significantly greater than in the case of the compounds previously described (Table XIV). The $Si^{29}—CH$ satellites should make up an ABX system. Six of the eight theoretical lines of the AB part were observed, the remaining two being presumably hidden under the main resonance. Analysis of this spectrum yielded the coupling parameters given in Table XI.

Study of the fine structure of the $C^{13}H$ satellites of the carbosilanes presents considerable difficulty because of the low natural abundance of $C^{13}$ ($\sim$1%). Observations made so far lead to the following picture. For the linear carbosilanes the $C^{13}H$ resonances appear in all cases as sharp lines on both sides of the main signal. Within the limits of observation these exhibit no further structure or broadening relative to the main signal. Some compounds give a further pair of lines which are symmetrical to the main signal. The origin of these has not yet been established; perhaps they are due to impurities (*18*). The $C^{13}H$ satellites of $SiCH_3$ groups in the ring also consist of single sharp lines. A point of some detail is that the $C^{13}H$ satellites of ring $CH_2$ groups appear to be somewhat broadened relative to the main signal (*18*). This is most clearly shown by $(Me_2Si—CH_2)_2$, the spectrum of which has been most studied (*40*). Fine structure is clearly recognizable in the $C^{13}H_2$ satellites of this compound (Fig. 8). The $C^{13}H_2$ satellite resonance of $(Me_3Si)_2CH_2$ is also shown for purposes of comparison. Splitting can arise only from $H^1—H^1$ coupling of the two ring $CH_2$ groups since the $C^{13}H$ satellites of the SiMe group are not broadened relative to the main signal. It follows that each of the $C^{13}H_2$ satellite multiplets must consist of half of a symmetrical $A_2X_2$ spectrum (*84*, p. 163). The corresponding coupling constants for this system may be derived from Fig. 9. The value of $J_A = J_B$ was assumed to be about 13 cycles/sec by comparison with carbon compounds. A possible interpretation of the spectrum (Fig. 8) then gives $J$ and $J'$ as 3 and 1 cycles/sec, respectively, the relative signs being unlike. Although the analysis of the pattern of the spectrum should not be regarded as fully conclusive, it may be seen quite clearly that, for this compound, coupling between $H_2CSiCH_2$ protons within the ring system is much stronger than between the $H_3CSiCH_2$ protons or the corresponding protons of both groups in the linear carbosilanes. No reliable measurements are available for the larger ring systems. It is to be expected, however, that with refined experimental conditions it will be possible to obtain further information on coupling parameters and consequently a fuller understanding of bonding in these compounds.

The PMR spectra of carbosilanes containing SiH groups are more complicated than those of the SiH-free compounds. Tables XIII and XIV summarize the NMR data for the linear compounds which have been examined so far. In these substances there is an additional parameter, namely, spin-spin coupling between protons of SiH and CH groups. Analysis of the spectra of the linear compounds is, however, simple, since the spectra are of the first order as a result of the small value of the ratio $J(H\mathrm{SiC}H):\nu_0\delta$. Assignment to the various possible SiH and CH groups is therefore readily made on the basis of the characteristic spin-spin splittings. Chemical shifts for SiCH and SiH groups lie in the same range as is found for the alkyl monosilanes (*89*). As in the case of the alkyl carbosilanes, resonances of the Si—CH₂—Si—group are displaced to high field relative to the $\mathrm{SiCH_3}$ group. Moreover, as with the methyl monosilanes (*89*), increasing methyl substitution in $\mathrm{Me}_n\mathrm{H}_{3-n}\mathrm{SiCH_2}$ groups results in displacement of SiC*H* resonances to high field, and of Si*H* resonances to low field. For $\mathrm{Me}_n\mathrm{H}_{3-n}\mathrm{SiCH_2}$

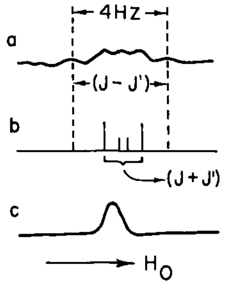


FIG. 8. $\mathrm{C^{13}H_2}$ satellite resonances. (a) High field satellite resonance signals of $\mathrm{Si_2C_6H_{16}}$. (b) their assignment, and (c) high field satellite resonance of $[(\mathrm{CH_3})_3\mathrm{Si}]_2\mathrm{CH_2}$ in approximately the same field scale.

