SILANES AND THEIR DERIVATIVES

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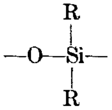
I. Introduction

The silanes or "silicon hydrides" may be regarded as the silicon analogues of the paraffin hydrocarbons, and form an analogous homologous series of compounds of the general formula Si_nH_{2n+2}. Just as one or more of the hydrogen atoms of a paraffin may be replaced by other elements or groups, so also can the hydrogen atoms of a silane be replaced either partly or completely by Cl, N, O, K, organic groups, etc. (*86, 87*). A very large number of silicon compounds in which all the hydrogen atoms of a silane (usually silane—SiH_4) have been replaced by organic groups are known, and many of these are relatively complex. A large number of derivatives are also known in which hydrogen atoms have been replaced by a combination of alkyl and aryl groups and oxygen, viz.,



$$-O-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{Si}}-$$

to give the "siloxanes," a class of compounds containing alternating —Si—O—Si—O— linkages such as are commonly found in "silicone" polymers. If all the hydrogen atoms are replaced by a combination of oxygen and OM groups (M = a metal, e.g., Na, Ca) then glasses—complex metal silicates—are formed. If they are all replaced by oxygen, SiO_2 results.

It is not possible to include in this chapter the enormous number of organosilicon compounds, siloxanes, and silicates which are known.* The discussion will instead be limited primarily to a description of the parent silanes and their simple derivatives.

Only after the introduction of the vacuum-system technique by Stock (*169*) during the years 1914–1920 was it possible to study satisfactorily volatile compounds which were unstable in air, such as the silanes and their simple derivatives. Stock and his co-workers prepared and thoroughly investigated the parent silanes and many of their simple derivatives during the years 1916 to 1923, and work in this field has continued up to the present time. A very large number of organosilicon compounds were studied by Kipping and his co-workers, and by other investigators during the first half of this century, and since then the amount of research conducted in this field has increased and still is increasing at a very rapid rate.

The fund of factual knowledge which has been built up concerning the descriptive chemistry of silicon compounds, combined with the advances of theoretical chemistry, now make it possible to establish many correlations and predict trends within the field of silicon chemistry itself, which promises to stand second only to that of carbon in its interest and diversity.

II. Relationship between the Chemistry of Analogous Carbon and Silicon Compounds

Since silicon falls immediately below carbon in the periodic table, and since both elements have similar electronic configurations (C, $1s^2$, $2s^2$, $2p^2$; Si, $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^2$, $3d^0$), it is to be expected that analogous carbon and

* For further information on organosilicon compounds and siloxanes, the reader is referred to several excellent books and review articles (*34, 49, 79, 81, 86, 137, 141, 143*). The nomenclature used in silicon chemistry is readily available from a number of sources (*43, 137*), and will not be described in this chapter.

silicon compounds would have similar physical and chemical properties; and in a broad sense, such is in fact the case. When carrying out research in this field, investigators frequently attempt the synthesis of a new compound or a prediction of its properties by direct analogy with what occurs in carbon chemistry, *modified* in certain ways, as will be shown in the following pages. However, as the knowledge of silicon chemistry increases, it becomes less necessary to rely on carbon chemistry as a guide, and one can draw more and more from trends within the field of silicon itself.

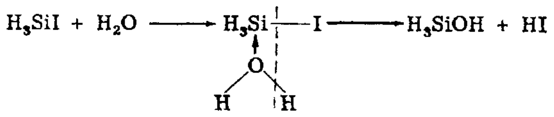
In general, silicon compounds are similar in formula type to their carbon analogues, e.g., $(CH_3)_3N$ and $(SiH_3)_3N$, but they do not necessarily have similar structures, e.g., $(CH_3)_3N$ is pyrimidal, whereas $(SiH_3)_3N$ is planar (*90*). They are usually more reactive than their corresponding carbon compounds, e.g., $HSiCl_3$ is hydrolyzed instantaneously by cold water with which, of course, $HCCl_3$ does not react. The greater "reactivity" of silicon compounds is not in general due to the fact that they are less thermodynamically stable in the presence of a particular reagent—in fact, bonds formed by silicon to other common elements are generally stronger than those formed by carbon (*39*, *49*, *81*), e.g., Si—O = 108 kcal/mole; C—O = 85.5 kcal/mole; Si—F = 135 kcal/mole, C—F = 116 kcal/mole; Si—Cl = 91 kcal/mole, C—Cl = 81 kcal/mole; Si—Br = 74 kcal/mole, C—Br = 68 kcal/mole; Si—I = 56 kcal/mole, C—I = 51 kcal/mole. The greater reactivity is rather a "kinetic" effect since the activated intermediate complexes will, in general, have a lower energy and will be formed more readily with silicon derivatives because of (i) the larger size, (ii) the smaller electronegativity, and (iii) the greater coordination number of silicon (*49*).

This may be exemplified by the hydrolysis of CH_3I and SiH_3I, both of which are thermodynamically unstable with respect to their possible hydrolysis products in the presence of pure water, viz.,

$$CH_3I + H_2O \rightarrow CH_3OH + HI \qquad (1)$$

$$SiH_3I + H_2O \rightarrow SiH_3OH + HI \qquad (2)$$

The first reaction occurs only slowly; the latter reaction occurs instantaneously (*54*). It is believed that the reaction of silicon compounds with other species generally proceeds via the formation of a five-coordinate intermediate complex in which the attacking species attaches itself to the silicon atom. In the above example this complex could be formulated as $H_2O \cdot SiH_3I$. (i) Since silicon is about half again as large as carbon (R_{Si} = 1.173 Å; R_C = 0.771 Å) it is sterically more vulnerable to attack, and hence an intermediate complex can be formed more readily. (ii) Since the electronegativity of the silicon is less than that of carbon (Si = 1.8; C = 2.5), the silicon linkage to most nonmetals is therefore more polar, i.e., has a greater ionic character than the corresponding carbon linkage, and it might therefore be expected to suffer attack by polar reagents more rapidly than the analogous carbon linkage. This effect facilitates the formation of an intermediate complex. (iii) The most important factor of all, however, is probably the ability of silicon to increase its coordination number to more than four, whereas carbon is limited to a maximum of four. The vacant 3*d* orbitals of silicon, which are readily available for the acceptance of a coordinate linkage, permit the easy formation of an intermediate complex which can then break down as indicated:



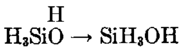
$$H_3SiI + H_2O \longrightarrow H_3\underset{\underset{\displaystyle \overset{}{H}\diagup O \diagdown H}{\uparrow}}{Si}{-}I \longrightarrow H_3SiOH + HI \qquad (3)$$

The above three factors all assist the silicon compound in reacting more rapidly than its carbon analog, for which such a low-energy reaction path is usually not available.

The SiH_3OH formed during hydrolysis immediately condenses:

$$2SiH_3OH \rightarrow (SiH_3)_2O + H_2O \qquad (4)$$

Reaction probably proceeds via an intermediate complex of the type



$$H_3Si\overset{H}{O} \rightarrow SiH_3OH$$

Steric factors are also very important when correlating trends within a series of related silicon compounds. If, for example, the hydrogen atoms of SiH_3OH are replaced by methyl groups to give a compound such as $(CH_3)_3SiOH$, we might expect to find that it would undergo condensation at a slower rate, since the silicon atom is no longer so sterically open to attack. This is actually observed experimentally, and pure $(CH_3)_3SiOH$ has been isolated and characterized. Similarly, SiH_3NH_2 condenses almost instantaneously to give the corresponding secondary and then tertiary amine, while $(C_2H_5)_3SiNH_2$ may be distilled (*18*) without the formation of $[(C_2H_5)_3Si]_2NH$. Hence, increasing size of the organic group attached to the silicon progressively decreases the rate of reaction. Other factors, such as inductive effects, most certainly are important also, but they are probably less important than steric effects in cases such as these.

If the above simple concepts are held in mind during the following discussion it will be found that qualitative explanations at least may frequently be formulated to explain and correlate changes in properties between analogous carbon and silicon compounds, and changes in properties within a given series of similar silicon compounds.

III. The Parent Silanes

The saturated silanes of the general formula Si_nH_{2n+2} so far isolated and characterized are given in Table I (*53, 169, 170, 180, 206*).

TABLE I

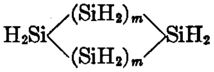
THE PARENT SILANES

Compound	M.P.	B.P.
SiH_4	−185.0°	−111.9°
Si_2H_6	−132.5°	−14.5°
Si_3H_8	−117.4°	52.9°
Si_4H_{10}	−84.3°	107.4°

The almost constant ratio of the boiling points of analogous silanes and hydrocarbons indicates that the physical constants given for tetrasilane are probably those for n-Si_4H_{10} (*169*).

Recently, the mixture of silanes obtained by reacting magnesium silicide with phosphoric acid has been separated into 21 components by means of gas-liquid chromatography (*27*). Two compounds of the formula Si_4H_{10} were obtained, one of which was definitely identified as n-Si_4H_{10} by nuclear magnetic resonance spectra, and in a similar manner both n-Si_5H_{12} and iso-Si_5H_{12} were identified. Tentative identification of n-Si_6H_{14}, n-Si_7H_{16}, and n-Si_8H_{18} has been made, but other isolated isomers of the last three compounds have not yet been identified.

Solid silanes, e.g., $(SiH_2)_x$, $(SiH)_x$, which in older works have been referred to as "unsaturated" are also known. Their lack of volatility indicates that they are not analogous to unsaturated hydrocarbons such as ethylene, $(CH_2)_2$, or acetylene, $(CH)_2$, and it appears most improbable that they contain Si═Si or Si≡Si linkages. It is possible that silicon exists in the divalent and monovalent states in these compounds, particularly since germanium, which falls below silicon in Group IV, is divalent in some compounds. However, until structural studies are carried out on these hydrides it appears advisable to assume that they contain tetravalent silicon in which SiH_2 or SiH units are joined together by Si—Si linkages. In this way $(SiH_2)_x$ could be regarded either as a linear molecule, $H_3Si(SiH_2)_nSiH_3$, in which n is large, or a cyclic species,



$$H_2Si\overset{(SiH_2)_m}{\underset{(SiH_2)_m}{\langle\quad\rangle}}SiH_2$$

where m is large. $(SiH)_x$ could similarly be regarded as consisting of a two- or three-dimensional network of Si—Si bonds. Solid silanes of variable composition $(SiH_{0.4-1.8})_x$ have also been reported. These could be considered to be mixtures of $(SiH_2)_x$, $(SiH)_x$, and silicon or a substance whose structure is intermediate between $(SiH_2)_x$ and $(SiH)_x$, or $(SiH)_x$ and silicon.

The failure of silicon to form stable compounds containing a Si=Si linkage (or a Si=C linkage) is not a property peculiar to this element alone, but rather one which is shared by most elements outside the first period of the periodic table. This is very possibly due to the fact that with the larger atoms the greater bond distance makes the overlap of p_π–p_π orbitals on the singly bonded atoms small (*122, 136*). Other explanations, however, have been offered (*136*). The conversion of any doubly bonded structure, if it should exist, to the singly bonded structure would also be greatly facilitated by the presence of the vacant 3*d*-orbitals of silicon. Such a conversion in carbon chemistry, e.g. the polymerization of $CH_2{=}CH_2$ to polyethylene, requires a catalyst.

Preparation. A mixture of all the known volatile silanes may be obtained by adding dilute hydrochloric acid to magnesium silicide (prepared by heating a mixture of magnesium and silicon, or more crudely, by heating SiO_2 and magnesium powder in an open test tube). Approximately 25% of the silicon is converted to volatile hydrides which can be separated by fractional distillation. The hydride mixture contains roughly 40% SiH_4, 30% Si_2H_6, 15% Si_3H_8, 10% Si_4H_{10}, and 5% higher silanes (*169, 170*).

The method of preparation of the magnesium silicide greatly affects both the over-all yield of silanes and the relative proportions of higher and lower silanes produced (*53*). With specially prepared magnesium silicide, high yields of disilane (up to 60% Si_2H_6) are obtained, and 70–80% yields of the lower silanes (SiH_4, Si_2H_6) can be obtained by reaction of magnesium silicide with ammonium bromide (an acid) in liquid ammonia (*94*). Similarly, high yields of SiH_4 are observed when $N_2H_4 \cdot 2HCl$ in anhydrous hydrazine is used (*67*). It is believed that experimental variations in the preparation of the magnesium silicide produce materials other than Mg_2Si, resulting in the observations noted above.

Disilane may also be produced easily, and in yields up to 67%, by means of a Wurtz-type reaction in which SiH_3I vapor reacts with sodium amalgam at room temperature (*42*):

$$2SiH_3I + 2Na \rightarrow Si_2H_6 + 2NaI \tag{5}$$

The best method for preparing both silane and disilane in high yields, however, is by the reduction of $SiCl_4$ and Si_2Cl_6 respectively with lithium hydride (*190*) or lithium aluminum hydride (*69*), e.g.,

$$2Si_2Cl_6 + 3LiAlH_4 \rightarrow 2Si_2H_6 + 3LiCl + 3AlCl_3 \tag{6}$$

In the reduction of Si_2Cl_6 considerable cleavage of the Si—Si bond occurs with consequent formation of SiH_4 if particular care is not taken to use appropriate concentrations of reagents, etc. (*198*).

The solid hydrides may be prepared in a variety of ways. Silane is decomposed to give a solid of variable composition, $(SiH_{0.4-0.9})_x$, when irradiated in the presence of mercury vapor with mercury resonance radiation (*61*). Except for SiH_4, the silanes yield solid hydrides on heating (*58*, *91*, *180*, *182*). With the higher silanes, decomposition is almost complete after several months at room temperature

$$Si_6H_{12} \rightarrow 2(SiH)_x + Si_2H_6 + SiH_4 \tag{7}$$

but with Si_2H_6 heating is necessary

$$Si_2H_6 \rightarrow SiH_4 + (SiH)_x + \tfrac{1}{2}H_2 \tag{8}$$

Silane is also decomposed into solid hydrides of composition $SiH_{1.2-1.7}$ by an electric discharge (*159*).

The compound $(SiH_2)_x$ is formed quite readily by treating calcium monosilicide (CaSi) with either absolute ethanol saturated with HCl or with glacial acetic acid (*159*). Reduction of $(SiBr_2)_x$ with $LiAlH_4$ also gives good yields of $(SiH_2)_x$ (*150*). Treatment of an ethereal solution of $HSiBr_3$ with magnesium (*151*) has been found to yield $(SiH)_x$:

$$2HSiBr_3 + 3Mg \rightarrow 3MgBr_2 + 2(SiH)_x \tag{9}$$

This compound may also be obtained from $HSiCl_3$ and sodium (*181*).

Physical Properties. All the lower silicon hydrides are colorless gases or liquids; their melting and boiling points are listed in Table I. A linear relationship has been shown to exist between the boiling points of analogous silanes and paraffins (*169*), and since the silanes have normal Trouton constants, a linear relationship also exists, therefore, between their molar heats of vaporization. A similar relationship is also found between the silyl and methyl halides and chalcogenides (*113*). The silanes are readily soluble in alcohol, benzene, and carbon disulfide, but they are almost insoluble in water (*169*).

The solid hydrides are all light brown or yellow amorphous materials with no definite melting points. They are insoluble in all inert solvents.

Chemical Properties. The chemical properties of the silanes given in this section are in general characteristic of the Si—H bond and, when modified by the factors described in Section II, may be used to predict, qualitatively at least, the chemical properties of an Si—H bond in almost any compound.

