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TRISILYL-SUBSTITUTED ORGANOPOLYSILANES.

Iowa State University of Science and Technology, Ph.D., 1966
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SYNTHESES AND REACTIONS OF
TETRA- AND TRISILYL-SUBSTITUTED ORGANOPOLYSILANES

by

Clifford Leon Smith

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
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DOCTOR OF PHILOSOPHY

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Head of Major Department

Signature was redacted for privacy.

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INTRODUCTION

Catenation of organosilicon compounds was initially studied by F. S. Kipping and co-workers (1, 2, 3) about forty years ago. Despite the phenomenal growth of organosilicon chemistry since that time, surprisingly few examples of silicon catenations were known before 1960. (4, 5). Since organically-substituted polysilane compounds have been found to possess a relatively high degree of stability, the paucity of organopolysilanes might well be attributed to the lack of equivalent methods of propagating silicon chains compared with carbon chains.

Although the first branched-chain compound, iso-tetrasilane was formed in 1923 (6) by a reaction between magnesium silicide and hydrochloric acid, the compound was not isolated until 1958 (7). To date more than a hundred tri- and tetra-Group IVB-substituted organometallic compounds have been prepared and characterized.

The objective of the work presented here was to extend the boundaries of catenated organosilicon chemistry to include the chemistry of some tri- and tetrasilyl-substituted compounds.

HISTORICAL

Tri- and Tetra-Group IVB-substituted Derivatives of Group IVB Compounds

Group IVB-substituted carbon compounds

Although tetra-*t*-butylmethane (I) is not known, in 1947 Tyler, Sommer and Whitmore unsuccessfully attempted the preparation of tri-*t*-butylchlorosilane (II) and tetra-*t*-butylsilane (III) by reactions between di-*t*-butyldichlorosilane *t*-butyllithium (8).

$$\underset{\text{I}}{\left[(CH_3)_3C\right]_4C} \qquad \underset{\text{II}}{\left[(CH_3)_3C\right]_3SiCl} \qquad \underset{\text{III}}{\left[(CH_3)_3C\right]_4Si}$$

The synthesis of the first class of organosilicon compounds in which three or four silicon atoms are bonded to one carbon atom was reported about 10 years later (9, 10).

Muller *et al.* (9, 10) obtained a mixture of perchlorinated compounds from a reaction between elemental silicon in the presence of copper as a catalyst and a polyhalide of carbon at high temperatures. For instance, tris(trichlorosilyl)methane (IV) and tetrakis(trichlorosilyl)methane (V) were produced, by using chloroform (9) and carbon tetrachloride (10), respectively, as the polyhalides.

$$Cl_3CH + Si/Cu \xrightarrow{\Delta} \underset{\text{IV}}{\left[Cl_3Si\right]_3CH}$$

$$CCl_4 + Si/Cu \xrightarrow{\Delta} \underset{\text{V}}{\left[Cl_3Si\right]_4C}$$

Several derivatives of IV were prepared in good yields. Treatment with methylmagnesium bromide gave tris(trimethylsilyl)methane (VI), while alcoholysis with methanol and ethanol afforded the respective alkoxides, tris(trimethoxysilyl)methane (VIIa) and tris(triethoxysilyl)methane (VIIb) (9):

$$\mathrm{IV} + 3\mathrm{CH_3MgBr} \longrightarrow \left[(\mathrm{CH_3})_3\mathrm{Si}\right]_3\mathrm{CH} + 3\mathrm{MgBrCl}$$

VI

$$\mathrm{IV} + 3\mathrm{ROH} \longrightarrow \left[(\mathrm{RO})_3\mathrm{Si}\right]_3\mathrm{CH} + 3\mathrm{MgBrCl}$$

VIIa, $R = CH_3$

VIIb, $R = C_2H_5$

The perchlorinated compound, tris(trichlorosilyl)chloromethane (VIII), was prepared by the ultraviolet irradiation of IV in the presence of chlorine (9):

$$\mathrm{IV} + \mathrm{Cl_2} \xrightarrow{h\nu} \left[\mathrm{Cl_3Si}\right]_3\mathrm{CCl} + \mathrm{HCl}$$

VIII

Conversion of VIII to V was accomplished by its reaction with silicon tetrachloride and elemental silicon using copper as catalyst (11). Muller <u>et</u> <u>al</u>. did not report the preparation of any derivatives of compound V, because of its molecular symmetry, one of particular interest would be tetrakis(trimethylsilyl)methane.