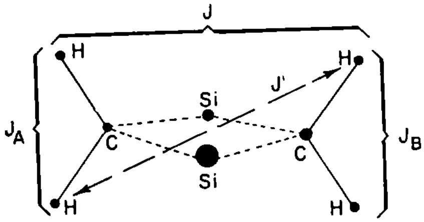


FIG. 9. Coupling constants of the $\mathrm{CH_2}$ groups in $\mathrm{Si_2C_6H_{16}}$.

## TABLE XIII

### CHEMICAL SHIFTS OF LINEAR CARBOSILANES WITH Si—H BONDS (*37*)[a]

| Compound | Chemical shift, τ units ± 0.01 (in ppm, TMS = 10.00) | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $SiH_3$ | $M^{++}$ | $SiH_2$ | $M^{++}$ | SiH | $M^{++}$ | $SiMe_3$ | $M^{++}$ | $SiMe_2$ | $M^{++}$ | SiMe | $M^{++}$ | $CH_2$ | $M^{++}$ |
| $H_3SiCH_2SiH_3$ | 6.37 | 3 | — | — | — | — | — | — | — | — | — | — | 10.08 | 7 |
| $Me_2HSiCH_2SiH_2Me$ | — | — | $6.18^+$ | 6 | 5.98 | 9 | — | — | 9.88 | 2 | $9.83^+$ | 3 | 10.16 | 4 |
| $Me_2HSiCH_2SiHMe_2$ | — | — | — | — | $5.98^+$ | 9 | — | — | $9.90^+$ | 2 | — | — | 10.20 | 3 |
| $Me_3SiCH_2SiHMe_2$ | — | — | — | — | $6.00^+$ | 9 | 9.97 | 1 | 9.91 | 2 | — | — | 10.25 | 2 |
| $H_3SiCH_2SiH_2CH_2SiH_3$ | 6.35 | 3 | 6.05 | 5 | — | — | — | — | — | — | — | — | 10.03 | 6 |
| $MeH_2{}^cSiCH_2{}^aSiH_2{}^dCH_2{}^bSiH_3$ | 6.37 | 3 | $6.16^c$ | 6 | — | — | — | — | — | — | 9.80 | 3 | $10.04^a$ | 5 |
| | | | $6.09^d$ | 5 | | | | | | | | | $10.04^b$ | 6 |

[a] All compounds were measured in dilute $CCl_4$ solution with $SiMe_4$ (TMS) as internal standard; $^+$ corrected, $^{++}$ multiplicity of the resonance signal.