The thermal stability of the volatile silanes is less than that of the analogous carbon compounds and decreases with increasing molecular weight. All the hydrides are decomposed to silicon and hydrogen at approximately 500°, but at intermediate temperatures a process analogous to the cracking of hydrocarbons occurs, with the formation of higher and lower hydrides. At 470° silane is partly converted to disilane, presumably through the formation of free SiH_3 radicals (*74*). At temperatures between 450°

and 510° in the presence of ethylene Si_3H_8 is produced in addition to Si_2H_6 (*200*). Irradiation of SiH_4 mixed with ethane, hydrogen and mercury vapor, by means of a mercury lamp, also produces small quantities of Si_2H_6, Si_3H_8 and Si_4H_{10} in addition to solid hydrides (*200*). It is of interest to note that the rate of thermal decomposition of SiD_4 is less than that of SiH_4 (*182*).

Silane and disilane appear to be stable indefinitely at room temperature, but the higher homologues decompose slowly. Studies on Si_4H_{10} (*53*) however, suggest that this instability may be due, at least in part, to impurities, since decomposition (by an autocatalytic reaction) was found to occur only with impure samples. On heating $(SiH_2)_x$ to 380° it undergoes cracking with production of a mixture of volatile silanes (*159*).

Although the Si—Si bond energy is relatively small (Si—Si = 53 kcal/mole; C—C = 82.6 kcal/mole) (*39, 49*), the ease of decomposition of the higher parent silanes cannot necessarily be attributed directly to this. For instance, Si_2H_6 undergoes thermal decomposition at 311° (*183*) whereas hexaphenyldisilane melts undecomposed at 354° (*148*) and octaphenylcyclotetrasilane may be distilled at temperatures greater than 400° under reduced pressure (*99*). It can be seen from the above that in actual fact the Si—Si bond in $(C_6H_5)_3SiSi(C_6H_5)_3$ is *more* stable thermally than the C—C bond in $(C_6H_5)_3CC(C_6H_5)_3$, which readily cleaves to give the free radical triphenyl methyl, $(C_6H_5)_3C$. No evidence of such a reaction has ever been observed with hexaphenyldisilane. These examples indicate that the frequently repeated statement that a bond with a lower energy will break (or react) before one with a higher energy can be, and often is, erroneous. The rate of breaking (or reaction) of a bond is dependent on many factors such as the reaction mechanism, steric factors, inductive effects, bond energies in the reactants and products, etc.

All the volatile silanes and many nonvolatile silanes, e.g., $(SiH_2)_x$, are spontaneously inflammable in air, but the lower silanes, SiH_4, Si_2H_6, Si_3H_8, can be mixed with oxygen under certain conditions of temperature, pressure, etc. without inflammation (*60*). Contrary to popular belief, most derivatives of silane containing Si—H bonds are *not* spontaneously inflammable in air under normal conditions. It is quite possible that those few which are, e.g., SiH_3Br, owe this property to minute traces of SiH_4 formed during very slow thermal decomposition. Many derivatives of the silanes, if they contain sufficient Si—H and/or C—H linkages will, however, burn in air when ignited.

Although the silanes are not affected by pure water (or slightly acidified water) in silica vessels, they do react with water in glass vessels or when glass is added to silanes and water in silica vessels. This is due to their extreme sensitivity to alkali, traces of which are dissolved from the glass. In alkaline solution the silanes are hydrolyzed quantitatively (*170, 172*), e.g.,

$$SiH_4 + 2KOH + H_2O \rightarrow K_2SiO_3 + 4H_2 \qquad (10)$$

It may be noted that one molecule of hydrogen is liberated for each Si—H bond present. A similar reaction occurs in substituted silanes, e.g.,

$$SiH_3I + 3KOH \rightarrow K_2SiO_3 + KI + 3H_2 \qquad (11)$$

In compounds containing the Si—Si linkage, one molecule of hydrogen is liberated for each Si—Si linkage ruptured

$$SiH_3SiH_2I + 5KOH + H_2O \rightarrow 2K_2SiO_3 + KI + 6H_2 \qquad (12)$$

Such reactions proceed with so few side reactions that the evolution of hydrogen is quantitative and measurement of the hydrogen evolved is commonly used in analysis for determining the number of Si—H and/or Si—Si linkages in a compound. However, under certain conditions the Si—Si bond is not cleaved readily by very concentrated aqueous alkali (*175*).

A reaction analogous to hydrolysis occurs with methanol; when added to SiH_4 it will yield $H_2Si(OCH_3)_2$, $HSi(OCH_3)_3$, $Si(OCH_3)_4$ and hydrogen (*167*). This type of reaction is somewhat general for all Si—H linkages, particularly in the presence of copper metal catalyst (*119*)

$$R_xSiH_{4-x} + yR'OH \rightarrow R_xSiH_{4-x-y}(OR')_y + yH_2 \qquad (13)$$

where R and R' are simple alkyl or aryl groups.

It is well known that many hydrides act as good reducing agents, e.g., HI, $LiAlH_4$, etc., and it is not therefore surprising to find that the Si—H bond, both in the parent silanes and in their derivatives, may act as a fairly strong reducing species. For instance, disilane will reduce aqueous solutions of $KMnO_4$ to MnO_2; $HgCl_2$ to Hg_2Cl_2 and Hg; $CuSO_4$ to copper hydride, etc. It does not, however, react with $NiSO_4$, $CrCl_3$, or $Pb(NO_3)_2$ solutions, or with dry NH_3 or concentrated H_2SO_4 (*170*). In certain circumstances the Si—H bond is able to convert a C—Cl linkage to C—H. For instance, all the silanes except monosilane react with carbon tetrachloride or with chloroform at 50–70° in the presence of aluminum chloride catalyst (*179*), e.g.,

$$Si_3H_8 + 4CHCl_3 \rightarrow Si_3H_4Cl_4 + 4CH_2Cl_2 \qquad (14)$$

The free halogens, in general, react vigorously with an Si—H bond, and with the parent silanes the reaction sometimes occurs with explosive violence to replace one or more of the hydrogen atoms (*171*). At low temperatures, the reactions can be made to occur more slowly and controllably, e.g., at −80° solid bromine reacts as shown to give SiH_3Br and some SiH_2Br_2 (*171*)

$$SiH_4 + Br_2 \rightarrow SiH_3Br + HBr \quad (15)$$

In the presence of the appropriate aluminum halide catalyst, HCl, HBr, or HI will replace the hydrogen of an Si—H bond by a halogen at 80–100° during several hours (*54, 126, 172, 173*), e.g.,

$$SiH_4 + HI \xrightarrow{Al_2I_6} SiH_3I + H_2 \quad (16)$$

Prolonged treatment produces more highly substituted products, e.g., SiH_2I_2, $SiHI_3$, and SiI_4. The analogous reaction with Si_2H_6 proceeds without heating to give SiH_3SiH_2I (*197*).

The Si—H bond in many compounds is able to *add* across a double or triple bond. This is a very general type of reaction which in some systems proceeds without a catalyst and in other systems occurs only in the presence of ultraviolet irradiation or an organic peroxide (*20, 33*), e.g.,

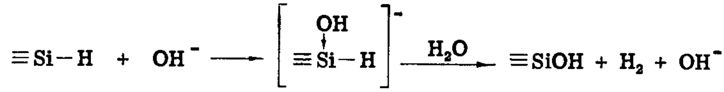
$$2HSiCl_3 + HC\equiv CH \rightarrow Cl_3SiCH_2CH_2SiCl_3 \quad (17)$$

It can be seen from the above that the Si—H bond reacts in many circumstances where a C—H bond will not, e.g., it is readily hydrolyzed and reacts with hydrogen halides. The Si—H bond is thermodynamically able to undergo many reactions not observed with C—H bonds, partly because it is weaker than the C—H bond (Si—H = 76 kcal/mole; C—H = 98.7 kcal/mole), and partly because the bonds which silicon forms with other common elements are usually stronger than those formed by carbon.

The rapidity with which an Si—H bond reacts, as compared with a C—H bond, depends primarily on: (i) the ability of silicon to increase its coordination number to above four; and (ii) on its greater size. The course of the reaction is greatly affected by the polarity of the Si—H bond, which is actually more similar to the C—Br link than to the C—H linkage. It is therefore reactive to nucleophilic polar reagents and, from (i) and (ii) above, it would be expected to react more rapidly than the C—Br bond (see the tabulation, where δ^+ and δ^- indicate some small part of the charge on one electron). However, it should be noted that in some instances the C—H bond can have a polarity of C^{δ^+}—H^{δ^-}, depending on the other groups attached to the carbon and its multiplicity of bonding (*78*).

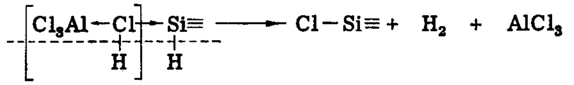
	$\overset{\delta^+}{\mathrm{Si}}$—	—$\overset{\delta^-}{\mathrm{H}}$	$\overset{\delta^-}{\mathrm{C}}$—	—$\overset{\delta^+}{\mathrm{H}}$	$\overset{\delta^+}{\mathrm{C}}$—	—$\overset{\delta^-}{\mathrm{Br}}$
Electronegativity	1.8	2.1	2.5	2.1	2.5	2.8
Electronegativity difference	+0.3		−0.4		+0.3	

In hydrolysis, for example, the positive silicon attracts a negative OH^- ion and, since it can accommodate extra electrons in its 3*d*-shell, a bond can be formed:



$$\equiv Si-H + OH^- \longrightarrow \left[\overset{OH}{\overset{\downarrow}{\equiv Si-H}}\right]^- \xrightarrow{H_2O} \equiv SiOH + H_2 + OH^- \qquad (18)$$

Since the rate-controlling step apparently involves the coordination of an OH^- to the silicon, it is clear why hydrolysis in acid solutions is slow. An analogous rapid reaction with a C—H bond is not likely since the carbon has no readily available vacant 3*d*-orbitals. Similarly, the reaction of an Si—H bond with HCl in the presence of anhydrous aluminum chloride would then be expected to proceed as indicated:



$$\left[Cl_3Al \leftarrow \underset{H}{Cl}\right] \leftarrow \underset{H}{Si\equiv} \longrightarrow Cl-Si\equiv + H_2 + AlCl_3 \qquad (19)$$

The intermediate complex formed could rearrange as shown.

For other reactions involving Si—H bonds see Eqs. (25), (28), (32–34), (35), (36), (39), (43), (44–50), (54), (65), (70), (74), (92), (100), and (122).

IV. Silane Derivatives Containing Silicon-Carbon Linkages

By far the greatest number of silane derivatives (excluding silicates) contain at least one Si—C linkage and these are of very great industrial importance in the preparation of a wide variety of polymeric materials. In this section, derivatives of the type $RSiH_3$, R_2SiH_2, R_3SiH and R_4Si (R = alkyl or aryl group) and derivatives of the higher silanes will be discussed. In following sections, compounds obtained from the above by replacing the hydrogen of the Si—H bonds by halogens, oxygen, nitrogen, etc., will be described.

Preparation. All of the above four types of compounds may, in general, be synthesized by a variety of different methods, several of which are given below.

1. The reaction of a silicon halide with an organometallic compound usually proceeds smoothly to give the desired products (*123*, *126*, *173*), e.g.,

$$2SiH_3Cl + Zn(CH_3)_2 \rightarrow 2SiH_3CH_3 + ZnCl_2 \qquad (20)$$

$$SiH_3Br + n\text{-}C_3H_7MgBr \rightarrow n\text{-}C_3H_7SiH_3 + MgBr_2 \qquad (21)$$

$$2SiH_3Br + BrMgC{\equiv}CMgBr \rightarrow H_3SiC{\equiv}CSiH_3 + 2MgBr_2 \qquad (22)$$

2. Organosilicon compounds containing Si—H bonds are generally prepared very easily and in high yields by reduction of the corresponding halosilane by means of lithium aluminum hydride (*69*, *98*), e.g.,

$$4C_6H_5SiCl_3 + 3LiAlH_4 \rightarrow 4C_6H_5SiH_3 + 3LiCl + 3AlCl_3 \qquad (23)$$

$$2(C_2H_5)_2SiCl_2 + LiAlH_4 \rightarrow 2(C_2H_5)_2SiH_2 + LiCl + AlCl_3 \qquad (24)$$

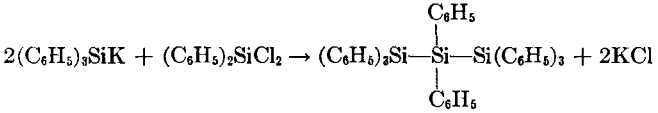
3. In the absence of silicon–halogen bonds a lithium alkyl may react with Si—H bonds (*132*), e.g.,

$$SiH_4 + 2C_2H_5Li \rightarrow (C_2H_5)_2SiH_2 + 2LiH \qquad (25)$$

Thus in silicon chemistry the hydrogen of an Si—H bond may act as a pseudohalide in certain cases.

4. Derivatives of the higher silanes may be conveniently prepared by means of silyl-metallic reagents (*85*, *92*), e.g.,

$$SiH_3SiH_2K + CH_3I \rightarrow SiH_3SiH_2CH_3 + KI \qquad (26)$$



$$2(C_6H_5)_3SiK + (C_6H_5)_2SiCl_2 \rightarrow (C_6H_5)_3Si\text{—}\overset{C_6H_5}{\underset{C_6H_5}{Si}}\text{—}Si(C_6H_5)_3 + 2KCl \qquad (27)$$

5. The higher organosilanes may also be prepared by means of a Wurtz-type reaction. When $(CH_3)_2SiCl_2$ in benzene is heated with sodium in an autoclave at 115° the cyclic, benzene-soluble crystalline compound $[(CH_3)_2Si]_6$ is obtained, together with the higher molecular weight species $[(CH_3)_2Si]_{55}$ (*32*). Compounds of this type may also be prepared by the action of Grignard reagents on $(SiBr_2)_x$, where $x \sim 16$. In this manner $(SiR_2)_x$ may be formed where R = methyl, ethyl, propyl or butyl (*150*).

Physical Properties. Organosilicon compounds are all colorless gases, liquids or solids, e.g., CH_3SiH_3 boils at −57°C, $CH_3(C_2H_5)_2SiH$ boils at 77.4°, and $(C_6H_5)_4Si$ melts at 233° (*141*).

Chemical Properties. In compounds containing Si—C and Si—H linkages it is found that, in general, the Si—H bond undergoes the same types of reactions as in the parent silanes but that the rate at which it reacts usually decreases with increasing number and size of the organic groups. For example, SiH_4 is spontaneously inflammable in air and is instantaneously attacked by even a slightly alkaline solution, whereas compounds such as SiH_3CH_3, $SiH_3C_2H_5$, $SiH_3C_3H_7$, $SiH_3C_4H_9$, $(SiH_3)_2CHCH_3$, etc. are not spontaneously inflammable in air, are thermally stable and react only very slowly with water but somewhat more rapidly with aqueous alkali (*63*, *69*, *126*, *133*, *173*, *200*); $(CH_3)_2SiH_2$ for example, is decomposed slowly by aqueous alkali

$$(CH_3)_2SiH_2 + 2NaOH \rightarrow (CH_3)_2Si(ONa)_2 + 2H_2 \qquad (28)$$

It is interesting to note that the sodium salt formed is soluble in the alkaline solution (*173*).

Similar effects are noted in the reaction of Si—H bonds with halogens; whereas bromine reacts explosively with SiH_4, $(C_6H_5)_3SiH$ reacts only slowly with bromine in refluxing carbon tetrachloride (*81*). Likewise, the rate of reaction of the Si—Si linkage toward a particular reagent is less in the substituted silanes than in the parent silanes. Again, this is what might be expected when steric factors are considered, although undoubtedly inductive and solubility effects, etc. are also important in certain cases. For example, the polymer $[(CH_3)_2Si]_{55}$ is stable to aqueous alkali hydroxide and is hydrolyzed only slowly on heating with alkali hydroxide in hexanol (*32*). This should be compared with the instantaneous reaction of the Si—Si linkage, e.g., in Si_2H_6 with aqueous alkali.