In 1963 Merker and Scott described a technique they termed the *in situ* Grignard reaction which involved the addition of a polyhalide of carbon to a solution of a monochlorosilane in tetrahydrofuran in which magnesium metal was suspended (12, 13, 14). The broad utility of this one-step reaction is illustrated by the variety of structurally novel compounds that have been synthesized from readily available starting materials. Of considerable interest is the preparation of some highly symmetrical compounds. The reaction between some polyhalide compounds (CBr_nCl_{4-n}), chlorotrimethylsilane and magnesium metal afforded tetrakis(trimethylsilyl)methane (IX) (12):

$$CBr_nCl_{4-n} + 4(CH_3)_3SiCl + 4Mg \longrightarrow \underset{\text{IX}}{[(CH_3)_3Si]_4C}$$

The yield of IX, using various polyhalide compounds (CBr_nCl_{4-n}) was low (<u>ca</u>. 30%) and no reaction was observed when silicon tetrachloride was used. When lithium metal was used, silicon tetrachloride gave excellent yields of IX, together with a small amount of VI (15, 16):

$$CCl_4 + 4(CH_3)_3SiCl + 8Li \longrightarrow IX + 8LiCl$$

The formation of IX by a reaction between carbon tetrabromide, chlorotrimethylsilane and lithium was explained by the following sequence of reactions (15):

$$\begin{aligned}
&CBr_4 + 2Li \longrightarrow Br_3CLi + LiBr\\
&Br_3CLi + (CH_3)_3SiCl \longrightarrow (CH_3)_3SiCBr_3 + LiCl\\
&(CH_3)_3SiCBr_3 + 2Li \longrightarrow (CH_3)_3SiCBr_2Li + LiBr\\
&(CH_3)_3SiCBr_2Li + (CH_3)_3Si\ Cl \longrightarrow [(CH_3)_3Si]_2CBr_2\\
&\qquad\qquad\qquad\qquad\qquad\qquad + LiCl, \text{ etc.}
\end{aligned}$$

A similar mechanism was also proposed for reactions involving magnesium (12).

Compound IX, a highly symmetrical molecule, can be envisaged as a sphere composed of twelve methyl groups surrounding the central carbon-silicon skeleton. X-ray powder data indicate that the crystal structure is face-centered cubic with a = 12.96 ± 0.08 Å (17). A calculated density for Z = 4 was found to be 0.929 g-cm^{-3} which is in good agreement with the observed value of 0.9113 g-cm^{-3} (17). The calculated molecular radius of the sphere is 4.58 A (17). Under ordinary conditions compound IX does not melt, but sublimes readily (12). Merker and Scott report that this compound appears to undergo some phase change to another crystalline compound between 195-210° (17) and melts, in a sealed tube, at 307-308° (15). Liu claims that the compound does not melt when heated above 420° and decomposes above 500° to an orange-brown gas which condenses to an orange liquid on cooling (16).

The less sterically hindered compound, tetrakis(dimethylsilyl)methane (X), was prepared in <u>ca</u>. 60% yield by the <u>in situ</u> Grignard reaction between carbon tetrabromide, chlorodimethylsilane and magnesium (12):

$$CBr_4 + 4H(CH_3)_2SiCl + 4Mg \longrightarrow \underset{\textstyle X}{[H(CH_3)_2Si]_4C} + 4MgBrCl$$

In view of the symmetrical arrangement of the four reactive silicon-hydrogen groups and its formation in high yield, this compound seemed particularly attractive as a precursor to other related types. Attempts to convert X to the corresponding tetraalkoxy derivatives under alkaline conditions resulted in extensive cleavage of the central carbon-silicon bonds (14). For instance, treatment of X with sodium methoxide afforded tris(dimethylmethoxysilyl)methane (XI) and other less-branched compounds:

$$X + 5CH_3OH \xrightarrow{CH_3ONa} \underset{XI}{[(CH_3O)(CH_3)_2Si]_3CH} + [(CH_3O)(CH_3)_2Si]_2CH_2 + 3H_2$$

Compounds which do not possess these reactive silicon-hydrogen groups, IX and VI, were not cleaved under these conditions (14). However, tetraalkoxy derivatives of X were obtained under acidic conditions, without detectable cleavage of the carbon-silicon bonds (14). Alcoholysis with methanol and ethanol, using chloroplatinic acid as catalyst, gave moderate to good yields of tetrakis(dimethylmethoxysilyl)methane (XIIa) and tetrakis(dimethylethoxysilyl)methane (XIIb), respectively (14):

$$X + 4ROH \xrightarrow{H_2PtCl_6} [(RO)(CH_3)_2Si]_4C + 4H_2$$

$$XIIa,\ R = CH_3$$

$$XIIb,\ R = C_2H_5$$

The _in situ_ Grignard reaction was also amenable to the preparation of some tri- and disilyl-substituted carbon compounds as well (13). Tris(trimethylsilyl)methane (VI), -methylmethane (XIIIa), and -phenylmethane (XIIIb) were prepared using chloroform, methyltrichloromethane, and phenyltrichloromethane as the polyhalide, respectively (13):