### TABLE XIV
### COUPLING CONSTANTS (CYCLES/SEC) OF LINEAR CARBOSILANES CONTAINING SiH GROUPS

| Compound | $J$(HSiCH) (± 0.2) | $J(C^{13}H_3)$ | $J(C^{13}H_2)$ | $J(Si^{29}CH_3)$ | $J(Si^{29}CH_2)$ | $J(Si^{29}H)$ (± 0.6) |
|---|---|---|---|---|---|---|
| $H_3SiCH_2SiH_3$ | $J(HSiCH) = 4.5$ | — | 119.0 ± 1 | — | — | 199.3 |
| $Me_2HSiCH_2SiH_2Me$ | $J(H_2SiCH_3) = 4.1$;<br>$J[HSi(CH_3)_2] = 3.6$ | SiMe 121.5 ± 0.8 | — | 6.9 ± 0.2 | — | 190.5 |
|  | $J(H_2SiCH_2) = 4.2$;<br>$J(HSiCH_2) = 3.7$ | $SiMe_2$ 120.0 ± 0.8 | — | 6.9 ± 0.4 | — | — |
| $Me_2HSiCH_2SiHMe_2$ | $J(HSiCH_3) = 3.6$;<br>$J(HSiCH_2) = 3.8$ | 120.0 ± 0.9 | 110.7 ± 0.9 | 7.0 ± 0.4 | 8.7 ± 0.4 | 185.5 |
| $Me_3SiCH_2SiHMe_2$ | $J(HSiCH_3) = 3.6$;<br>$J(HSiCH_2) = 3.8$ | $SiMe_2$ 119.1 ± 0.3 | 110.4 ± 0.3 | 6.9 ± 0.2 | 8.9 ± 0.3 | 184.5 |
|  |  | $SiMe_3$ 118.6 ± 0.3 | — | 6.5 ± 0.2 | — | — |
| $H_3SiCH_2SiH_2CH_2SiH_3$ | $J(H_3SiCH_2) = 4.5$;<br>$J(H_2SiCH_2) = 4.2$ | — | — | — | — | $SiH_3$ 199.0<br>$SiH_2$ 196.5 |
| $MeH_2{}^cSiCH_2{}^aSiH_2{}^dCH_2{}^bSiH_3$ | $J(H_3SiCH_2{}^b) = 4.5$;<br>$J(H_2{}^cSiCH_3) = 4.1$<br>$J(H_2{}^dSiCH_2{}^b) \simeq$<br>$J(H_2{}^dSiCH_2{}^a) \simeq$<br>$J(H_2{}^cSiCH_2{}^a) \simeq 4.2 \pm 0.3$ | — | — | — | — | $SiH_3$ 199.0 |

groups attached to the same molecular moiety, it is also possible to establish a linear relationship between the chemical shift of the SiCH group and the magnitude of $n$ (*65*). The number of compounds studied is, however, not sufficient to establish this relationship firmly, especially the change in the SiH chemical shift.

As in the case of simple silyl compounds (*20*), the chemical shift for the SiH and SiCH resonances in carbosilanes is relatively insensitive to dilution (*65*). Individual resonance lines in the SiH and SiCH multiplets show no further splitting under high resolution conditions (~0.3 cycles/sec) at 60 megacycles/sec and are not broadened relative to the signals from tetramethyl silane, due to $H^1$—$H^1$ long-range coupling ($H$SiCSi$H$ or $H$SiCSiC$H$). Satellite lines arising from $C^{13}$—$H^1$ and $Si^{29}CH^1$ coupling occur on both sides of the SiCH main resonance as for the SiH-free carbosilanes. For all compounds more or less symmetrically placed satellites of the SiH signals due to $Si^{29}H$ interaction were observed. Satellites associated with $C^{13}SiH^1$ coupling have not yet been identified. For some compounds it is impossible to measure the $Si^{29}CH$ satellites because of overlapping with the main resonance lines, whereas $C^{13}H$ satellites of some other compounds have not yet been found because the quantities of material available were too small. Parameters so far recorded are summarized in Table XIV.

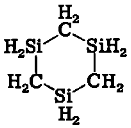
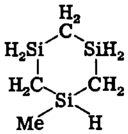
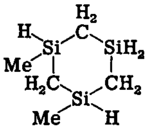
The data show certain regularities. As for the SiH-free carbosilanes, values of $J(Si^{29}CH_2)$ are 2–3 cps greater than those of $J(Si^{29}CH_3)$. $J(Si^{29}H)$ and, to a lesser extent, $J(Si^{29}CH_3)$ decrease with increasing methyl substitution in the compound. Only small changes occur in $J(C^{13}H)$. Interpretation of values of $J$(SiH) would be premature in view of the present state of the theory of spin-spin coupling and also because of the limited number of compounds investigated. Study of a series of simple silicon compounds has shown (*19*, *59b*) that experience gained in interpreting $J(C^{13}H)$ for corresponding carbon compounds cannot be applied in explaining values for $Si^{29}H$ couplings without modifications. Presumably the difficulties arise because of the participation of the *d* orbitals of silicon. On the other hand, the results described may be used quite simply for analytical purposes and in determining structures of unknown compounds. The fine structure of $Si^{29}H$ and $C^{13}H$ satellites has not been studied so far. Preliminary investigations of the $Si^{29}H$ satellites of $H_3SiCH_2SiH_3$, however, show a splitting of the satellite lines due to $H_3Si^{29}CSi^{28}H_3$ long-range coupling (*65*).