The Si—C bond is relatively inert and the most characteristic chemical properties of organosilicon compounds are generally those of the silicon linkage to other elements such as hydrogen, halogens, oxygen, nitrogen, etc. present in the molecule. Substituents attached to the organic groups generally affect the over-all chemical properties of an organosilicon compound only to a lesser extent. This is understandable since the bond between silicon and a given element is usually more labile than any bond formed by carbon to another element. For example, in $ClCH_2SiCl_3$, the Si—Cl linkage will react with most reagents before the C—Cl bond (*96*), e.g.,

$$4ClCH_2SiCl_3 + 3LiAlH_4 \rightarrow 4ClCH_2SiH_3 + 3LiCl + 3AlCl_3 \tag{29}$$

The relative chemical inertness of the Si—C bond is not related directly to its bond energy, since this is approximately the same as that of the Si—Br bond, which is very reactive; (Si—C = 76 kcal/mole; Si—Br = 74 kcal/mole). It must be remembered that whether a chemical reaction will take place depends first on whether the reaction is thermodynamically possible, and second on the reaction mechanism and dependent factors.

The relative inertness of the Si—C bond toward polar reagents is due primarily to the relatively small polarity of the Si—C bond. If we take the two analogous reactions below, we find that the first occurs instantaneously at room temperature, while the second does not take place under similar conditions

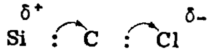
$$SiBr_4 + 2H_2O \rightarrow SiO_2 + 4HBr \tag{30}$$

$$(CH_3)_4Si + 2H_2O \rightarrow SiO_2 + 4CH_4 \tag{31}$$

On examining the polarity of the Si—C and Si—Br bonds it is found that it lies in the same direction in both cases but that its magnitude is considerably greater in the Si—Br linkage (as shown in the tabulation). It can therefore be seen that the silicon atom in the less polar Si—C linkage in, for example, an Si—CH_3 bond, will undergo attack by nucleophilic reagents,

	$\overset{\delta^+}{\text{Si}}$—	$\overset{\delta^-}{\text{C}}$	$\overset{\delta^+}{\text{Si}}$—	$\overset{\delta^-}{\text{Br}}$
Electronegativity	1.8	2.5	1.8	2.8
Electronegativity difference	+0.7		+1.0	

e.g., H_2O, OH^- ion, etc., with subsequent cleavage of the bond, less readily than that in the more polar Si—Br linkage. However, if one now replaces the relatively weak electron-attracting hydrogen atoms on the carbon by strongly electron-attracting atoms such as chlorine, then the polarity of the Si—C bond will be increased *and in a direction to make the silicon even more positive*, i.e., the Si—C bond electrons are withdrawn even more from the silicon and toward the carbon,



and the Si—C bond will now tend to react *more* readily with nucleophilic reagents, e.g., the Si—C bond in Cl_3CSiCl_3 is cleaved by cold water to give $CHCl_3$ (*81*). In this example the positive charge on the silicon is also increased by the presence of the Si—Cl bonds.

V. Silane Derivatives Containing Silicon-Halogen Linkages

A. SiH_3X AND DERIVATIVES

Preparation. The silyl halides (*113*), with the exception of the fluoride which has not been investigated in this type of reaction, may be prepared by the action of the gaseous hydrogen halide on monosilane at slightly elevated temperatures in the presence of the appropriate aluminium halide catalyst as indicated by the general equation (*54*, *126*, *172*, *173*)

$$SiH_4 + HX \rightarrow SiH_3X + H_2 \qquad (32)$$

Silyl halides may also be prepared by the interaction of a dihalosilane with silane in the presence of the appropriate aluminium halide catalyst (*173*), e.g.,

$$SiH_2Cl_2 + SiH_4 \rightarrow 2SiH_3Cl \qquad (33)$$

while an alternative preparation of the bromide involves the reaction of monosilane with solid bromine at low temperatures (*171*). Silyl fluoride has been prepared by the action of silyl chloride on antimony trifluoride (*52*).

Mono- or diorganosilyl halides may be prepared by analogous reactions; methylsilyl iodide, CH_3SiH_2I, and dimethylsilyl iodide, $(CH_3)_2SiHI$ for instance, can be prepared from HI and CH_3SiH_3 (*57*) and $(CH_3)_2SiH_2$ (*59*) respectively. Addition of iodine to a refluxing organosilane may replace one, two, or three of the hydrogen atoms (*12*),

$$n\text{-}C_7H_5SiH_3 + I_2 \rightarrow n\text{-}C_7H_5SiH_2I + n\text{-}C_7H_5SiHI_2 + n\text{-}C_7H_5SiI_3 + HI \qquad (34)$$

Iodides may also be prepared by the unexpected interaction of a disiloxane with elemental iodine at room, or slightly elevated, temperatures. In this manner $(SiH_3)_2O$ forms SiH_3I (*51*) and (cyclo-$C_6H_{11}SiH_2)_2O$ forms cyclo-$C_6H_{11}SiH_2I$ (*10*), e.g.,

$$3(\text{cyclo-}C_6H_{11}SiH_2)_2O + 3I_2 \rightarrow 3\text{cyclo-}C_6H_{11}SiH_2I + 3HI + (\text{cyclo-}C_6H_{11}SiHO)_3 \quad (35)$$

A very convenient method of preparation of chlorides and bromides involves the reduction of a metal halide (e.g., $HgCl_2$, AgCl, $CuCl_2$, etc.) by an Si—H bond at the boiling point of the silane (*9, 12*), e.g.,

$$n\text{-}C_7H_{15}SiH_3 + HgBr_2 \rightarrow n\text{-}C_7H_{15}SiH_2Br + HBr + Hg \quad (36)$$

Organohalosilanes of the type R_ySiX_{4-y} (R = alkyl or aryl groups) can usually be prepared on a small scale from the appropriate silicon tetrahalide and Grignard reagent. The chlorosilanes are of great industrial importance in the preparation of silicone polymers and are produced commercially on a large scale directly from silicon-copper mixtures and CH_3Cl or C_6H_5Cl (*142*). Trimethyl- and triethyl-, chloro-, and fluorosilanes have been prepared by the action of the hydrogen halide (generated *in situ* from concentrated sulfuric acid and the appropriate sodium or ammonium halide) on the corresponding disiloxane (*70, 163*). Mono-, di-, and trifluorosilanes have been synthesized by the action of ZnF_2 or SbF_3 on the corresponding chlorosilanes (*62, 124*). An organosilyl fluoride containing Si—H bonds has also been prepared by refluxing the appropriate disiloxane with concentrated aqueous hydrofluoric acid (*10*):

$$(\text{cyclo-}C_6H_{11}SiH_2)_2O + 2HF \rightarrow 2\text{cyclo-}C_6H_{11}SiH_2F + H_2O \quad (37)$$

This is completely analogous to the well-known reaction

$$SiO_2 + 4HF \rightleftharpoons SiF_4 + 2H_2O \quad (38)$$

The driving force behind the reaction is principally the formation of the very strong Si—F bonds (Si—O = 108 kcal/mole; Si—F = 135 kcal/mole); consequently, the analogous reaction with HCl (Si—Cl = 91 kcal/mole) does not proceed so readily although 25% yields of cyclo-$C_6H_{11}SiH_2Cl$ can be obtained if hot gaseous HCl is used in the presence of P_2O_5 (to remove water and force the equilibrium to the right) (*10*).

Physical Properties. The melting and boiling points of the parent silyl halides are given in Table II. The substituted silyl halides boil at higher

TABLE II
THE PARENT SILYL HALIDES

Compound	M.P.	B.P.
SiH_3F (*52, 189*)	—	−88.1°
SiH_3Cl (*173*)	−118.1°	−30.4°
SiH_3Br (*171*)	−94°	1.9°
SiH_3I (*54*)	−57.0°	45.4°

temperatures and, as expected, substitution of a phenyl group raises the boiling point more than methyl or ethyl groups. An approximately linear relationship exists between the boiling points of analogous pairs of silyl and methyl halides (*113*). (See also Section III.) In general, all silyl compounds boil at a higher temperature than their methyl analogs (*113*) with the exception of silyl fluoride, chloride, bromide, and pseudohalides which have lower boiling points. The Trouton constants for SiH_3F, SiH_2F_2, and $SiHF_3$ indicate that the compounds are considerably associated in the liquid state (*52*). This might be caused by hydrogen bonding or by bonding of the type $H_3SiF \rightarrow SiH_3F$. (See also Section IX,A.) It is therefore somewhat surprising to find that SiH_3F boils at a lower temperature than CH_3F.

It has been shown that when Si is attached to an element of Group V, VI, or VII by means of a σ-bond, then d_π–p_π "back-bonding" frequently occurs, and that the strength of the π bond formed is *greater* the *more* electronegative the donor atom, i.e., the $Si\overset{\leftarrow}{-}F$ bond involves "back-bonding" to a greater extent than the $Si\overset{\leftarrow}{-}Cl$ bond (*16*, *41*, *184*). This may be regarded qualitatively as an attempt to partly neutralize the large positive charge on the silicon induced by the electronegative halogen atoms. In the smaller fluorine atom better overlap of the filled *p*-orbitals of the fluorine with the empty *d*-orbitals of the silicon can occur. The vacant 3*d*-orbitals of the silicon thus permit the appearance of a certain amount of double bond character in the bonds. This is consistent with the experimental observation that silicon–halogen bonds are frequently shorter than the calculated values, assuming single bond linkages (*46*, *80*, *121*, *161*). Alternative explanations have also been advanced (*136*). The π-bonding concept also explains why many simple halogenated silanes have smaller dipole moments than their carbon analogs (*29*, *45*, *138*, *166*) when the relative electronegativity values of silicon and carbon ($Si = 1.8$; $C = 2.5$) would suggest that the silicon compounds should have the larger values.

Chemical Properties. None of the silyl halides are spontaneously inflammable in air except SiH_3Br, although they will all burn when ignited. All the hydrogen atoms in silyl halides, or in those organoderivatives containing Si—H bonds may be successively replaced by halogen by prolonged treatment with the appropriate hydrogen halide and aluminium halide catalyst (see Eq. 16), e.g.,

$$SiH_3I + HI \xrightarrow{Al_2I_6} SiH_2I_2 + H_2, \qquad \text{etc.} \tag{39}$$

In general, all the silyl halides and their partly or completely substituted organic derivatives are hydrolyzed to give the corresponding silicon ether or "disiloxane" (see Section VIII,A,*2*), e.g.,

$$2SiH_3Cl + H_2O \rightarrow (SiH_3)_2O + 2HCl \tag{40}$$

$$2(CH_3)_3SiCl + H_2O \rightarrow [(CH_3)_3Si]_2O + 2HCl \tag{41}$$

In some cases the intermediate alcohol or "silanol" [e.g., $(CH_3)_3SiOH$] which can be assumed to be formed in the above reactions, can actually be isolated. As might be expected from the steric factors mentioned previously, the rate of reaction of the silicon-halogen bond decreases as the hydrogen atoms on the silicon are replaced by progressively more bulky groups, e.g., the parent silyl halides are hydrolyzed instantaneously, whereas $(iso\text{-}C_3H_7)_3SiCl$ is hydrolyzed only very slowly (*1*). It is interesting to note that whereas $(C_2H_5)_3SiCl$, $(C_2H_5)_2SiCl_2$, and $(C_2H_5)SiCl_3$ are all hydrolyzed rapidly, $(C_2H_5)_3SiF$ is hydrolyzed only very slowly by aqueous alkali; $(C_2H_5)_2SiF_2$ is hydrolyzed rapidly by aqueous alkali but only slowly by water, and $C_2H_5SiF_3$ is hydrolyzed rapidly by water alone (*62*). This is characteristic of organofluorosilanes in general. Alcohols react with Si–halogen linkages in an analogous manner to water, but intermediate alcoholysis products can generally be obtained, e.g., $SiCl_4$ and CH_3OH react readily to give CH_3OSiCl_3, $(CH_3O)_2SiCl_2$, $(CH_3O)_3SiCl$, and $(CH_3O)_4Si$ (*88*).

An unexpected reaction occurs between SiH_3Cl and formaldehyde at 200°

$$SiH_3Cl + HCHO \rightarrow ClCH_2OSiH_3 \tag{42}$$

Analogous reactions occur with $HSiCl_3$ and $SiCl_4$ to give $ClCH_2OSiHCl_2$ and $ClCH_2OSiCl_3$ respectively (*77*).

All the silyl halides have a tendency to disproportionate in the absence of catalyst at room temperature:

$$2SiH_3X \rightarrow SiH_2X_2 + SiH_4 \tag{43}$$

However, SiH_3I suffers only negligible decomposition on being stored at room temperatures for several months. Since the total number of Si—H and Si—X bonds broken and formed in this process is zero, it appears probable that the ΔH term in the free energy equation,* $\Delta F = \Delta H - T\Delta S$, is not far removed from zero since the Si—H and Si—X bond lengths in the reactants and products should not differ too greatly. Thermodynamically, however, the reactions might be expected to proceed at least to a measurable extent primarily because of the increase in entropy involved in the redistribution of the hydrogen and halogen atoms. The greater rate of this type of decomposition with silyl compounds as compared to methyl compounds is undoubtedly related, at least in part, to the low-energy reaction path made available by the ability of silicon to increase its coordination number to above four, viz.,

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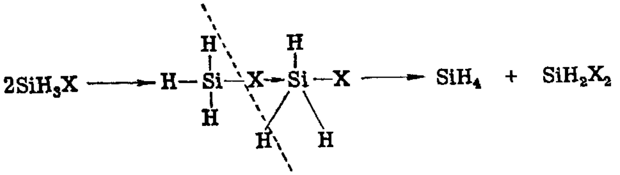
* The symbols ΔF, ΔH, and ΔS refer to the free energy, enthalpy, and entropy differences, respectively, between the reactants and products at temperature, T.



(44)

followed by cleavage of the intermediate complex as shown.

The silyl halides are the chief reagents used in the synthesis of silyl compounds. The iodides in particular may be used to prepare other derivatives by reaction with the appropriate silver salt as illustrated in the "Conversion Series" below. Treatment of a compound with the appropriate silver salt will bring about a conversion into any compound later in the series but into none earlier therein (*11*, *48*, *113*). This has been thoroughly tested with triorganosilyl derivatives and all parent silyl compounds so far investigated substantiate the order.

$$H_3SiI \rightarrow (H_3Si)_2Se \rightarrow (H_3Si)_2S \rightarrow H_3SiBr \rightarrow H_3SiCN \rightarrow H_3SiCl \rightarrow H_3SiNCS \rightarrow H_3SiNCO \rightarrow (H_3Si)_2O \rightarrow H_3SiF$$

For example, SiH_3I reacts with Ag_2Se to give $(SiH_3)_2Se$ (*51*) but $(SiH_3)_2O$ does not react with AgCl to give SiH_3Cl. Equilibrium conditions appear to exist between the chloride and cyanide (*66*). There is also evidence of a similar conversion series involving mercuric salts, but only a few reactions have so far been investigated (*113*).

For other reactions involving silicon–halogen bonds, see Eqs. (2), (3), (5), (6), (9) (11), (12), (20–24), (27), (29), (30), (48–51), (53–57), (67), (68), (72), (81), (83–85), (89), (90), (94–99), (102), (104), (108), (110–115), (119), (120), (129), (133), (137), (138).

B. SiH_2X_2 AND DERIVATIVES

Preparation. The parent compounds may be conveniently prepared by the controlled action of a hydrogen halide on monosilane or a silyl halide, and in the case of SiH_2Br_2, from silane and bromine (*54*, *57*, *126*, *171*, *172*, *173*), e.g.,

$$SiH_3Cl + HCl \xrightarrow{Al_2Cl_6} SiH_2Cl_2 + H_2 \tag{45}$$

$$CH_3SiH_2I + HI \xrightarrow{Al_2I_6} CH_3SiHI_2 + H_2 \tag{46}$$

$$SiH_4 + 2Br_2 \longrightarrow SiH_2Br_2 + 2HBr \tag{47}$$

Good yields of SiH_2Cl_2 may be obtained by the disproportionation of $HSiCl_3$ (one of the few commercially available materials containing Si—H linkages) in the presence of catalysts, e.g., dimethylcyanamide, at temperatures below 150° (*19*).

$$2HSiCl_3 \rightarrow H_2SiCl_2 + SiCl_4 \tag{48}$$

It may also be prepared from SiH_4 and $SiCl_4$ at 300° in the presence of anhydrous aluminium chloride catalyst (*37*)

$$SiH_4 + SiCl_4 \rightarrow 2SiH_2Cl_2 \qquad (49)$$

This type of reaction also occurs with organochlorosilanes.