$$RCCl_3 + 3(CH_3)_3SiCl + 3Mg \longrightarrow [(CH_3)_3Si]_3CR + 3MgCl_2$$

VI, $R = H$

XIIIa, $R = CH_3$

XIIIb, $R = Ph$

When dichlorodiphenylmethane was used as the polyhalide, bis(trimethylsilyl)diphenylmethane (XIV) was obtained (13):

$$Ph_2CCl_2 + 2(CH_3)_3SiCl + 2Mg \longrightarrow \underset{\text{XIV}}{[(CH_3)_3Si]_2CPh_2} + 2MgCl_2$$

An attempted preparation of tetrakis(dimethylphenylsilyl)methane by a reaction between chlorodimethylphenylsilane, carbon tetrabromide and magnesium gave bis(dimethylphenylsilyl)methane (XV) in a 68% yield but no tetrakis compound was isolated (12):

$$2Ph(CH_3)_2SiCl + CBr_4 + 4Mg \xrightarrow{H_3O^+} \underset{\text{XV}}{[Ph(CH_3)_2Si]_2CH_2}$$

Merker and Scott (15) also described the preparation of compound VI and bis(trimethylsilyl)methane (XVI) by reactions of chlorotrimethylsilane and lithium with the respective polyhalides, chloroform and methylene chloride (15):

$$CHCl_3 + 3(CH_3)_3SiCl + 6Li \longrightarrow VI + 6LiCl$$

$$CH_2Cl_2 + 2(CH_3)_3SiCl + 4Li \longrightarrow \underset{\text{XVI}}{[(CH_3)_3Si]_2CH_2} + 4LiCl$$

Andreev (18) has also reported the preparation of VI by the reaction between methylmagnesium bromide and a mixture of chloro compounds obtained by the action of a silent discharge on dichlorodimethylsilane.

Gilman and Aoki (19, 20) studied the reactions between triphenylsilyllithium and polyhalide derivatives of carbon. The main product of these reactions was hexaphenyldisilane and only in the case of methylene chloride were small amounts of the anticipated coupling product obtained. The high yield of hexaphenyldisilane might well be attributed to: (1) a lithium-halogen exchange reaction followed by coupling of the silyllithium with the silicon halide (Path A); or (2) a coupling reaction of triphenylsilyllithium with the polyhalide followed by cleavage of the newly formed silicon-carbon bonds by triphenylsilyllithium (Path B) (19, 20).

Path A:

$$Ph_3SiLi + CX_4 \longrightarrow Ph_3SiX + LiCX_3$$

$$Ph_3SiLi + Ph_3SiX \longrightarrow Ph_3SiSiPh_3 + LiX$$

Path B:

$$Ph_3SiLi + CX_4 \longrightarrow Ph_3SiCX_3 + LiX$$

$$Ph_3SiLi + Ph_3SiCX_3 \longrightarrow Ph_3SiSiPh_3 + LiCX_3$$

Kraus and Nutting (21) report that, in a reaction between triphenylgermylsodium and chloroform in liquid ammonia, complete substitution of the chlorine atoms does not occur. In ether or benzene, only bis(triphenylgermyl)methane and hexaphenyldigermane were obtained (21).

Willemsens and van der Kerk (22) prepared tetrakis(triphenylplumbyl)methane (XVII) in <u>ca</u>. 60% yield by a reaction between triphenylplumbyllithium and carbon tetrachloride:

$$4\ Ph_3PbLi + CCl_4 \longrightarrow \left[Ph_3Pb\right]_4C + 4LiCl$$

XVII

From a stereochemical point of view, the formation of this compound is most remarkable. The reaction between triphenylplumbyllithium and chloroform or methylene chloride afforded tris(triphenylplumbyl)methane (XVIII) and bis(triphenylplumbyl)methane (XIX), respectively (22):

$$3\ Ph_3PbLi + CHCl_3 \longrightarrow \left[Ph_3Pb\right]_3CH + 3LiCl$$

XVIII

$$2\ Ph_3PbLi + CH_2Cl_2 \longrightarrow \left[Ph_3Pb\right]_2CH_2 + 2LiCl$$

XIX

A tabulation of known Group IVB tri- and tetra-Group IVB-substituted derivatives of carbon is given in Table 1.