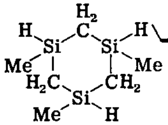
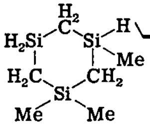
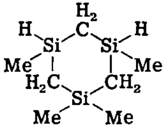
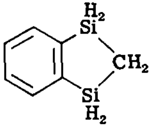
Spectra of cyclic carbosilanes containing SiH groups are much more complicated and cannot be explained yet in detail. Compounds which have been examined are shown with their NMR parameters in Table XV.

Chemical shifts for the individual groups of protons correspond with the values found for linear compounds. Again, the signals of the different

## TABLE XV

### NMR PARAMETERS OF CYCLIC SiH-CONTAINING CARBOSILANES (*37*, *65*)

| Compound | Chemical shift, τ units ± 0.01[a] (in ppm, TMS = 10) | | | | | | | | | | Coupling constant (± 0.2) (cps) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $SiH_2$ | $M^+$ | SiH | $M^+$ | $SiMe_2$ | $M^+$ | SiMe | $M^+$ | $CH_2$ | $M^+$ | |
|  | 5.85 | 5 | – | – | – | – | – | – | 9.98 | 5 | $J(HSiCH) = 3.6$<br>$J(Si^{29}H) = 197 \pm 1$ |
|  | 5.89 | 5 | Masked | – | – | – | 9.79 | 2 | 10.08 | x | $J(H_3CSiH) = 3.6$<br>$J(Si^{29}H) = 196 \pm 1$ |
|  | 5.99 | x | | – | – | – | 9.81 | 2 | 10.07 | x | $J(H_3CSiH) = 3.6$ |

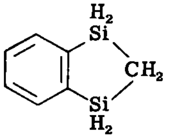
|  |  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  | 5.86 | x |  | – | – | – | 9.83 | 2 | 10.15 | x | $J(H_3CSiH) = 3.6$ |
|  | 5.86 | x |  | – | 9.89 | 1 | 9.82 | 2 | 10.15 | x | $J(H_3CSiH) = 3.6$ |
|  | – | – | 5.77 | 8 | 9.91 | 1 | 9.84 | 2 | 10.19 | x | $J(H_3CSiH) = 3.6$ |
|  | 5.37 | 3 | – | – | – | – | – | – | 9.75 | 5 | $J(HCSiH) = 4.0$<br>$J(Si^{29}H) = 200.5 \pm 0.8$ |

[a] Compounds were investigated in dilute $CCl_4$ solution with $SiMe_4$ (TMS) as internal standard.
$M^+$ indicates a multiplicity of resonance signals.
The signal designated by x indicates a complex multiplet, in which the τ-value arbitrarily refers to the maximum of the absorption.

SiH and CH groups are split, in the main, by *H*SiC*H* coupling. The multiplets do not, however, consist of sharp single lines but present a complicated appearance. Only for the terminal $SiMe_3$ groups are multiplets with sharp lines observed. While this complication may be understood in the case of the unsymmetrically substituted rings in terms of the increased coupling parameters as compared to the linear compounds, the spectra of the symmetrically substituted rings and the fully hydrogenated parent compound $(H_2SiCH_2)_3$ (*64*) show that other factors must play an important role. Thus the SiH and CH resonance signals of $(H_2SiCH_2)_3$, in spite of the high molecular symmetry of the compound, both show a quintet pattern of broad overlapping maxima with no resolvable fine structure (*65*). These observations may be explained by the presence of conformational effects or(and) stronger long-range couplings (e.g., *H*SiCSi*H*, *H*CSiCSi*H*, etc.) than in the linear compounds. Further discussion of these interesting possibilities must be postponed until complete analyses of these spectra are available.