Substances such as CH_3SiHCl_2 may be prepared by passing a mixture of hydrogen and CH_3SiCl_3, for example, over a halogen acceptor such as heated aluminium or zinc. In general, compounds of the type R_2SiX_2 may be synthesized in a similar manner to triorganohalosilanes (*141*). (See Section V,A.)

Physical Properties. The physical properties of the parent compounds are given in Table III.

TABLE III
THE PARENT SILYLENE HALIDES

Compound	M.P.	B.P.
SiH_2F_2 (*52*)	−122.0°	−77.8°
SiH_2Cl_2 (*173*)	−122°	8.3°
SiH_2Br_2 (*171*)	−70.1°	66°
SiH_2I_2 (*54*)	−1.0°	149.5°

Chemical Properties. The chemical properties of the Si—H, Si–halogen, and Si—C (if present) bonds in these compounds are similar to the properties already ascribed to these linkages in previous sections. An analogous reaction to that given in Eq. (49) occurs with SiH_2Cl_2 (*173*)

$$SiH_4 + SiH_2Cl_2 \xrightarrow{Al_2Cl_6} 2SiH_3Cl \qquad (50)$$

C. $SiHX_3$ AND DERIVATIVES

Preparation. Although $HSiCl_3$, $HSiBr_3$, and $HSiI_3$ may be obtained by prolonged treatment of silane with hydrogen halide (see Section III), the compounds are much more easily prepared by treating silicon, ferrosilicon, or calcium silicide with anhydrous hydrogen halide at 350–450°. The trihalosilane can be distilled readily from the mixture of silicon tetrahalide and higher silicon halides also produced (*25*, *152*, *158*, *201*). A particularly novel synthetic method for $HSiCl_3$ involves the interaction of ammonium halides with Si_2Cl_6 or $C_2H_5Si_2Cl_5$ at reflux temperatures (*204*). The preparation of $HSiI_3$ from $HSiCl_3$ may be readily carried out by the use of aniline followed by HI (*144*)

$$HSiCl_3 + 3C_6H_5NH_2 \rightarrow HSi(NHC_6H_5)_3 + 3HCl \qquad (51)$$

$$HSi(NHC_6H_5)_3 + 3HI \rightarrow HSiI_3 + 3C_6H_5NH_2 \qquad (52)$$

$HSiF_3$ may be prepared by fluorinating the chloride by means of SbF_3 (catalyst $SbCl_5$), SnF_4 etc. (*26, 52, 145*), e.g.,

$$HSiCl_3 + SbF_3 \rightarrow HSiF_3 + SbCl_3 \qquad (53)$$

or from SiF_4 and hydrogen (*208*). During the above fluorination reaction, considerable quantities of $HSiCl_2F$ and $HSiClF_2$ are also formed (*26*).

Organic derivatives of the type $RSiX_3$ may in general be prepared by similar methods to those used for R_3SiX. (See Section V,A.)

Physical Properties. The physical properties of the parent trihalosilanes are given in Table IV.

TABLE IV

THE PARENT SILYLIDYNE HALIDES

Compound	M.P.	B.P.
$HSiF_3$ (*52*)	−131.4°	−95.0°
$HSiCl_3$ (*181*)	−126.5°	31.8°
$HSiBr_3$ (*152*)	−73.5°	111.8°
$HSiI_3$ (*144*)	8°	220°
$HSiCl_2F$ (*26*)	−149.5°	−18.4°
$HSiClF_2$ (*26*)	~−144°	~−50°

Chemical Properties. It has been stated that $HSiF_3$ disproportionates even at very low temperatures (*26*), but recent evidence indicates that it is completely stable if free from traces of HF (*208*). All other properties of the parent and organoderivatives are those expected from previous discussions of the reactions of Si—H, Si–halogen, and Si—C (if present) linkages.

D. SiH_3SiH_2X AND DERIVATIVES

Si_2H_6 reacts with HCl, HBr, and HI in the presence of aluminium halide catalyst in an analogous manner to silane to give compounds in which one or more of the hydrogen atoms are replaced by halogen (*175, 197*). Reaction proceeds much more rapidly than with SiH_4. The HI, for instance, in a mixture of HI with excess Si_2H_6 is completely consumed in 3 to 4 hours at room temperature (*197*).

Disilanyl chloride, SiH_3SiH_2Cl, and disilanyl bromide, SiH_3SiH_2Br, disproportionate so rapidly that it has not been possible to obtain them in the pure state (*175*), viz.,

$$2SiH_3SiH_2X \rightarrow Si_2H_6 + Si_2H_4X_2 \qquad (54)$$

The iodide, however, is much more stable and has been completely characterized (*197*). Disilanyl iodide is spontaneously inflammable in air, melts at −86.1° and boils at 102.8°. Considerable decomposition of the compound occurs after 5 hours at 90°. It is rapidly hydrolyzed by pure water to the corresponding ether.

$$2SiH_3SiH_2I + H_2O \rightarrow (SiH_3SiH_2)_2O + 2HI \qquad (55)$$

Pentamethyldisilanyl chloride, $(CH_3)_3SiSi(CH_3)_2Cl$, may be prepared by stirring $(CH_3)_3SiSi(CH_3)_3$ with concentrated sulfuric acid, then with NH_4Cl (*106, 107*). The fluoride may be prepared in an analogous manner. It is interesting to note that the Si—Si bond survives treatment with sulfuric acid under conditions in which Si—C bonds are broken. The pentaphenylchloro derivative is prepared by the use of $(C_6H_5)_3SiK$ (*85*)

$$(C_6H_5)_3SiK + (C_6H_5)_2SiCl_2 \rightarrow (C_6H_5)_3SiSi(C_6H_5)_2Cl + KCl \qquad (56)$$

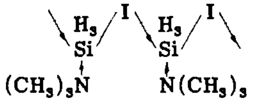
VI. Addition Compounds of Silicon Halides with Amines, Phosphines, or Arsines

Since silicon has vacant 3d orbitals available for bond formation it might be expected that SiH_4 would act as a Lewis acid and form addition compounds with Lewis bases such as tertiary amines. This, however, does not occur unless the "acid strength" of the silicon has been increased by substituting one or more of the hydrogen atoms by a halogen. This then makes the silicon more positive and hence more susceptible to nucleophilic attack. Trimethylamine, for instance, reacts instantaneously even at low temperatures with halosilanes to form solid addition compounds such as $SiH_3I \cdot N(CH_3)_3$, $SiH_3Cl \cdot N(CH_3)_3$, $HSiCl_3 \cdot NMe_3$, etc. (*16, 30, 55, 68, 113, 196, 205*). On examining their relative stabilities given by the series

$$SiCl_4 \cdot N(CH_3)_3 < HSiCl_3 \cdot N(CH_3)_3 < H_2SiCl_2 \cdot N(CH_3)_3 = H_3SiCl \cdot N(CH_3)_3$$

it is found that $SiCl_4 \cdot N(CH_3)_3$ is the least stable and that $H_2SiCl_2 \cdot N(CH_3)_3$ and $H_3SiCl \cdot N(CH_3)_3$ are the most stable (*184*). From electronegativity aspects one would expect $SiCl_4 \cdot N(CH_3)_3$ to be the most stable compound; however, it has been suggested (*30*) that the steric effect of the bulky chlorine atoms tends to decrease the stability of the compounds, and in this series the latter effect predominates. As expected from the electronegativities of fluorine and chlorine, $SiF_4 \cdot N(CH_3)_3$ and $HSiF_3 \cdot N(CH_3)_3$ are more stable than their chlorine analogs; however, $SiF_4 \cdot N(CH_3)_3$ is *more* stable than $HSiF_3 \cdot N(CH_3)_3$, whereas $SiCl_4 \cdot N(CH_3)_3$ is *less* stable than $HSiCl_3 \cdot N(CH_3)_3$. Thus in the fluorosilanes the electronegativity factor apparently overcomes any opposing steric factor.

Although these substances could be formulated as simple five-coordinate silicon compounds it appears more likely that they are ionic quaternary ammonium compounds (*68*), viz., $[H_3SiN(CH_3)_3]^+I^-$ or hexacoordinated halogen-bridged structures (A).



(A)

The two extreme types of structures suggested can be given as shown below, where X = a halogen (*113*).

$$(H_ySiX_{4-y}) \cdot N(CH_3)_3 \qquad (a)$$

and

$$[(H_yX_{3-y}Si)N(CH_3)_3]^+X^- \qquad (b)$$

Structure (*b*) will be most favored when there are no halogen atoms in the cation, since the presence of halogen atoms attached to the silicon would increase the electron-attracting power of the cation as a whole, and consequently reduce the tendency to ionize. These two structures are similar in form but differ only to the extent to which an electron may migrate toward a halogen atom. Structure (*b*) will therefore be most favored with a silyl halide, and consequently silyl halide adducts with tertiary amines are the most likely to have the quaternary ammonium salt structure. In this respect it is interesting to note that $[H_3SiN(CH_3)_3]Cl$ and $[H_3SiN(CH_3)_3]I$ are good electrical conductors when dissolved in appropriate organic solvents. It should be noted that a solution of $SiH_3I \cdot 2N(CH_3)_3$ does not conduct electricity under identical experimental conditions.

It is shown in Sections V,A and IX,A that a silyl group may attract electrons strongly by π-bonding, and hence it is not surprising to find that no stable compounds of the above type are known in which there is more than one silyl group. For example, $[(SiH_3)_2N(CH_3)_2]Cl$ is not sufficiently stable to be isolated in the pure state (*55*). Likewise, CH_3SiH_2I and $(CH_3)_2N(SiH_2CH_3)$ combine in a 1:1 ratio at low temperatures to form a compound which is completely dissociated in the vapor state (*50*). No reaction is found to take place between SiH_3I and $N(SiH_3)_3$.

Phosphine derivatives (*16*, *188*) of the above type are also known, viz., $[SiH_3P(CH_3)_3]I$, $[SiH_3P(C_2H_5)_3]I$, $[SiH_3PH(CH_3)_2]Br$, $[SiH_3PH(CH_3)_2]I$, and $[SiH_3PH_2CH_3]Br$. They are all white solid materials formed by instantaneous direct reaction between the appropriate silyl halide and alkylphosphine at or below room temperatures. $[SiH_3PH(CH_3)_2]Br$ and $[SiH_3PH_2CH_3]Br$ are largely dissociated even at low temperatures, whereas $[SiH_3P(C_2H_5)_3]I$ is very stable at room temperatures and its solution in acetonitrile conducts a nelectric current.

The white solid, $[(SiH_3)_4P]I$, tetrasilylphosphonium iodide (*16*), may be considered as being formed from SiH_3I and the $(SiH_3)_3P$ produced during the reaction of SiH_3I with white phosphorus. The compound $[SiH_3As(CH_3)_3]I$ (*16*), which may be formulated as an arsonium compound, is formed in the reaction of SiH_3I with $As(CH_3)_3$. It melts at 8.1–9.6° and has a high dissociation pressure at low temperatures. The interaction of SiH_3I with $As(SiH_3)_3$ (prepared *in situ* by the action of SiH_3I on mercuric arsenide) produces $[(SiH_3)_4As]I$, an unstable white solid (*16*).

VII. Silane Derivatives Containing Silicon-Pseudohalogen Linkages

A. SiH_3CN AND DERIVATIVES

Although silyl cyanide, SiH_3CN, appears to have the normal cyanide structure, in many cases it is not clear whether the compounds should be formulated as the normal or iso-derivatives. For the sake of convenience, the compounds will be referred to as the normal cyanides without implying that this is their actual structure.

Preparation. SiH_3CN may be prepared in good yields by passing the vapor of SiH_3I over AgCN at room temperature (*111*)

$$SiH_3I + AgCN \rightarrow SiH_3CN + AgI \tag{57}$$

The compounds CH_3SiH_2CN and $(CH_3)_2SiHCN$ can be prepared in a similar manner (*57*, *104*), while $(CH_3)_3SiCN$ may be obtained by refluxing $(CH_3)_3SiCl$ with AgCN (*66*). The chloro derivative, Cl_3SiCN, is produced by cleaving the Si—Si bond in Si_2Cl_6 with $Hg(CN)_2$ at 100° (*95*)

$$Cl_3SiSiCl_3 + Hg(CN)_2 \rightarrow 2Cl_3SiCN + Hg \tag{58}$$

Compounds of the type $R_2Si(CN)_2$ may also be synthesized from the corresponding halides (*47*, *117*).

Physical Properties. SiH_3CN is a white solid with a high vapor pressure at room temperature. It melts at 32.4° and boils at 49.6° (*111*). The methylated derivatives melt at considerably lower temperatures.

Whether the silyl cyanides have the normal or the iso-structure has invoked considerable discussion. Hydrolysis cannot be used to distinguish between the isomers as with the carbon analogs, since the silicon–cyanide bond is cleaved very rapidly by water, and substances analogous to CH_3COONH_4 or CH_3NH_2 produced by hydrolysis of the carbon compounds cannot therefore be obtained (*111*). Infrared studies on SiH_3CN and SiD_3CN strongly suggest the normal structure for the parent compound (*109*); this conclusion has recently been substantiated by an examination of the microwave spectrum of SiH_3CN (*162*).

The infrared spectrum of $(CH_3)_3SiCN$ favors the normal cyanide structure, but it also suggests that a small quantity of isocyanide is always present in the pure material (*23*, *110*, *117*, *160*). The chemical properties of $(CH_3)_3SiCN$ indicate that the substance may be an equilibrium mixture of the normal and isocyanide, in which equilibrium conditions are established very rapidly—hence the pure material may react as if it consisted completely of either of the pure species (*23*, *160*). For example, $(CH_3)_3SiCN$ and $(C_6H_5)_3SiCN$ readily add sulfur, thus indicating an isocyanide structure (*23*, *117*), e.g.,

$$(CH_3)_3SiNC + S \rightarrow (CH_3)_3SiNCS \qquad (59)$$

In comparison, it should be noted that SiH_3CN does not add sulfur at room temperature, and complex decomposition occurs when the temperature is raised (*109*). The trimethylsilyl derivative also reacts with $Fe(CO)_5$ to give 93 per cent yields of the yellow, crystalline compound $(CH_3)_3Si{-}N\overset{\rightarrow}{=}C{\rightarrow}Fe(CO)_4$ (*160*)

$$(CH_3)_3SiNC + Fe(CO)_5 \rightarrow (CH_3)_3SiNCFe(CO)_4 + CO \qquad (60)$$

Organic isocyanides undergo a similar type of reaction. It is interesting to find that analogous equilibrium systems apparently exist in the germanium and tin analogues of $(CH_3)_3SiCN$ (*160*).

Chemical Properties. Both SiH_3CN and $(CH_3)_3SiCN$ react at approximately $-100°$ to give the addition compounds $SiH_3CN \cdot BH_3$ and $(CH_3)_3SiCN \cdot BH_3$ which decompose on heating to 100° (*66*)

$$SiH_3CN \cdot BH_3 \rightarrow (BH_2CN)_x + SiH_4 \qquad (61)$$

$$(CH_3)_3SiCN \cdot BH_3 \rightarrow (BH_2CN)_n + (CH_3)_3SiH \qquad (62)$$

The polymeric $(BH_2CN)_n$ formed is remarkably stable to water, oxygen, and heat. On decomposing $(CH_3)_3SiCN \cdot BH_3$ in the presence of excess $(CH_3)_3SiCN$, a liquid of composition $(CH_3)_3SiCN \cdot BH_2CN$ is obtained (*66*).