Group IVB-substituted silicon compounds

In 1923, Stock *et al.* (6) obtained *n*-tetrasilane from the products of the reaction of magnesium silicide with hydrochloric acid, but they were unable to isolate the branched isomer, *iso*-tetrasilane (XX). Geher *et al.* achieved a partial separation of the two isomers by fractional distillation, and reported the boiling and freezing points, densities and refractive indices of both isomers (7). Borer and Phillips (23), and Feher and Strack (24) showed that the mixture of silanes obtained from the reaction of magnesium silicide with aqueous

$$\left[H_3Si\right]_3SiH$$

XX

Table 1. Known tri- and tetra-Group IVB-substituted derivatives of carbon

Formula	Name	MP(b.p.)	Reference
<u>A. Trisubstituted</u>			
$CCl_{10}Si_3$	Tris(trichlorosilyl)chloromethane	(290.6-291.6/758)	9
$CHCl_9Si_3$	Tris(trichlorosilyl)methane	(124-126/10)	9
$C_{10}H_{28}Si_3$	Tris(trimethylsilyl)methane	(93-95/13)	13
$C_{11}H_{30}Si_3$	Tris(trimethylsilyl)methylmethane	115	14
$C_{16}H_{22}Si_4$	Tris(trimethylsilyl)phenylmethane	158-160	14
$C_{19}H_{46}O_9Si_3$	Tris(triethoxysilyl)methane	(144.5/4)	9
$C_{55}H_{46}Pb_3$	Tris(triphenylplumbyl)methane	167-168	22
<u>B. Tetrasubstituted</u>			
$CCl_{12}Si_4$	Tetrakis(trichlorosilyl)methane	sublimes[a]	10
$C_9H_{28}Si_4$	Tetrakis(dimethylsilyl)methane	115	13
$C_{13}H_{36}Si_4$	Tetrakis(trimethylsilyl)methane	307-308[b]	16
$C_{13}H_{36}O_4Si_4$	Tetrakis(dimethylmethoxysilyl)methane	sublimes[a]	15
$C_{17}H_{44}O_4Si_4$	Tetrakis(dimethylethoxysilyl)methane	114-115	15
$C_{73}H_{60}Pb_4$	Tetrakis(triphenylplumbyl)methane	292-294[c]	

[a] No melting point was reported.

[b] In a sealed tube.

[c] Decomposition point.

acid can be separated into many components, including *n*- and *iso*-tetrasilane (XX), by gas chromatography. The *iso*-tetrasilane (XX) was recently prepared by Gokhale and Jolly (25) from pure silane by an ozonizer-type electric discharge method. The isomers of tetrasilane were separated by gas chromatography and identified by their relative volatilities and, by their infrared and n.m.r. spectra (25).

In 1950 Milligan and Kraus (26) prepared tris(triphenylgermyl)silane (XXI) by a reaction between triphenylgermylsodium and trichlorosilane in ether:

$$3\ Ph_3GeNa + SiHCl_3 \longrightarrow \left[Ph_3Ge\right]_3SiH + 3NaCl$$

XXI

Unexpectedly, the silicon-hydrogen bond of this compound was found to exhibit a reactivity not commonly associated with that of trialkyl- and triarylsilane compounds. Upon treatment of XXI with lithium in ethylamine, tris(triphenylgermyl)silyllithium (XXII) was obtained:

$$XXI + Li \longrightarrow \left[Ph_3Ge\right]_3SiLi + 1/2\ H_2$$

XXII

Derivatization of XXII with ethyl bromide afforded tris(triphenylgermyl)ethylsilane (XXIII):

$$XXII + C_2H_5Br \longrightarrow \left[Ph_3Ge\right]_3SiC_2H_5 + LiBr$$

XXIII

In contrast, triethylsilane (27) and triphenylsilane (28) reacted with lithium in ethylamine, affording triethylsilylamine and bis(triphenylsilyl)ethylamine, respectively:

$$(C_2H_5)_3SiH + Li \xrightarrow{C_2H_5NH_2} (C_2H_5)_3SiNHC_2H_5$$

$$Ph_3SiH + Li \xrightarrow{C_2H_5NH_2} [Ph_3Si]_2NC_2H_5$$

Milligan and Kraus (26) also prepared the bromide, tris(triphenylgermyl)bromosilane (XXIV), by the reaction of XXI with bromine in ethylamine:

$$XXI + Br_2 \longrightarrow [Ph_3Ge]_3SiBr + HBr$$

XXIV

The bromide, compound XXIV, was not hydrolyzed by water, but ammonia in moist benzene converted it to tris(triphenylgermyl)silanol (XXV):

$$XXIV + NH_3 \longrightarrow [Ph_3Ge]_3SiOH$$

XXV

In liquid ammonia at -33°, compound XXIV ammonolyzed to tris(triphenylgermyl)silylamine (XXVI):

$$XXIV + 2NH_3 \longrightarrow [Ph_3Ge]_3SiNH_2 + HBr$$

XXVI

Tris(triphenylgermyl)chlorosilane (XXVII) was obtained by the reaction between XXVI and hydrogen chloride:

$$XXVI + HCl \longrightarrow [Ph_3Ge]_3SiCl + NH_3$$

XXVII

The first reported compound containing a Ge-Si-Sn linkage, tris(triphenylgermyl)(triphenylstannyl)tin (XXVIII), was prepared by the treatment of XXII with chlorotriphenylstannane (29):

$$XXII + Ph_3SnCl \longrightarrow [Ph_3Ge]_3SiSnPh_3 + LiCl$$

XXVIII

Milligan and Kraus (26) also attempted the preparation of tetrakis(triphenylgermyl)silane by a reaction between triphenylgermylsodium and silicon tetrachloride. The products of this reaction were hexaphenyldigermane and an amorphous material:

$$4\ Ph_3GeNa + SiCl_4 \xrightarrow[C_6H_6]{Et_2O\ or} Ph_3GeGePh_3 + \text{an amorphous material} + 4NaCl$$

It was suggested that the amorphous material might be tetrakis(triphenylgermyl)silicoethylene, $[Ph_3Ge]_2Si = Si[GePh_3]_2$, based on elemental analyses.

In 1959, about 10 years after Milligan and Kraus described the synthesis of XXI (26), Gilman et al. (30) reported the preparation of the first branched-chain organosilicon compound containing contiguous silicon atoms: namely, tris(triphenylsilyl)silane (XXIX). This compound was isolated in a low yield (4.4%) from a reaction of triphenylsilyllithium and trichlorosilane:

$$3\ Ph_3SiLi + Cl_3SiH \longrightarrow \underset{\text{XXIX}}{[Ph_3Si]_3SiH} + 3LiCl$$

Under similar conditions, no tetrakis compound was isolated when silicon tetrachloride or tetraethoxysilane was used instead of trichlorosilane (30). The formation of hexaphenyldisilane in a high yield, from a reaction of triphenylsilyllithium and silicon tetrachloride, was explained by the following sequence of reactions:

$$Ph_3SiLi + SiCl_4 \longrightarrow Ph_3SiSiCl_3 + LiCl$$

$$Ph_3SiLi + Ph_3SiSiCl_3 \longrightarrow Ph_3SiSiPh_3 + LiSiCl_3$$

Gilman and Sim prepared tetrakis(triphenylstannyl)silane (XXX) by a reaction between triphenylstannyllithium and silicon tetrachloride (31):

$$4\ Ph_3SnLi + SiCl_4 \longrightarrow \left[Ph_3Sn\right]_4Si + 4LiCl$$

XXX

Urry *et al.* prepared tetrakis(trichlorosilyl)silane (XXXI) by trimethylamine-induced disproportionation reactions of hexachlorodisilane and octachlorotrisilane (32, 33):

$$4\ Si_2Cl_6 \xrightarrow{(CH_3)_3N} \left[Cl_3Si\right]_4Si + 3SiCl_4$$

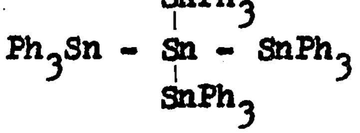
XXXI

$$3\ Si_3Cl_8 \xrightarrow{(CH_3)_3N} XXXI + 2Si_2Cl_6$$

A tabulation of known tri- and tetra-Group IVB-substituted derivatives of silicon is given in Table 2.

Group IVB-substituted germanium, tin and lead compounds

In 1923 Boeseken and Rutger (34) isolated a product with an empirical formula of $Ph_{12}Sn_5$ from a reaction of phenylmagnesium bromide with stannous chloride. Of the possible isomers, XXXII, XXIII and XXXIV, they thought XXXIII to be the most likely structure.



$$Ph_3Sn - \underset{\displaystyle SnPh_3}{\overset{\displaystyle SnPh_3}{Sn}} - SnPh_3$$