The same consideration applies to the methyl-substituted rings. It is found that $H^1$—$H^1$ coupling of exocyclic methyl groups with neighboring CH groups in these compounds is below the limit of measurement (<0.3 cps). A complete analysis of the PMR spectra will be extremely difficult and requires a better understanding of the nature of line broadening.

In contrast to these findings the protons in the $CH_2$ and $SiH_2$ groups of the compound

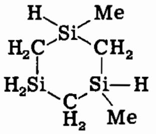


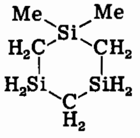
give rise to resonance multiplets which consist of narrow lines. No long-range coupling of these groups with the α—H atom of the phenyl ring is observed (*37*).

In spite of the difficulties discussed above, the spectra of the cyclocarbosilanes may be used in solving structural problems such as those associated with position isomerism in unsymmetrical methyl-substituted rings. This type of analytical application of nuclear magnetic resonance spectroscopy is particularly valuable for the carbosilanes, as the possibilities of establishing structures by chemical means are very restricted. The carbosilanes are not reactive and, unlike carbon compounds, undergo few reactions which yield information concerning their structures. In fact the structures of a number of compounds were first established with the aid of nuclear resonance.

Chemical and analytical investigations showed the six-membered ring

$Si_3C_5H_{16}$ to contain four protons and two methyl groups bonded to silicon. Their position in the ring was unknown. Determination of the relative intensities of the $CH_2$, $CH_3$, and SiH resonances in the proton resonance spectrum of this compound agreed satisfactorily with the chemical results. There are two possibilities, (*a*) and (*b*), for the arrangement of the two methyl groups in the ring, and it is possible to differentiate between them with the aid of Si-methyl resonance, which is characteristic in this case:

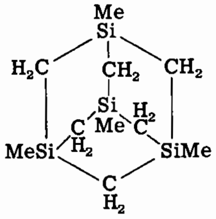

(*a*)

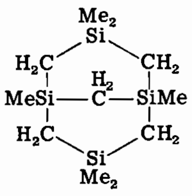

(*b*)

The resonance for the Si-methyl group in the compound consisted of a doublet which shows the presence of isomer (*a*) quite unambiguously (*37*).

In the case of the compound $MeH_2Si—CH_2—SiH_2—CH_2—SiH_3$ (I) or $H_3Si—CH_2—SiHMe—CH_2—SiH_3$ (II) it had proved impossible with other analytical means to differentiate between the isomers (I) and (II). The PMR spectrum shows the pure isomer (I) to be present. The signals in the spectrum may be assigned to a quintet at $\tau$ = 10.04, a sextet at 10.04, a triplet at 9.80, a triplet at 6.37, a sextet at 6.17, and a quintet at 6.09. If the proton groups are indexed as $MeH_2{}^cSi—CH_2{}^a—SiH_2{}^d—CH_2{}^b—SiH_3$ (I) it is possible, from the relative intensities and the position and characteristic multiplet splittings, to assign the appropriate multiplets to the $CH_2{}^a$—, $CH_2{}^b$—, $CH_3{}^c$—, $SiH_3$—, $SiH_2{}^c$—, or $SiH_2{}^d$ group (*37*).