In a similar manner, both SiH_3CN and $(CH_3)_3SiCN$ react at low temperatures with BF_3, BCl_3, and BBr_3 to give addition compounds which decompose slowly at or below room temperature (*65*)

$$SiH_3CN + BX_3 \rightarrow SiH_3CN \cdot BX_3 \rightarrow (BX_2CN)_n + SiH_3X \qquad (63)$$

It can be seen that this type of reaction is completely analogous to reactions shown in Eq. (61) and (62) as is also the reaction below (*64*)

$$20(CH_3)_3SiCN + 20(n\text{-}C_4H_9)_2BCl \rightarrow [(n\text{-}C_4H_9)_2BCN]_{20} + 20(CH_3)_3SiCl \qquad (64)$$

B. SiH_3NCO AND DERIVATIVES

The parent compounds, silyl cyanate and silyl isocyanate, have not been prepared, but cyclo-$C_6H_{11}SiH_2NCO$ has been made by refluxing a solution of cyclo-$C_6H_{11}SiH_3$ in carbon tetrachloride with silver cyanate (*10*)

$$\text{cyclo-}C_6H_{11}SiH_3 + 2AgNCO \rightarrow \text{cyclo-}C_6H_{11}SiH_2NCO + 2Ag + HOCN \qquad (65)$$

Compounds such as $SiCl_3NCO$ and cyclo-$C_6H_{11}Si(NCO)_3$, etc., may be obtained from the appropriate halide or hydride and silver cyanate (*2*, *10*, *48*), and those of the type $R_xSi(NCO)_{4-x}$ (R = alkyl group) have been prepared by reacting the appropriate chlorosilane with silver cyanate (*7*, *72*).

Properties. The substances are colorless solids or liquids and on the basis of their molecular refractions and boiling points it is thought that most of them probably have the isocyanate structure (*72*, *73*). The compounds are similar to the halides in the ease with which they undergo hydrolysis.

C. SiH_3NCS AND DERIVATIVES

Silyl isothiocyanate, SiH_3NCS, may be obtained by passing the vapor of SiH_3I over silver thiocyanate (*111*), while compounds such as cyclo-$C_6H_{11}SiH_2NCS$, $(C_6H_5)_3SiNCS$, $R_2Si(NCS)_2$, and $SiCl_3NCS$ have been prepared by methods analogous to those used for the corresponding isocyanates (*3*, *4*, *6*, *10*, *71*, *83*).

Properties. SiH_3NCS melts at −51.8° and boils at 84.0° (*111*). It is believed to have the isothiocyanate structure since the infrared spectrum indicates that it is a linear molecule (in distinction to CH_3NCS, which is nonlinear); this suggests a structure such as $H_3Si\substack{\leftarrow \\ -}N{=}C{=}S$ (*115*). (See also Section IX,A.) Molecular refractions, boiling points, and spectral data indicate that all compounds containing the NCS grouping are probably isothiocyanates (*5*, *71*, *89*) which is consistent with the appreciable double-bond character found in the Si—N linkage in $(CH_3)_3SiNCS$ (*89*).

SiH_3NCS decomposes during 2–3 weeks at room temperature, and both it and its organo-derivatives are readily hydrolyzed.

VIII. Silane Derivatives Containing Silicon Linked to Oxygen, Sulfur, or Selenium

A. OXYGEN COMPOUNDS

1. SiH_3OH *and Derivatives*

The parent silanol, the silicon analog of CH_3OH, has not been isolated although there is a little evidence for its transitory existence during the hydrolysis of SiH_3I (*114*). It condenses extremely rapidly to $(SiH_3)_2O$ even at very low temperatures (*177*)

$$2SiH_3OH \rightarrow (SiH_3)_2O + H_2O \qquad (66)$$

Careful hydrolysis of trialkyl or triaryl halosilanes, however, leads to the formation of the corresponding silanol, R_3SiOH, many of which are known (*164*).

Properties. The silanols are colorless solids or liquids. Trimethylsilanol, $(CH_3)_3SiOH$, for instance, may be distilled at 99° without decomposition

(*164*) and has a camphor-like odor. The most characteristic chemical property of silanols is their relative ease of condensation as compared with their carbon analogues, the rate decreasing with increasing size of the attached organic groups. Some sterically hindered silanols are in fact very resistant to condensation.

2. $(SiH_3)_2O$ *and Derivatives*

The condensation of silanols, which may occur spontaneously or only in the presence of acid or alkali catalysts, yields silicon "ethers" or siloxanes.

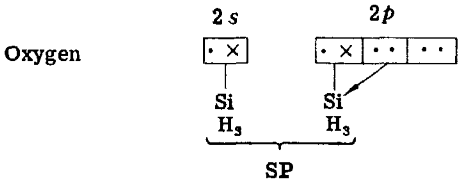
Preparation. Disilyl ether or disiloxane, $(SiH_3)_2O$, may be prepared in good yields by the instantaneous hydrolysis of almost any silyl compound (*113*). In some cases, secondary reactions may destroy the disiloxane; e.g., the liberation of NH_3 in the hydrolysis of $(SiH_3)_3N$ produces an alkaline solution which decomposes any Si—H linkages present. Disiloxane is most commonly prepared by the hydrolysis of a silyl halide, and in general, partly and completely organo-substituted disiloxanes such as $(CH_3SiH_2)_2O$, $[(CH_3)_3Si]_2O$, etc. can be easily prepared by the hydrolysis of the corresponding silyl halide (*57*). Silver carbonate may also be used (*59*):

$$2(CH_3)_2SiHI + Ag_2CO_3 \rightarrow [(CH_3)_2SiH]_2O + 2AgI + CO_2 \qquad (67)$$

Derivatives of $(SiH_3)_2O$ in which the hydrogen atoms are completely replaced by chlorine or bromine may be obtained by passing a mixture of either chlorine and oxygen or bromine and oxygen over silicon at dull red heat (*153*, *154*). Hexachlorodisiloxane, $(SiCl_3)_2O$, has also been prepared by the partial hydrolysis of $SiCl_4$ (*156*). In a similar manner $(H_2SiCl)_2O$ and $(HSiCl_2)_2O$ are produced by the partial hydrolysis of H_2SiCl_2 and $HSiCl_3$ respectively (*199*). Fluorination of the chloride yields $(SiF_3)_2O$ (*24*).

The ether, SiH_3OCH_3, intermediate between disilyl and dimethyl ethers, has recently been prepared by the interaction of CH_3OH with $[SiH_3N(CH_3)_3]I$ at low temperatures (*168*).

Physical Properties. The parent disiloxane, $(SiH_3)_2O$, melts at −144° and boils at −15.2° (*177*) while SiH_3OCH_3 melts at −98.5° and boils at −21.1° (*168*). It is interesting to note that whereas the C—O—C bond angle in $(CH_3)_2O$ is 111° (*131*), the Si—O—Si angle in $(SiH_3)_2O$ is 155° (*44*), and that in $[(CH_3)_3Si]_2O$ it is 150° (*102*). A considerable amount of double-bond character in the Si—O bond is therefore indicated. (See also Section IX,A.) This may be shown diagrammatically as



i.e., $H_3Si\text{—}O\overset{\rightarrow}{\text{—}}SiH_3$ and other resonance forms. Although the relative electronegativities of silicon and carbon ($Si = 1.8$; $C = 2.5$) indicate that $(SiH_3)_2O$ might be a stronger base than $(CH_3)_2O$, the reverse is found to be the case experimentally. For instance, B_2H_6 forms an addition compound with $(CH_3)_2O$ but not with $(SiH_3)_2O$ (*186*) or with SiH_3OCH_3 (*168*). The large Si—O—Si bond angle in $(SiH_3)_2O$ suggests that the lone pairs of electrons on the oxygen atom are employed, at least in part, in "back-bonding" to the silicon atoms, and they are not therefore readily available as in $(CH_3)_2O$, to form Lewis acid–base compounds of the type $(SiH_3)_2O \rightarrow BH_3$. (See also Section IX,A.)

Chemical Properties. $(SiH_3)_2O$ is not spontaneously inflammable in air, although it will burn when ignited; it is very stable thermally and may be heated to 300–400° without much decomposition occurring. It reacts explosively with chlorine even at low temperatures to give a mixture of $SiCl_4$ and $(SiCl_3)_2O$ (*177*). Although $(SiH_3)_2O$ does not react with HI, cleavage of the Si—O bond occurs in the case of $(CH_3SiH_2)_2O$ with the formation of CH_3SiH_2I (*56*).

For other reactions involving Si—O bonds, see Eqs. (4), (35), (37), (38), (69), (71), (73), (75–80).

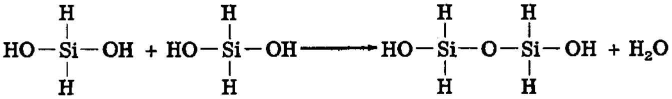
3. $SiH_2(OH)_2$, $SiH(OH)_3$ *and Derivatives*

Preparation. The parent compounds $SiH_2(OH)_2$ and $SiH(OH)_3$ have not been isolated but several organic derivatives have been prepared by the careful hydrolysis of the corresponding chlorides. Dimethylsilanediol, $(CH_3)_2Si(OH)_2$, and phenylsilanetriol, $C_6H_5Si(OH)_3$, for example, have been obtained by the hydrolysis of the appropriate chloro compounds (*191*), e.g.,

$$(CH_3)_2SiCl_2 + 2H_2O \rightarrow (CH_3)_2Si(OH)_2 + 2HCl \qquad (68)$$

Properties. The silanediols and -triols are colorless solids which condense even more readily (to either cyclic or linear siloxanes), by heating or by acid or base catalysis, than the corresponding silanols. As expected, $(C_6H_5)_2Si(OH)_2$ exhibits a much smaller tendency to condense than $(CH_3)_2Si(OH)_2$, for example, and it can be stored more or less indefinitely under normal laboratory conditions.

When benzene solutions of H_2SiCl_2 are hydrolyzed, the $SiH_2(OH)_2$, which may be assumed to be formed momentarily, condenses to give benzene-soluble cyclic $(H_2SiO)_6$ (*174*). Condensation presumably occurs stepwise, e.g.,



$$HO-\underset{H}{\overset{H}{Si}}-OH + HO-\underset{H}{\overset{H}{Si}}-OH \longrightarrow HO-\underset{H}{\overset{H}{Si}}-O-\underset{H}{\overset{H}{Si}}-OH + H_2O \qquad (69)$$

The molecule formed may react with a similar molecule or with a $H_2Si(OH)_2$ molecule with further elimination of water to give cyclic or linear (Si—OH terminal groups) siloxanes. Hydrolysis of organohalosilanes of the type $RSiHX_2$ and R_2SiX_2 proceeds in a similar manner. Polysiloxanes may also be obtained from the reaction of $(C_2H_5)_2SiH_2$ with either silver or mercury oxides at room temperature (*38*)

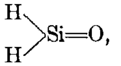
$$(C_2H_5)_2SiH_2 + 2HgO \rightarrow [Si(C_2H_5)_2O]_x + 2Hg + H_2O \qquad (70)$$

Because of the great thermal and hydrolytic stability of the Si—C and Si—O bonds, the organosiloxanes, by slight modification, have been converted into extremely useful polymeric materials called "silicones." For instance, by hydrolyzing a mixture of $(CH_3)_3SiCl$ and $(CH_3)_2SiCl_2$ in the appropriate proportions, linear polymers in which the end groups are —$Si(CH_3)_3$ have been obtained (*141*), e.g.,

$$2(CH_3)_3SiOH + 4(CH_3)_2Si(OH)_2 \rightarrow (CH_3)_3SiO[(CH_3)_2SiO]_4Si(CH_3)_3 + 5H_2O \quad (71)$$

The siloxanes, depending on their structure and molecular weights, may be liquids or solids.

If condensation were to proceed in an *intra-* rather than an *inter*molecular fashion, then hydrolysis of H_2SiCl_2 or SiH_2Br_2 might be expected to yield



$H_2Si{=}O$,

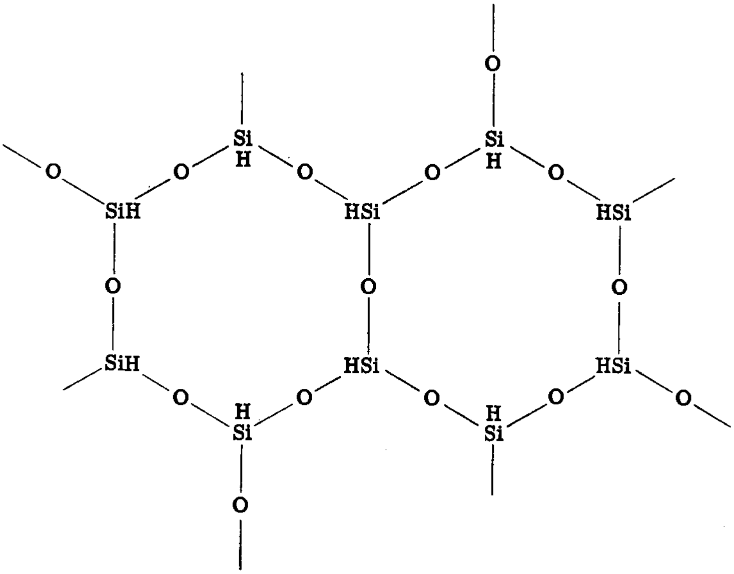
the silicon analogue of formaldehyde

$$H_2SiCl_2 + 2H_2O \rightarrow H_2Si(OH)_2 + 2HCl \qquad (72)$$
$$H_2Si(OH)_2 \rightarrow H_2Si{=}O + H_2O \qquad (73)$$

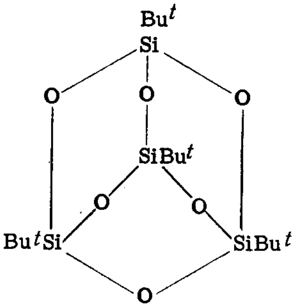
A volatile compound, presumably $H_2Si{=}O$, is actually formed by the hydrolysis of the above two compounds in the vapor phase, and this then rapidly polymerizes to a liquid, which then further polymerizes to a silica-like solid (*174, 178*). This process is analogous to the polymerization of formaldehyde to paraformaldehyde.

Hydrolysis of $HSiCl_3$ presumably produces $HSi(OH)_3$, which then immediately condenses to give a highly polymerized white solid, $HSiO_{1.5}$, i.e., $[(H_2Si_2O_3)]_x$, which has a mica-like, two-dimensional structure (*203*) shown on opposite page (B).

A material of similar structure is obtained by the hydrolysis of $C_2H_5SiCl_3$, but *tert*-butyltrichlorosilane (Bu^t), because of steric hindrance, gives (C) a less highly polymerized species, $(tert\text{-}C_4H_9SiO_{1.5})_4$ (*203*)



(B)



(C)

On heating $HSiO_{1.5}$ at 500° it slowly loses hydrogen (*203*):

$$(HSiO_{1.5})_6 \quad \text{i.e., } H_6Si_6O_9 \rightarrow H_4Si_6O_9 \rightarrow H_2Si_6O_9 \rightarrow Si_6O_9 \qquad (74)$$

The silicon oxide Si_6O_9 finally formed is believed to have Si—Si bonds in place of Si—H bonds, i.e., $2{\equiv}Si{-}H \rightarrow Si{-}Si + H_2$.

The chemical properties of polymeric organosiloxanes are, in general, those expected for compounds containing both Si—C and Si—O bonds, e.g.,

$$(R_2SiO)_3 + 2BCl_3 \rightarrow 3R_2SiCl_2 + B_2O_3. \qquad (75)$$

Intermediate species are also formed as in the analogous reaction with disiloxanes (see Eqs. 79, 80) (*118*).