XXXII

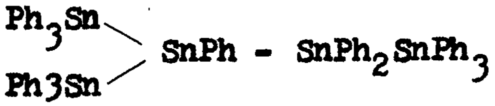
$$Ph_3SnSnPh_2SnPh_2SnPh_2SnPh_2$$

XXXIII

Table 2. Known tri- and tetra-Group IVB-substituted derivatives of silicon

Formula	Name	M.P.(b.p.)	Reference
A. Trisubstituted			
$H_{10}Si_4$	Trisilylsilane	(101.4/760)	24
$C_{54}H_{45}BrGe_3Si$	Tris(triphenylgermyl)bromosilane	242	26
$C_{54}H_{45}ClGe_3Si$	Tris(triphenylgermyl)chlorosilane	230-231	26
$C_{54}H_{46}Ge_3Si$	Tris(triphenylgermyl)silane	187-188	26
$C_{54}H_{46}OGe_3Si$	Tris(triphenylgermyl)silanol	197	26
$C_{54}H_{46}Si_4$	Tris(triphenylsilyl)silane	206-209	30
$C_{54}H_{47}NGe_3Si$	Tris(triphenylgermyl)silylamine	206	26
$C_{58}H_{50}Ge_3Si$	Tris(triphenylgermyl)ethylsilane	293	26
B. Tetrasubstituted			
$Cl_{12}Si_4$	Tetrakis(trichlorosilyl)silane	345 ± 2[a]	32
$C_{72}H_{50}Sn_4Si$	Tetrakis(triphenylstannyl)silane	390-395[a]	31
$C_{72}H_{60}Ge_3SnSi$	Tris(triphenylgermyl)(triphenylstannyl) silane	340-342	29

[a] Decomposition point.



XXXIV

Recently, Gilman and Cartledge (35, 36) reported the synthesis of this compound by several procedures:

$$3\ Ph_3SnLi + SnCl_2 \longrightarrow \left[Ph_3Sn\right]_3SnLi \xrightarrow{Ph_3SnCl} XXXII$$

$$2\ SnCl_2 \xrightarrow[2)\ 2Ph_3SnCl]{1)\ 3\ Ph_3Sn\ {}_2Mg} XXXII + Ph_3SnSnPh_3$$

$$4\ Ph_3SnLi + SnCl_4 \longrightarrow XXXII + Ph_3SnSnPh_3$$

$$4\ Ph_3SnCl + 8Li + SnCl_4 \longrightarrow XXXII + Ph_3SnSnPh_3$$

The highest yield of XXXII was obtained by the reaction of triphenyltinlithium and stannous chloride followdd by derivatization of the reaction mixture with triphenyltin chloride. In order to test for the presence of tris(triphenylstannyl)-tinlithium, the reaction mixture was derivatized with chlorotriphenylgermane, instead of triphenyltin chloride, to give tris(triphenylstannyl)(triphenylgermyl)tin (XXXV) (36):

$$3\ Ph_3SnLi + SnCl_2 \longrightarrow \left[Ph_3Sn\right]_3SnLi \xrightarrow{Ph_3GeCl} \underset{XXXV}{\left[Ph_3Sn\right]_3SnGePh_3}$$

Hydrolysis of the supposed tris(triphenylstannyl)tinlithium with saturated aqueous ammonium chloride gave the tetrakis compound instead of the expected tris(triphenylstannyl)tin hydride (XXXVI):

$$3\ Ph_3SnLi + SnCl_2 \longrightarrow \left[Ph_3Sn\right]_3SnLi \xrightarrow{Aq.\ NH_4Cl} \underset{XXXVI}{\left[Ph_3Sn\right]_3SnH}$$

In like manner, reaction of the supposed tris(triphenylstannyl)tinlithium with chlorotriphenylsilane or tri-n-butyltin chloride afforded only tetrakis(triphenylstannyl)tin. It is believed that tris(triphenylstannyl)tinlithium is formed on reaction of triphenyltinlithium with stannous chloride, but there are limits to the synthetic possibilities of the reagent.

The reaction of XXXII with one mole of iodine afforded an 81.9% yield of triphenyltin iodide; however, the only other product isolated was unreacted tetrakis compound in a 57% yield. When XXXII was treated with one mole of sym-tetrachloroethane in refluxing xylene, no reaction was observed, and the tetrakis compound was recovered in 94.2% yield. In like manner the nucleophilic reagent, methyllithium, gave only tetraphenyltin in addition to recovered starting material.

Incidental to the work of Gilman and Cartledge, van der Kerk and Willemsens (37, 38) prepared a number of related compounds of the type: $\left[Ph_3M\right]_4M'$ (where M = Pb, Sn and M' = Sn, Ge). They were obtained according to the following reaction:

$$4\ Ph_3MLi + M'Cl_4 \longrightarrow \left[Ph_3M\right]_4M' + 4LiCl$$

$$M = Pb,\ Sn$$

$$M' = Sn,\ Ge$$

Varying amounts of Ph_6M_2 were always formed as a by-product, probably as a result of metal-halogen interconversion reactions. Owing to the ease of oxidation and general instability of lead tetrachloride, compounds with M' = Pb were obtained from lead dichloride (37):

$$Ph_3MLi + PbCl_2 \longrightarrow (Ph_3M)_2Pb$$

$$(Ph_3M)_2Pb \longrightarrow [Ph_3M]_4Pb + Pb$$

The compound containing lead-lead bonds, tetrakis(triphenylplumyl)plumbane (XXXVII), has been obtained by simultaneous hydrolysis and oxidation of ether-free triphenylplumbyllithium at a low temperature (39):

$$Ph_3PbLi \xrightarrow[H_2O_2]{\text{ice-salt}} \underset{\text{XXXVII}}{[Ph_3Pb]_4Pb}$$