In the fully alkylated compound $Si_4C_{10}H_{24}$ (*30*) the limit of error in the analytical results made it impossible to decide between structural formulas (*c*) and (*d*):


(*c*) $Si_4C_{10}H_{24}$

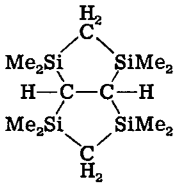

(*28, 85*)

(*d*) $Si_4C_{11}H_{28}$

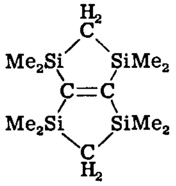
The PMR spectrum consisted of two unsplit signals of equal areas which, from their $\tau$ values, are due to a $SiCH_2Si$ and a SiMe group (*18*)

(Table XI). This shows the presence of structure (*c*) in which all $SiCH_2$ and SiMe groups are equivalent and in which the ratio of the number of protons in each group is 1:1.

The carbosilane which is obtained from the Grignard reaction of the SiCl-containing cyclocarbosilane from the pyrolysis of $MeSiCl_3$ (*45*) may, on chemical evidence, have either formula (*e*) or (*f*).



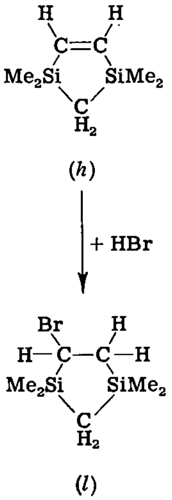
(*e*)



(*f*)

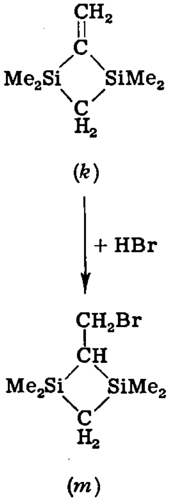
The PMR spectrum shows two resonances with an area ratio of 6:1. The $\tau$ value for the smaller signal corresponds with a $SiCH_2Si$ group and that of the larger with an SiMe group. The absence of further signals and the area ratio show the structure to be (*f*) (*18*). This result was confirmed by an X-ray structure determination on the compound (*46*).

With carbosilanes containing no SiH groups it is not always possible to determine the structure unambiguously from the PMR spectra because of the lack of characteristic spin-spin couplings. In such cases a solution of the structural problem may be possible by using nuclear resonance to follow the course of a chemical reaction of the compound in question. The small amount of substance required is a distinct advantage. For example,



(*h*)

(*l*)



(*k*)

(*m*)

the PMR spectrum of $Si_2C_7H_{16}$ (Table XI) is consistent with either of the structures (*h*) or (*k*), and it is impossible to decide between them (*18*).

The PMR investigation of numerous reactions of this compound with halogens and hydrogen halides under various conditions showed that when HBr was passed into a $CCl_4$ solution of $Si_2C_7H_{16}$, the HBr addition compound $Si_2C_7H_{17}Br$ was formed together with other products (*54*). The PMR spectrum of the addition compound may be identified unambiguously as belonging to (*l*). The proton signals of the $C_2H_3Br$ group have an ABX structure. The chemical shift of the X proton corresponds with that for a proton bonded to a CBr group, while the AB part of the spectrum lies to higher field ($\tau_X < \tau_A$, $\tau_B$). In the simplest case an $A_2B$ or $A_2X$ spectrum would be expected for the corresponding protons in (*m*), with $\tau_A$ being smaller than $\tau_B$ ($\tau_X$). This would be true also in the event of possible complications of the spectrum due to hindered rotation of the $CH_2Br$ group. The compound $Si_2C_7H_{16}$ is thus proved to have formula (*h*) (*54*).

## IV. Conclusion

In this review the authors have traced the development of the chemistry of compounds containing in their structures alternate Si and C atoms, although in all probability the literature coverage is not complete at all points. The article does not represent an area of research which has been fully explored; indeed, in many places the subject is still in its infancy. Thus the high molecular weight compounds formed in the pyrolysis of $Si(CH_3)_4$ and the methyl chlorosilanes have scarcely been examined, and the possibilities of further reactions of carbosilanes substituted on the bridge carbon atom are also not completely known. In part the text reports only the experimental material available at the moment and discusses its possible interpretation. Further research will have to provide the final answers. It seems certain in any case that the subject will develop far more in the years ahead.

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