4. $(SiH_3SiH_2)_2O$ *and Derivatives*

Bisdisilanyl ether, $(SiH_3SiH_2)_2O$, may be prepared in good yields by the hydrolysis of SiH_3SiH_2I. It melts at −111.7° and boils at 94.8°. It is spontaneously inflammable in air, is not as stable thermally as $(SiH_3)_2O$, and decomposes slightly on heating at 70° for several hours (*197*).

The chlorinated derivative, $(SiCl_3SiCl_2)_2O$ may be prepared in a manner similar to $(SiCl_3)_2O$ by the partial hydrolysis of Si_2Cl_6 (*155*).

5. Siloxy (H_3SiO—) *Compounds*

A large number of compounds are known in which R_3SiO— groups are attached to metal or nonmetal atoms, but very few containing the SiH_3O— group are known.

Preparation. Many methods for preparing the above type of siloxy compounds are known, but space does not permit a discussion of the triorganosiloxy derivatives.*

Disiloxane and organodisiloxanes (*127*) react with anhydrous aluminium halides and, as expected, the reaction with the parent compound occurs the most readily. Even at −65° the Si—O—Si bond is cleaved (*103*), e.g.,

$$2(SiH_3)_2O + Al_2Cl_6 \rightarrow 2SiH_3OAlCl_2 + 2SiH_3Cl \qquad (76)$$

$$2(SiH_3)_2O + (CH_3)_4Al_2Br_2 \rightarrow (CH_3)_4Al_2(OSiH_3)_2 + 2SiH_3Br \qquad (77)$$

$$2[(CH_3)_3Si]_2O + Al_2Cl_6 \rightarrow 2(CH_3)_3SiOAlCl_2 + 2(CH_3)_3SiCl \qquad (78)$$

In a similar manner, certain of the boron halides react rapidly with $(SiH_3)_2O$, $(CH_3SiH_2)_2O$, $[(CH_3)_2SiH]_2O$, or $[(CH_3)_3Si]_2O$ at low temperatures (*56, 202*), e.g.,

$$(SiH_3)_2O + BCl_3 \rightarrow SiH_3Cl + SiH_3OBCl_2 \qquad (79)$$

Silyl methyl ether, SiH_3OCH_3, also reacts with BF_3 producing SiH_3F and CH_3OBF_2 (*168*). No evidence for stable addition compounds between $(SiH_3)_2O$ and BF_3, BCl_3, or $B(CH_3)_3$ has been obtained (*56*).

Properties. Parent siloxy compounds of the type SiH_3OAlX_2 decompose spontaneously below room temperature with the production of SiH_3X, SiH_2X_2, and SiH_4 (*103*). $(CH_3)_4Al_2(OSiH_3)_2$ melts at 41–42°, boils at 109–112°, and is considerably more stable thermally. It is dimeric in the vapor state and presumably has the structure (D).

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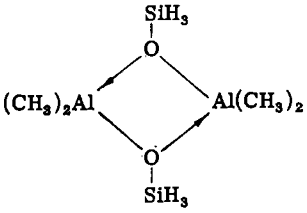
* For a summary of compounds of the type R_3SiO—M, see p. 319 in reference (*49*).



(D)

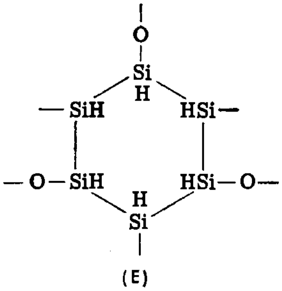
Both the parent and organosiloxyboron halides also decompose spontaneously (*56, 202*)

$$3SiH_3OBCl_2 \rightarrow 3SiH_3Cl + BCl_3 + B_2O_3 \qquad (80)$$

6. *Siloxene,* $(Si_2H_2O)_x$*, and Derivatives*

When calcium silicide, $CaSi_2$, is allowed to react with a mixture of hydrochloric acid and alcohol, hydrogen is evolved and a white solid with the empirical formula Si_2H_2O is formed (*97*). It is believed that this material has a somewhat similar structure to $HSiO_{1.5}$, but that Si—Si linkages are present in addition to Si—H and Si—O bonds.

Calcium silicide has a layer lattice structure with calcium atoms arranged in sheets between layers of silicon atoms. It is believed that the acid removes the metal atoms and leaves the silicon atoms in the form of a two-dimensional structure, in which three of the hydrogen atoms are above the plane of the paper and three below (E).



(E)

Siloxene is a spontaneously inflammable, flaky solid which is pseudomorphic with the calcium silicide from which it is formed. Both siloxene and its derivatives readily absorb many materials. The parent compound reacts with halogens with partial or complete replacement of the hydrogen atoms to give substances such as $(Si_2HBrO)_x$. The halogen compounds, which are greenish to bright yellow in color, react with water to give the corresponding hydroxy derivatives, e.g., $(Si_2H(OH)O)_x$, the colors of which deepen from yellow to black as the number of OH groups is increased. On treating the hydroxy derivatives with acids, acidic groups such as Cl, Br, and CH_3COO are introduced into the compound. The halogen compounds also react with ammonia, amines, or ethanol to yield a series of amino, alkylamino, or ethoxy derivatives. Complete chlorination or bromination of siloxene breaks the Si—Si linkage to form $(SiCl_3)_2O$ and $(SiBr_3)_2O$ respectively. All derivatives of siloxene are solids.

Oxidation of siloxene either by air or potassium permanganate is accompanied by bright chemiluminescence. If a fluorescent dye, such as rhodamine, is adsorbed on the siloxene, then permanganate oxidation gives a luminescence having an identical spectrum to the fluorescence spectrum of the dye used.

B. Sulfur and Selenium Compounds

1. $(SiH_3)_2S$, SiH_3SH, *and Derivatives*

Preparation. Disilyl sulfide, $(SiH_3)_2S$, may be prepared readily by the reaction of SiH_3I vapor with mercuric sulfide at room temperature (*51*)

$$2SiH_3I + HgS \rightarrow (SiH_3)_2S + HgI_2. \qquad (81)$$

"Silyl mercaptan" (silanethiol), SiH_3SH, is formed in an equilibrium reaction between disilyl sulfide and hydrogen sulfide at room temperature (*51*)

$$(SiH_3)_2S + H_2S \rightleftarrows 2SiH_3SH. \qquad (82)$$

The compound $SiH_3SC_2H_5$ may be prepared by the reduction of $SiCl_3SC_2H_5$ with $LiAlH_4$ (*149*), the $SiCl_3SC_2H_5$ itself being prepared from $SiCl_4$ and $Pb(SC_2H_5)_2$.

The sulfide, SiH_3SCH_3, intermediate between disilyl and dimethyl sulfides, has recently been prepared by the interaction of CH_3SH with $[SiH_3N(CH_3)_3]I$ (*168*).

Partly and completely organo-substituted derivatives may be obtained by several methods (*36*, *57*), e.g.,

$$CH_3SiH_2I + HgS \rightarrow (CH_3SiH_2)_2S + HgI_2 \qquad (83)$$

$$2(C_2H_5)_2SiCl_2 + 2H_2S + 4C_6H_5N \rightarrow [(C_2H_5)_2SiS]_2 + 4C_6H_5N \cdot HCl \qquad (84)$$

$$(CH_3)_3SiCl + LiSH \rightarrow (CH_3)_3SiSH + LiCl \qquad (85)$$

Derivatives such as $(SiCl_3)_2S$ and $SiCl_3SH$, in which the hydrogen has been replaced by chlorine, are formed by passing $SiCl_4$ and H_2S vapors through a tube at 700–1100° (*129*).

Physical Properties. Melting and boiling points of the parent silyl compounds are given in Table V.

Chemical Properties. $(SiH_3)_2S$ is spontaneously inflammable in moist, but not in dry air, and it suffers only slight thermal decomposition when held at 100–125° for several hours. It is instantaneously hydrolyzed to the ether,

$$(SiH_3)_2S + H_2O \rightarrow (SiH_3)_2O + H_2S, \qquad (86)$$

TABLE V
THE PARENT SILYL SULFIDES

Compound	M.P.	B.P.
$(SiH_3)_2S$ (*51*)	−70.0°	58.8°
$H_3SiSC_2H_5$ (*149*)	—	15–20° (0.1 mm)
SiH_3SH (*51*)	−134°	14.2°
H_3SiSCH_3 (*168*)	−116.7°	46.8°

and reacts with iodine at room temperature,

$$(SiH_3)_2S + I_2 \rightarrow 2SiH_3I + S, \tag{87}$$

and also with HI (*51*),

$$(SiH_3)_2S + 2HI \rightarrow 2SiH_3I + H_2S. \tag{88}$$

The organosubstituted sulfides undergo analogous reactions with water and HI (*56*).

The absence of basic character in both $(SiH_3)_2S$ and SiH_3SCH_3 is illustrated by the fact that neither compound forms an adduct with B_2H_6 even at −78° (*168, 186*). At this temperature $(CH_3)_2S$ forms the stable species $(CH_3)_2S \cdot BH_3$.

The compound $(SiH_3)_2S$ reacts neither with CH_3I nor with SiH_3I to form sulfonium compounds and it forms no addition compounds with either $HgCl_2$ or HgI_2. With $HgCl_2$, SiH_3Cl and HgS are formed quantitatively (*51*). Similar observations are noted with $[(CH_3)_2SiH]_2S$ (*59*). Although $(CH_3)_2S$ forms addition compounds with BF_3 and $(CH_3)_3B$, no such species are formed by $(CH_3SiH_2)_2S$ (*56*). It would seem likely that the absence of basic character in the sulfur is related to the "electron-withdrawing" capacity of the silicon in the parent or substituted silyl groups in a manner analogous to that proposed for $(SiH_3)_2O$ and $(SiH_3)_3N$. Although the parachor of the Si—S bond in $(SiH_3)_2S$ indicates some d_π–p_π bonding character (*112*), it seems that this cannot be great if an exactly similar type of bonding to that in $(SiH_3)_2O$ is postulated, since the Si—S—Si bond angle in $(SiH_3)_2S$ is only 101° (*108*). However, the above experimental observations are not necessarily incompatible since bond angles in simple sulfur compounds are usually less than those in analogous oxygen compounds.

2. $(SiH_3SiH_2)_2S$

Bis-disilanyl sulfide can be formed in good yields from SiH_3SiH_2I and HgS in a manner analogous to $(SiH_3)_2S$. It is spontaneously inflammable in air and melts at −70.4° and boils at 143.8°. It decomposes slightly when held near its boiling point for several hours (*198*).

3. $(SiH_3)_2Se$ *and Derivatives*

Disilyl selenide, $(SiH_3)_2Se$, may be prepared by the reaction of SiH_3I with Ag_2Se (*51*). It melts at −68.0° and boils at 85.2°. Although it is stable at room temperature, it decomposes when held near its boiling point for several hours. It is hydrolyzed instantaneously to the ether and reacts with iodine and with HI in a manner analogous to $(SiH_3)_2S$. Like the sulfide, it does not react with methyl iodide to form a selenonium compound.

Completely substituted derivatives may be prepared from selenophenols (*17*), e.g.,

$$4C_6H_5SeH + SiCl_4 \rightarrow Si(SeC_6H_5)_4 + 4HCl \qquad (89)$$

IX. Silane Derivatives Containing Silicon Linked to Nitrogen, Phosphorus, or Arsenic

A. NITROGEN COMPOUNDS

1. SiH_3NH_2, $(SiH_3)_2NH$, $(SiH_3)_3N$, *and Derivatives*

Preparation. The mono- and disilylamines, SiH_3NH_2 and $(SiH_3)_2NH$, are apparently formed in the instantaneous reaction of SiH_3Cl with excess NH_3, but they have never been isolated since they either condense or decompose very rapidly (*176*). When excess SiH_3Cl is used, $(SiH_3)_3N$ is formed quantitatively.

$$SiH_3Cl + 2NH_3 \rightarrow SiH_3NH_2 + NH_4Cl \qquad (90)$$

$$2SiH_3NH_2 \rightarrow (SiH_3)_2NH + NH_3 \qquad (91)$$

then

$$x(SiH_3)_2NH \rightarrow xSiH_4 + [SiH_2(NH)]_x \qquad (92)$$

and

$$3(SiH_3)_2NH \rightarrow 2(SiH_3)_3N + NH_3 \qquad (93)$$

The alkyl-substituted amines such as $(SiH_3)_2NCH_3$, $(SiH_3)_2NC_2H_5$, and $SiH_3N(CH_3)_2$ are formed readily in the reaction between silyl chloride or bromide and the appropriate amine at room temperature (*55, 187*), e.g.,

$$SiH_3Br + HN(CH_3)_2 \rightarrow SiH_3N(CH_3)_2 + HBr \qquad (94)$$

For a description of silyl quaternary ammonium compounds see Section VI.

Partly or completely organo-substituted silyl amines may be prepared by analogous methods (*8, 18, 50, 101, 128, 147*), e.g.,

$$2(CH_3)_3SiCl + 3NH_3 \rightarrow [(CH_3)_3Si]_2NH + 2NH_4Cl \qquad (95)$$

$$(C_2H_5)_3SiCl + 2NH_3 \rightarrow (C_2H_5)_3SiNH_2 + NH_4Cl \qquad (96)$$

$$(C_6H_5)_3SiCl + 2NH_3 \rightarrow (C_6H_5)_3SiNH_2 + NH_4Cl \qquad (97)$$

$$(CH_3)_3SiCl + 2HN(C_2H_5)_2 \rightarrow (CH_3)_3SiN(C_2H_5)_2 + (C_2H_5)_2NH \cdot HCl \qquad (98)$$

$$3CH_3SiH_2Cl + 4NH_3 \rightarrow (CH_3SiH_2)_3N + 3NH_4Cl \qquad (99)$$

In liquid ammonia, a potassium derivative may be obtained (*100*).

$$2(C_2H_5)_3SiH + KNH_2 \rightarrow [(C_2H_5)_3Si]_2NK + 2H_2 \qquad (100)$$

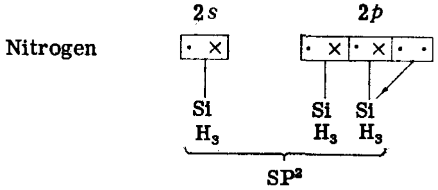
Several (chlorosilyl) amines have also been synthesized by a variety of methods. When $SiCl_4$ and NH_3 vapors are held at 825° for 35 hours $(SiCl_3)_2NH$ is obtained (*157*), whereas $SiCl_3N(CH_3)_2$ is formed by mixing pentane solutions of $SiCl_4$ and $(CH_3)_2NH$ at 0° (*35*). The direct reaction of $SiCl_4$ vapor and nitrogen in a glow discharge yields $(SiCl_3)_3N$ (*134*).

Physical Properties. The silyl amines are colorless liquids or solids. Melting and boiling points of the parent compounds are given in Table VI.

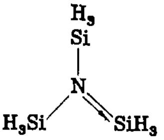
TABLE VI
THE PARENT SILYLAMINES

Compound	M.P.	B.P.
$(SiH_3)_3N$ (*176*)	−105.6°	52°
$(SiH_3)_2NCH_3$ (*55, 187*)	−124.1°	32.3°
$SiH_3N(CH_3)_2$ (*55, 187*)	3.4°	—
$(SiH_3)_2NC_2H_5$ (*55*)	−127°	65.9°

Whereas $(CH_3)_3N$ is a pyrimidal molecule, $(SiH_3)_3N$ is planar (*90, 140*). It appears that resonance forms exist in which the lone pair of electrons on the nitrogen "back-coordinate" by means of a π bond to the silicon atoms. This is substantiated by the observation that the Si—N bond is shorter than that expected for a single bond:

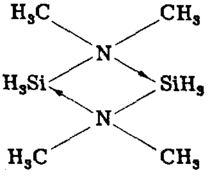


i.e.,



and other resonance forms. A similar structure for $(CH_3)_3N$ in which a *d*-orbital of carbon is utilized is most unlikely.