The compound was described as unstable and decomposed in a few days in the presence of air to hexaphenyldilead and lead oxide. It decomposed more slowly under a nitrogen atmosphere and very rapidly in polar solvents. Due to its instability in ethereal solvents, compound XXXVII could not be prepared from a reaction between triphenylplumbyllithium and lead dichloride (39). Willemsens and van der Kerk (37) report that the lead compounds were prepared most easily; and compounds of the type, $[Ph_3Ge]_4M'$, could not be obtained. Gilman and Sim (31), however, have prepared tetrakis(triphenylgermyl)tin (XXXVIII) from a reaction between triphenylgermyllithium and stannous chloride followed by derivatization of the reaction mixture with chlorotriphenylgermane:

$$3\ Ph_3GeLi + SnCl_2 \longrightarrow [Ph_3Ge]_3SnLi \xrightarrow{Ph_3GeCl} \underset{\text{XXXVIII}}{[Ph_3Ge]_4Sn}$$

Tetrakis(triphenylsilyl)tin (XXXIX) could be prepared from stannous chloride, but not stannic chloride, by the following reactions:

$$3\ Ph_3SiLi + SnCl_2 \longrightarrow [Ph_3Si]_3SnLi \xrightarrow{Ph_3SiCl} \underset{\text{XXXIX}}{[Ph_3Si]_4Sn}$$

A tabulation of known tetra-Group IVB-substituted derivatives of germanium, tin and lead is given in Table 3. In the solid state all compounds prepared, except compound XXXVI, are stable at room temperature. In solution, the compounds with lead atoms as the surrounding metal atoms, $[Ph_3Pb]_4M'$, show much higher stability (25).

All of the compounds listed in Table 3 show ultraviolet absorption maxima in the 298 to 444 mμ region (ε = 59,000 to 73,000) which have been attributed to the excitation of the electrons of the metal-metal system (39).

The Chemistry of Methylated Polysilane Compounds

The chemistry of methylated polysilane compounds has recently been reviewed (5). As a basis for the work presented here, a cursory survey of the chemistry of permethylated polysilane compounds and compounds in which at least one silicon atom is bonded to three methyl group will be emphasized.

Methods of preparation

The reactions of a silicon halide with a metal or a silylmetallic compound are the two most widely used methods

Table 3. Known tetra-Group IVB-substituted derivatives of germanium, tin and lead

Formula	Name	Decomposition point	Reference
$C_{72}H_{60}Ge_4Pb$	Tetrakis(triphenylgermyl)plumbane[a]	- - -	25
$C_{72}H_{60}GeSn_4$	Tris(triphenylstannyl)(triphenylgermyl)tin	315-330	36
$C_{72}H_{60}Ge_4Sn$	Tetrakis(triphenylgermyl)tin	407-410	31
$C_{72}H_{60}Pb_5$	Tetrakis(triphenylplumbyl)plumbane[a, b]	- - -	39
$C_{72}H_{60}Pb_4Ge$	Tetrakis(triphenylplumbyl)germane	210	37
$C_{72}H_{60}Pb_4Sn$	Tetrakis(triphenylplumbyl)tin	160	37
$C_{72}H_{60}Si_4Sn$	Tetrakis(triphenylsilyl)tin	390-394	31
$C_{72}H_{60}Sn_4$	Tetrakis(triphenylstannyl)tin	315-325	35
$C_{72}H_{60}Sn_4Ge$	Tetrakis(triphenylstannyl)germane	324	37
$C_{72}H_{60}Sn_4Pb$	Tetrakis(triphenylstannyl)plumbane	200	37

[a] Could not be isolated in the pure state.

[b] Solutions are not stable and become turbid after a while.

for preparing organopolysilane compounds (4, 5, 40).

Symmetrical permethylated polysilane compounds, straight-chain and cyclic, are conveniently prepared by a reaction between the appropriate silicon halide and lithium metal in THF (41, 42), molten sodium in xylene or the absence of a solvent (43, 44, 45), and sodium potassium alloy in hydrocarbon or ether (46, 47, 48, 49). The synthesis of an homologous series of methylated polysilane compounds of the type, $CH_3\ Si(CH_3)_2\ _n CH_3$, has been reported (44, 45, 49). They were prepared according to the following reactions:

$$(CH_3)_3SiCl + (CH_3)_3SiSi(CH_3)_2Cl \xrightarrow[Na/K]{Na\ or} CH_3\left[Si(CH_3)_2\right]_3CH_3$$

$$(CH_3)_3SiSi(CH_3)_2Cl + Cl(CH_3)_2Si\text{-}Si(CH_3)_2Cl \xrightarrow[Na/K]{Na\ or} CH_3\left[Si(CH_3)_2\right]_nCH_3$$