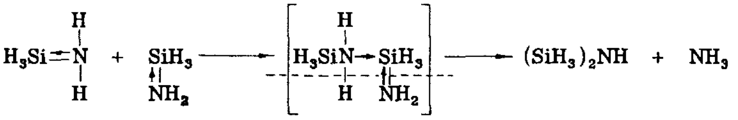
It has been noted that $SiH_3N(CH_3)_2$ is slightly associated in the solid and vapor state, whereas $(SiH_3)_2NCH_3$ is not (*187*). This may be explained qualitatively if it is assumed that the lone pair electrons on the nitrogen are not totally employed in back-bonding in $SiH_3N(CH_3)_2$ (since there is only one silicon atom to attract them), and consequently they are free to form intermolecular bonds (*187*) of the type shown (F).



(F)

In $(SiH_3)_2NCH_3$ and $(SiH_3)_3N$, however, with two and three silicon atoms in the molecule respectively, the nitrogen electron pair is totally consumed in back-bonding within the molecule, and is therefore no longer available to form an associated structure such as that shown above.

Chemical Properties. Silyl amines tend to condense readily. The rate of condensation and also the nature of the final product is entirely analogous to the condensation of silanols and is controlled by similar factors. The larger the attached atom, the slower is the rate of condensation. The likelihood of condensation stopping when the secondary amine has been formed also increases with increasing size of the attached group. Thus, SiH_3NH_2 (*176*) and $CH_3SiH_2NH_2$ (*50*) condense spontaneously to give $(SiH_3)_3N$ and $(CH_3SiH_2)_3N$, presumably through the formation of the corresponding secondary amine, e.g.,



$$H_3Si \overset{\leftarrow}{=} \underset{H}{\overset{H}{N}} + \underset{NH_2}{\overset{}{SiH_3}} \longrightarrow \left[H_3Si\underset{H}{\overset{H}{N}} \rightarrow \underset{NH_2}{SiH_3} \right] \longrightarrow (SiH_3)_2NH + NH_3 \qquad (101)$$

The $(SiH_3)_2NH$ could then combine with another molecule of SiH_3NH_2 in a similar manner to give $(SiH_3)_3N$. $(CH_3)_3SiNH_2$ condenses spontaneously to give the secondary amine, hexamethyldisilazane, $[(CH_3)_3Si]_2NH$ (*128*), while $(C_2H_5)_3SiNH_2$ can be isolated and condenses to $[(C_2H_5)_3Si]_2NH$ less readily (*18*), while $(C_6H_5)_3SiNH_2$ apparently shows no tendency to condense (*101*). It is believed that three relatively large organic groups attached to the silicon prevent the formation of the tertiary, and in the case of phenyl groups, the secondary amine. However, it appears likely that other factors may also be involved since $(SiCl_3)_3N$ is known and a methyl group and a chlorine atom have approximately the same size. It should be noted that the reaction of amines with triorganosilyl halides is reversible, and that the direction of the reaction can be changed by modifying the experimental conditions (*8*, *21*):

$$(C_6H_5)_3SiCl + 2C_2H_5NH_2 \rightleftharpoons (C_6H_5)_3SiNHC_2H_5 + C_2H_5NH_2 \cdot HCl \qquad (102)$$

The most outstanding characteristic of all silyl amines is that they are only weak Lewis bases. This is not surprising in view of the fact that $(SiH_3)_3N$ has a planar structure and the nitrogen lone pair of electrons is therefore no longer available to allow the nitrogen to act as a Lewis base. If it were not for this, it would be expected that silyl amines would be stronger bases than methyl amines since silicon is less electronegative than carbon (Si = 1.8; C = 2.5). It is therefore understandable why the basic properties of the following series of amines increases as shown (*116*, *189*):

$$(SiH_3)_3N < (SiH_3)_2N(CH_3) < SiH_3N(CH_3)_2 < N(CH_3)_3.$$

Addition compounds are formed with $B(CH_3)_3$ by the last two but not with the first two. At −78°, B_2H_6, $[(CH_3)_3Al]_2$, and $(CH_3)_3Ga$ form adducts with the last three compounds but only the very strong Lewis acid, $[(CH_3)_3Al]_2$, combines with $(SiH_3)_3N$ (*116*). Whereas BF_3 and BCl_3 form unstable addition compounds with $(SiH_3)_3N$, stable adducts are formed with $(CH_3)_3N$ (*31*). The fewer the number of silyl groups present in the molecule, the fewer will be the possible resonance structures involving the π bond, and the greater will be the donor properties of the lone pair electrons on the nitrogen. Similar observations with $B(CH_3)_3$, BCl_3, and BF_3 are noted in the series $(CH_3SiH_2)_3N$, $(CH_3SiH_2)_2NCH_3$, and $CH_3SiH_2N(CH_3)_2$ (*50*). With B_2H_6 and $[(CH_3)_3Si]_2NH$, the addition compound $[(CH_3)_3Si]_2NH \cdot BH_3$ is formed (*185*).

The increasing basicity with decreasing number of silyl groups attached to the nitrogen is also exemplified by the fact that $CH_3SiH_2N(CH_3)_2$ and $(CH_3)_3SiN(CH_3)_2$ react with CH_3I to give stable solids which appear to be ionic quaternary ammonium compounds, e.g.,

$$(CH_3)_3SiN(CH_3)_2 + CH_3I \rightarrow [(CH_3)_3SiN(CH_3)_3]^+I^-, \qquad (103)$$

whereas the related compounds with two or three silicon atoms attached to a nitrogen do not (*50*). The interaction of CH_3SiH_2I and $CH_3SiH_2N(CH_3)_2$ at low temperatures gives a compound which is so unstable that it is completely dissociated in the vapor state (*50*).

$$CH_3SiH_2I + CH_3SiH_2N(CH_3)_2 \rightleftharpoons [(CH_3SiH_2)_2N(CH_3)_2]I \qquad (104)$$

Similarly, there is evidence that $[(SiH_3)_2N(CH_3)_2]Cl$ decomposes readily and it has not been isolated in the pure state (*55*). In light of the above, it is not surprising to find that $(SiH_3)_3N$ and SiH_3Cl do not combine to form tetrasilylammonium chloride (*176*).

With the exception of $SiCl_3N(CH_3)_2$ (*35*), which forms a hydrochloride, hydrogen halides cleave the Si—N bonds in silicon amines to form the corresponding silyl chloride (*55*, *176*):

$$(SiH_3)_3N + 4HCl \rightarrow 3SiH_3Cl + NH_4Cl \qquad (105)$$

$$(SiH_3)_2NCH_3 + 3HCl \rightarrow 2SiH_3Cl + CH_3NH_2 \cdot HCl. \qquad (106)$$

However, it is interesting to observe that HI does not react with $[SiH_3N(CH_3)_3]I$ or even with $SiH_3I \cdot 2N(CH_3)_3$ (*13*). The above type of reaction is an example of an even more general type which occurs between Si—N bonds and a variety of covalent halides (*8*) e.g.,

$$4(CH_3)_3SiNH(C_6H_5) + GeBr_4 \rightarrow 4(CH_3)_3SiBr + Ge(HNC_6H_5)_4 \qquad (107)$$

The Si—N bond is usually cleaved readily by water and by alcohols to give the corresponding silanol, disiloxane, or alkoxide. $(SiH_3)_3N$ is spontaneously inflammable in air but is thermally stable. The alkyl-substituted amines, however, are less thermally stable, and $SiH_3N(CH_3)_2$ decomposes at a measurable rate at its melting point (*176*, *187*). In this case, intermediate complexes involving two amine molecules, which may be important in thermal decomposition, can be formed readily, as indicated by the observed association of $SiH_3N(CH_3)_2$ discussed previously.

Reactions between silyl amines and boron compounds are discussed more fully in Section IX,A,*5*.

2. $SiH_2(NH_2)_2$, $SiH(NH_2)_3$, *and Derivatives*

Just as the condensation of silanediols or silanetriols can lead to a variety of complex species, so also does the condensation of species having two or three NH_2 groups attached to a silicon atom give a variety of substances. Compounds with more than one NH_2 group are rare, although as might be expected, the presence of large organic groups increases the stability of such compounds, e.g., $(\textit{tert}\text{-}C_4H_9)_2Si(NH_2)_2$ can be distilled at 190° without decomposition (*165*). In general, however, NH_3 splits off instantaneously with the formation of polymeric materials, e.g.,

$$SiH_2Cl_2 + 4NH_3 \rightarrow SiH_2(NH_2)_2 + 2NH_4Cl \qquad (108)$$

$$xSiH_2(NH_2)_2 \rightarrow (SiH_2NH)_x + xNH_3 \qquad (109)$$

Preparation. When SiH_2Cl_2 and NH_3 are mixed in the absence of a solvent a highly polymeric amorphous white powder is obtained, but when the reaction is carried out in benzene solution a soluble polymer is produced where $x \sim 8$ (*176*). With $HSiCl_3$ and $SiCl_4$ solid polymeric materials such as $\{[SiH(NH)]_2NH\}_x$ and $[Si(NH_2)_2NH]_x$ are obtained (*181*). Under different reaction conditions, more complex (*22*) or more simple products, e.g., $(SiCl_3)_2NH$ can be formed. It should be noted that $[SiH_2(NH)]_x$ is also produced during the decomposition of SiH_3NH_2.

Analogous reactions occur with diorganodihalosilanes to give polymeric silazanes which frequently are formed as cyclic species (*28*):

$$3(CH_3)_2SiCl_2 + 9NH_3 \rightarrow [(CH_3)_2SiNH]_3 + 6NH_4Cl. \qquad (110)$$

Compounds such as $(Cl_3SiNSiCl_2)_4$ and $[(SiCl_3)_2N]_2SiCl_2$ are formed in the reactions of $SiCl_4$ with NH_3 (*157*) or with nitrogen in a glow discharge (*134*).

If primary or secondary organic amines are used instead of NH_3 in the types of reactions mentioned above, the expected substances containing both silicon and carbon attached to the nitrogen are obtained (*35*, *93*), e.g.,

$$(C_2H_5)_2SiCl_2 + 4HN(C_2H_5)_2 \rightarrow (C_2H_5)_2Si[N(C_2H_5)_2]_2 + 2(C_2H_5)_2HN \cdot HCl \quad (111)$$

$$(C_2H_5)_2SiCl_2 + 2HN(C_2H_5)_2 \rightarrow (C_2H_5)_2SiCl[N(C_2H_5)_2] + (C_2H_5)_2NH \cdot HCl \quad (112)$$

$$SiCl_4 + 4HN(CH_3)_2 \rightarrow Cl_2Si[N(CH_3)_2]_2 + 2(CH_3)_2NH \cdot HCl \quad (113)$$

Properties. In general, the chemical properties of the compounds given above are exactly those expected from reactions of the Si—N bond previously discussed. For example, with HCl, $[SiH_2(NH)]_x$ gives SiH_2Cl_2 and $\{[SiH(NH)]_2(NH)\}_x$ gives $HSiCl_3$, though the reactions proceed less readily than with $(SiH_3)_3N$ (*176*, *181*).

3. $(SiH_3SiH_2)_3N$

The instantaneous reaction of SiH_3SiH_2I with NH_3 gives good yields of tris-disilanylamine, which melts at −97.1° and boils at 178.8°. It is spontaneously inflammable in air but shows no sign of decomposition even when held at 100–120° for several hours (*198*).

4. $(SiH_3)_2NN(SiH_3)_2$ *and Derivatives*

Tetrasilylhydrazine, $(SiH_3)_2NN(SiH_3)_2$, has been prepared by the reaction of SiH_3I with N_2H_4. It explodes in air, melts at −24°, and boils at 109°. The lone pairs of electrons of the nitrogen atoms in $(CH_3)_2NN(CH_3)_2$ are sufficiently labile to form the addition compounds $SiH_3I \cdot (CH_3)_4N_2$ (vapor and liquid phases) and $2SiH_3I \cdot (CH_3)_4N_2$ (liquid phase only). However, in $(SiH_3)_2NN(SiH_3)_2$, as in $(SiH_3)_3N$, the lone pairs are so completely involved in back-coordination to the SiH_3 groups within the molecule that analogous addition compounds are not formed with SiH_3I (*14*, *15*).

Organosilyl derivatives of hydrazine have also been prepared by similar reactions (*193*, *194*), e.g.,

$$2(C_2H_5)_3SiCl + H_2NNH_2 \rightarrow (C_2H_5)_3SiNHNHSi(C_2H_5)_3 + 2HCl \quad (114)$$

$$(C_6H_5)_3SiCl + H_2NNH_2 \rightarrow (C_6H_5)_3SiNHNH_2 + HCl \quad (115)$$

Substances such as $(C_6H_5)_2Si[NHN(CH_3)_2]_2$ have also been isolated (*195*). No compounds have been isolated in which all four of the hydrogen atoms of hydrazine have been replaced by R_3Si groups.

5. Derivatives Containing Si—N—B *Linkages*

The thermal decomposition products of the addition compounds formed by silyl amines with substances such as BF_3, BCl_3, and B_2H_5Br are of particular interest (*31*, *189*).

$(SiH_3)_3N$ reacts at −78° with both BF_3 and BCl_3 to give the solid addition compounds $(SiH_3)_3N \cdot BF_3$ and $(SiH_3)_3N \cdot BCl_3$. On warming to room temperature, these compounds decompose smoothly to give the volatile species $(SiH_3)_2NBF_2$ and $(SiH_3)_2NBCl_2$ respectively, e.g.,

$$(SiH_3)_3N \cdot BCl_3 \rightarrow (SiH_3)_2NBCl_2 + SiH_3Cl \qquad (116)$$

$(SiH_3)_2NBCl_2$ is spontaneously inflammable in air and both it and $(SiH_3)_2NBF_2$ slowly decompose on standing. In the case of the latter compound, a silyl borazine derivative has been identified, viz.,

$$3(SiH_3)_2NBF_2 \rightarrow (SiH_3NBF)_3 + 3SiH_3F \qquad (117)$$

With B_2H_5Br, at −78°, $(SiH_3)_3N$ reacts quantitatively to give $(SiH_3)_2NBH_2$ and $[(SiH_3)_2NBH_2]_2$:

$$2(SiH_3)_3N + 2B_2H_5Br \rightarrow 2(SiH_3)_2NBH_2 + 2SiH_3Br + B_2H_6 \qquad (118)$$

The compound $(SiH_3)_2NBH_2$ readily adds B_2H_6 to form $(SiH_3)_2NB_2H_5$, which melts at −69.4° and boils at ~54°. It is regarded as having a hydrogen-bridged structure similar to B_2H_6. At room temperature $(CH_3)_2BBr$ also reacts with $(SiH_3)_3N$ to give $(CH_3)_2BN(SiH_2Br)_2$.

Silyl amines with methyl groups on either the nitrogen or silicon undergo reactions similar to those mentioned above. With BCl_3 for example, $CH_3N(SiH_3)_2$ gives $(CH_3NSiH_3)BCl_2$, which decomposes quantitatively to solid $(CH_3NBCl)_3$ and SiH_3Cl. With BF_3 the analogous fluorine derivatives are obtained. With $(CH_3)_2NSiH_3$ and BF_3, $(CH_3)_2NBF_2$ is formed. In a similar manner, $CH_3N(SiH_3)_2$ and B_2H_5Br produce the volatile compound $(CH_3NSiH_3)B_2H_5$, which melts at −39.0° and boils at ~51°. Analogously, BF_3 with $(CH_3SiH_2)_3N$ and $(CH_3)_3SiN(CH_3)_2$ gives adducts which decompose to produce $(CH_3SiH_2)_2NBF_2$ and $(CH_3)_2NBF_2$ respectively (*50*).

Both BF_3 and BCl_3 react with $[(CH_3)_3Si]_2NH$ to give addition compounds which readily decompose. With BCl_3 there is formed $(CH_3)_3SiCl$ and $(HNBCl)_3$ (*185*).

B. PHOSPHORUS COMPOUNDS

Preparation. Monosilylphosphine, SiH_3PH_2, can be prepared by heating a mixture of silane and phosphine (*75*) while trisilylphosphine, $(SiH_3)_3P$, iododisilylphosphine, $(SiH_3)_2PI$, diiodosilylphosphine, SiH_3PI_2, and tetrasilylphosphonium iodide, $[(SiH_3)_4P]I$, are found among the products of the reaction between SiH_3I and white phosphorus (*16*). Trisilylphosphine and iododisilylphosphine have not yet been isolated in the pure state. For the preparation and properties of silylphosphonium compounds, see Section VI.

Triorganosilyl phosphorus compounds have been prepared by the reaction of R_3SiCl with alkali metal phosphides and their derivatives (*130*), e.g.,

$$(CH_3)_3SiCl + LiPH_2 \rightarrow (CH_3)_3SiPH_2 + LiCl \qquad (119)$$

From Li_2PH and Li_3P, similarly, were prepared $[(CH_3)_3Si]_2PH$ and $[(CH_3)_3Si]_3P$, respectively. By the use of $(C_6H_5)_2PNa$, the compound $(C_6H_5)_2PSi(CH_3)_3$ has been obtained (*105*). Pentavalent phosphorus compounds have been synthesized as shown below (*125*), e.g.,

$$(CH_3O)_2P(O)Na + (CH_3)_3SiCl \rightarrow (CH_3O)_2P(O)Si(CH_3)_3 + NaCl \qquad (120)$$

By using $(C_2H_5)_2SiCl_2$ instead of $(CH_3)_3SiCl$ with the appropriate lithium compound, the interesting cyclic species $P[Si(C_2H_5)_2]_3P$, $C_6H_5P[Si(C_2H_5)_2]_2PC_6H_5$, and $HP[Si(C_2H_5)_2]_2PH$ have been obtained (*130*).

Properties. SiH_3PH_2 boils at 12.7° and reacts with ammonium hydroxide to produce SiH_4, PH_3, and H_2. With anhydrous HBr, a reaction analogous to that with silyl amines occurs,

$$SiH_3PH_2 + HBr \rightarrow SiH_3Br + PH_3 \qquad (121)$$

It is thermally stable and begins to decompose at about 400° (*75, 76*). SiH_3PI_2 melts at $-1.8°$, boils at 190°, but decomposes at a measurable rate at room temperature (*16*).

The alkylsilyl phosphines are colorless liquids or low-melting solids which are extremely sensitive to air and water. Those compounds containing P—H bonds are spontaneously inflammable. All the compounds appear to have high thermal stability. $[(CH_3)_3Si]_3P$ may be refluxed in an inert atmosphere at 243° for 8 hours without appreciable decomposition (*130*).

It appears that when $(CH_3)_3SiPH_2$ is mixed with butyl lithium the compound $(CH_3)_3SiPLi_2$ is formed (*130*), since addition of $(C_2H_5)_2SiCl_2$ to the above mixture yields $(CH_3)_3SiP[Si(C_2H_5)_2]_2PSi(CH_3)_3$.

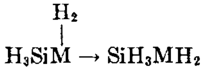
B_2H_6 reacts with $[(CH_3)_3Si]_3P$ to give a crystalline compound, $[(CH_3)_3Si]_3P \cdot BH_3$, which slowly decomposes at room temperature. It is surprising to find that oxidation of $[(CH_3)_3Si]_3P$ with NO_2 yields not the phosphine oxide, but rather the phosphate, $[(CH_3)_3SiO]_3PO$ (*130*).

C. Arsenic Compounds

Preparation. Monosilylarsine, SiH_3AsH_2, iododisilylarsine, $(SiH_3)_2AsI$, and di-iodosilylarsine, SiH_3AsI_2, have been reported among the products of the reaction between SiH_3I and arsenic (*13, 16*). Disilylarsine, $(SiH_3)_2AsH$, and trisilylarsine, $(SiH_3)_3As$, are formed by the reaction of SiH_3I with K_3As, but they have not been obtained in the pure state. For the preparation and properties of silyl arsonium compounds, see Section VI.

Properties. Di-iodosilylarsine, SiH_3AsI_2, is the only silyl-arsenic compound which has been characterized to any extent. It melts at 4° and boils at 210°. $(SiH_3)_3As$ boils at 97–98°, and arsine is formed when it is hydrolyzed with aqueous alkali.

It should be noted that whereas SiH_3NH_2 condenses instantaneously upon formation, SiH_3PH_2 and SiH_3AsH_2 do not. It appears probable that as Group V is descended, the formation of an intermolecular bond of the type



$$H_3Si\overset{H_2}{\overset{|}{M}} \rightarrow SiH_3MH_2$$

(M = N, P, or As) in an intermediate complex (see Sections V,A and IX,A,*1*) might occur less readily since the positive charge induced on the silicon by M will decrease with the decreasing electronegativity of M. Since the electronegativity of M decreases as the group is descended, the rate of condensation by such a mechanism might also be expected to decrease. A similar argument could be applied to explain the observation that SiH_3OH condenses instantaneously, whereas SiH_3SH condenses relatively slowly.

X. Silyl-Metallic Compounds

A. Compounds Containing Alkali Metals

Preparation. When SiH_4 or Si_2H_6 are allowed to react with potassium dissolved in liquid ammonia, silyl potassium, $KSiH_3$, is formed

$$SiH_4 + K \rightarrow KSiH_3 + \tfrac{1}{2}H_2 \tag{122}$$

$$Si_2H_6 + 2K \rightarrow 2KSiH_3 \tag{123}$$

Rapid ammonolysis of the product has prevented its isolation but its existence can be deduced from the fact that its solution in liquid ammonia with ammonium ions generates SiH_4

$$KSiH_3 + NH_4^+ \rightarrow SiH_4 + K^+ + NH_3 \tag{124}$$

and with CH_3Cl, methylsilane

$$KSiH_3 + CH_3Cl \rightarrow CH_3SiH_3 + KCl \tag{125}$$

In the reaction with Si_2H_6, disilanyl potassium, $KSiH_2SiH_3$, is also formed as indicated by the evolution of some $CH_3SiH_2SiH_3$ on treating the solution with CH_3Cl (*92*).

More convenient methods of preparation have recently been discovered (*139*). A solution of $KSiH_3$ in 1,2-dimethoxyethane ("monoglyme") may be prepared by treating potassium or sodium potassium alloy with SiH_4 or Si_2H_6. It may also be prepared from Si_2H_6 and KH in monoglyme:

$$Si_2H_6 + KH \rightarrow KSiH_3 + SiH_4 \tag{126}$$

The reaction with SiH_4 takes several weeks but those with Si_2H_6 are complete within a day. Slow evaporation of the monoglyme solutions yields pure, colorless, crystalline $KSiH_3$.

A number of triorganosilyl metallic compounds have been prepared, all except one of which contain at least one phenyl group (*207*). They are generally prepared as solutions in diethyl ether, ethyleneglycoldimethyl ether, or tetrahydrofuran by the cleavage of Si—C, Si—Si, or Si—Cl bonds by sodium, sodium-potassium alloy, or lithium. The best combination of solvent and metal to be employed depends on the type of silicon compound used, e.g.,

$$(C_6H_5)_3SiC(CH_3)_2(C_6H_5) + Na/K \xrightarrow{\text{ether}} (C_6H_5)_3SiK + C_6H_5(CH_3)_2CK \quad (127)$$

$$(C_6H_5)_3SiSi(C_6H_5)_3 + 2Na \xrightarrow{(MeOCH_2)_2} 2(C_6H_5)_3SiNa \quad (128)$$

$$(C_6H_5)_2(CH_3)SiCl + 2Li \xrightarrow{\text{T.H.F.}} (C_6H_5)_2CH_3SiLi + LiCl \quad (129)$$

Although trialkylsilyl metal compounds have not been prepared by cleavage of hexalkyl disilanes, trimethylsilyl potassium has been prepared as shown below:

$$(C_6H_5)_3SiSi(CH_3)_3 + Na/K \xrightarrow{\text{ether}} (C_6H_5)_3SiK + (CH_3)_3SiK \quad (130)$$

Cleavage of completely phenylated tri- and tetrasilanes by Li in tetrahydrofuran produces pentaphenyldisilanyl lithium, $(C_6H_5)_3SiSi(C_6H_5)_2Li$, and heptaphenyltrisilanyl lithium, $(C_6H_5)_3Si(C_6H_5)_2Si(C_6H_5)_2SiLi$, respectively.

Properties. Solutions of $KSiH_3$ vary from colorless to yellow or green while those of the triorgano-derivatives are generally yellow to brown. Solid $KSiH_3$ appears to be surprisingly stable thermally, and rapid decomposition does not occur below 240°. Solid $KSiH_3$ is hydrolyzed quantitatively, and also reacts quantitatively with HCl and CH_3Cl as shown below:

$$KSiH_3 + HCl \rightarrow SiH_4 + KCl \quad (131)$$

$$KSiH_3 + CH_3Cl \rightarrow SiH_3CH_3 + KCl \quad (132)$$

With SiD_3Br and $SiBr_4$ complex reactions occur to give primarily monosilanes (*139*).

The triorganosilyl metal compounds are used in the solvents in which they are prepared without isolation of the pure material. A discussion of the large number of interesting reactions of these materials (*207*) cannot be given here, but in general, they react with silicon-halogen or carbon-halogen bonds to give the expected products, e.g.,

$$(CH_3)_2(C_6H_5)SiLi + (CH_3)_3SiCl \rightarrow (CH_3)_2(C_6H_5)SiSi(CH_3)_3 + LiCl \quad (133)$$

$$(C_6H_5)_3SiK + C_6H_5Br \rightarrow (C_6H_5)_4Si + KBr \quad (134)$$

The latter reaction is complicated by the fact that halogen-metal interchange may occur, e.g.,

$$(C_6H_5)_3SiK + C_6H_5Br \rightarrow C_6H_5K + (C_6H_5)_3SiBr \qquad (135)$$

With CO_2, a carboxylic acid, $(C_6H_5)_3SiCOOH$, is obtained.

The derivatives of the higher silanes have not been extensively investigated. Acid hydrolysis yields the corresponding silane (*207*), e.g.,

$$(C_6H_5)_3SiSi(C_6H_5)_2Li + H_2O \xrightarrow{\text{acid}} (C_6H_5)_3SiSi(C_6H_5)_2H + LiOH \qquad (136)$$

B. COMPOUNDS CONTAINING GERMANIUM, TIN, BORON, OR IRON

No definite evidence for the existence of any silylmetallic compound other than $KSiH_3$ has ever been found. SiH_3I in diethyl ether or diisoamyl ether (*42, 54*) rapidly dissolves magnesium with the liberation of SiH_4 and H_2, but no material having a Si—Mg bond has been isolated. Similar results were obtained with SiH_3Br (*192*). Unsuccessful attempts to prepare silicon-magnesium compounds have also been made with $(C_2H_5)_3SiI$ (*47*).

An interesting series of compounds containing Si—Ge bonds in the form of the tris(triphenylgermyl)silyl group has been prepared

$$3(C_6H_5)_3GeNa + HSiCl_3 \rightarrow [(C_6H_5)_3Ge]_3SiH + 3NaCl \qquad (137)$$

From the parent silane, species of the type $[(C_6H_5)_3Ge]_3SiX$ have been isolated where X = Cl, Br, OH, NH_2 (*120*). Compounds with Si—Ge bonds may also be prepared from $(C_6H_5)_3SiK$ and $(C_6H_5)_3GeCl$ (*82*). Species containing Si—Sn bonds have been synthesized by analogous methods (*84*) e.g.,

$$(C_6H_5)_3SnLi + (C_6H_5)_3SiCl \rightarrow (C_6H_5)_3SiSn(C_6H_5)_3 + LiCl \qquad (138)$$

$(C_6H_5)_3SiGe(C_6H_5)_3$ is not cleaved by iodine in boiling xylene, but it is cleaved by sodium-potassium alloy in ether.

Only two compounds containing silicon-boron bonds have been reported (*40*). They are derivatives of borazene and were prepared from triphenylsilyl potassium and *B*-chloroborazenes, e.g.,

$$B_3Cl_3N_3(CH_3)_3 + 3(C_6H_5)_3SiK \rightarrow B_3[Si(C_6H_5)_3]_3N_3(CH_3)_3 + 3KCl \qquad (139)$$

Also prepared was *B*-tris(triphenylsilyl)-*N*-triphenylborazene. Both compounds react with moist air and the Si—B bond is cleaved by a carbon tetrachloride solution of bromine at room temperature, with the formation of $(C_6H_5)_3SiBr$.

A cyclopentadienyl derivative, $C_5H_5Fe(CO)_2Si(CH_3)_3$, containing a silicon-iron σ bond has been reported (*135*).

Notes Added in Proof

Interesting information on silane derivatives has been published since the manuscript went to press. This is summarized below

1. Halides and Pseudohalides. SiH_3I has been prepared by the reaction of HI with $C_6H_5SiH_3$ or $ClC_6H_4SiH_3$. In a similar manner, SiH_2I_2 has been obtained from $(C_6H_5)_2SiH_2$. [Aylett, B. J., and Ellis, I. A., *J. Chem. Soc.* p. 3415 (1960); Fritz, G., and Kummer, D., *Z. anorg. Chem.* **306,** 191 (1960).]

Pure SiH_3SiH_2Br (M.P., −97.2°, B.P., 69.5°) has been prepared from SiH_3SiH_2I and AgBr. When completely pure it is thermally stable but traces of Al_2Br_6 cause rapid decomposition. (Ward, L. G. L., and MacDiarmid, A. G., unpublished results, 1960.)

A study has been made of the strengths of addition compounds formed between SiH_3I and a number of ethers and sulfides. [Aylett, B. J., *J. Inorg. & Nuclear Chem.* **15,** 87 (1960).]

The microwave spectrum of SiH_3NCS has been investigated and the linear, iso-structure of the compound has been confirmed. [Jenkins, D. R., Kewley, R. and Sugden, T. M., *Proc. Chem. Soc.* p. 220 (1960).]

A further study of the microwave spectrum of SiH_3CN confirms the normal cyanide structure of this compound. [Muller, N., and Brachen, R. C., *J. Chem. Phys.* **32,** 1577 (1960).]

Infrared and Raman spectra of the following compounds have been examined: $(CH_3)_3SiNCO$; $(CH_3)_2Si(NCO)_2$; $CH_3Si(NCO)_3$; $Si(NCO)_4$; and $Si_2O(NCO)_6$. All compounds have the isocyanate structure. A small multiple bond character is present in the Si—N bonds. [Goubeau, J., Heubach, E., Paulin, D., and Widmaier, I., *Z. anorg. Chem.* **300,** 194 (1959).]

2. Nitrogen Compounds. Infrared and Raman spectra have been obtained for $(SiH_3)_2NN(SiH_3)_2$ and $(SiD_3)_2NN(SiD_3)_2$. They are interpreted in terms of a D_{2d} (staggered) configuration for the molecular skeleton. [Aylett, B. J., Hall, J. R., McKean, D. C., Taylor, R., and Woodward, L. A., *Spectrochim. Acta* **16,** 747 (1960).]

The compound $[(CH_3)_3Si]_3N$ has been isolated as a stable solid by the interaction of $[(CH_3)_3Si]_2NNa$ with $(CH_3)_3SiCl$. [Goubeau, J. and Jiménez-Barberá, J., *Z. anorg. Chem.* **303,** 217 (1960).]

3. Sulfides. The compound SiH_3SCF_3 (M.P., −127°; B.P., 13.6°) has been prepared from SiH_3I and $(CF_3S)_2Hg$. [Downes, A. J., and Ebsworth, E. A. V., *J. Chem. Soc.* p. 3516 (1960).]

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