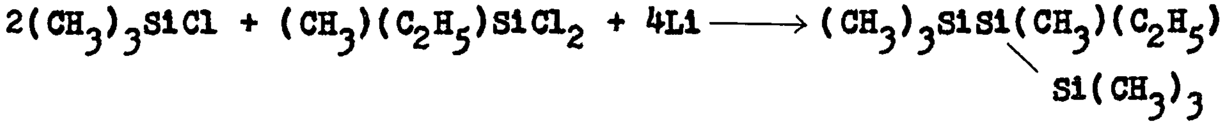
n = 4, 6, 7, 8, 9, 10, 11, 12

Recently, a one-step procedure has been described for the preparation of some straight-chain methylated polysilane compounds by a reaction between a dichlorosilane compound (RCH_3SiCl_2, where R = CH_3, C_2H_5 or Ph), chlorotrimethylsilane and lithium (42). The reaction between dichlorodimethylsilane, chlorotrimethylsilane, and lithium gave 60-70% yields of octamethyltrisilane, together with small amounts of the next two higher homologues (42):

$$2(CH_3)_3SiCl + (CH_3)_2SiCl_2 + 4Li \longrightarrow CH_3\left[Si(CH_3)_2\right]_nCH_3$$

n = 3-5

When a smaller ratio of chlorotrimethylsilane to dichlorodimethylsilane was used, compounds of the type, $CH_3[Si(CH_3)_2]_n$-CH_3, n = 3-8 and 10, were isolated and identified. Using methylethyldichlorosilane as the dichloro silicon compound, a 66% yield of 2-ethylheptamethyltrisilane was obtained, and methylphenyldichlorosilane gave a 25% yield of heptamethyl-2-phenyltrisilane (42):



$$2(CH_3)_3SiCl + (CH_3)(C_2H_5)SiCl_2 + 4Li \longrightarrow (CH_3)_3SiSi(CH_3)(C_2H_5)Si(CH_3)_3$$

$$2(CH_3)_3SiCl + (CH_3)PhSiCl_2 + 4Li \longrightarrow (CH_3)_3SiSi(CH_3)PhSi(CH_3)_3$$

Hexamethyldisilane has also been prepared by a similar procedure from a reaction between chlorotrimethylsilane and lithium.[1]

$$2(CH_3)_3SiCl + 2Li \longrightarrow (CH_3)_3SiSi(CH_3)_3$$

Dodecamethylcyolohexasilane, the only well-characterized permethylated cyclopolysilane compound, has been prepared by a reaction between dichlorodimethylsilane and sodium (45), sodium potassium alloy (48) and lithium (41):

$$6(CH_3)_2SiCl_2 \xrightarrow[Li]{Na,\ Na/K\ or} [(CH_3)_2Si]_6$$

The method of choice for the preparation of dodecamethylcyclohexasilane is the use of lithium, with triphenylsilyllithium as catalyst (41).

Unsymmetrical polysilane compounds, in which one silicon

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[1] Dr. K. Shiina, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the preparation of hexamethyldisilane. Private communication. 1966.

atom is bonded to three methyl groups, are easily obtained by a reaction between a silylmetallic compound and chlorotrimethylsilane (4, 5, 50, 51), and use has been made of this procedure for the characterization of organometallic species.

Chemical properties

The silicon-silicon bond of organopolysilanes is cleaved by aqueous or methanolic alkali (52), aqueous piperidine (1, 53) and alkali in hexanol (45), affording one mole of hydrogen gas per silicon-silicon bond:

$$R_3SiSiR_3 + ROH \longrightarrow 2R_3SiOR + H_2$$

These reactions can be considered as an attack by the basic or nucleophilic species on a silicon atom and are represented generally as follows:

$$R_3Si-SiR_3 + R'^{} \longrightarrow R_3SiR' + R_3Si^-$$
$$R_3Si-SiR_3 + R_3'Si \longrightarrow R_3Si-SiR_3' + R_3Si^-$$
$$R_3Si-SiR_3 + H^- \longrightarrow R_3Si-H + R_3Si^-$$
$$R_3Si-SiR_3 + OH^- \longrightarrow R_3SiOH + R_3Si^-$$

The last reaction is carried out in hydroxylic media, which effect immediate hydrolysis of the intermediate silanion to an Si-H compound which is in turn hydrolyzed to a silanol with the evolution of hydrogen (54, 55):

$$R_3Si^- + R'OH \longrightarrow R_3SiH + R'O^-$$
$$R_3SiH + R'OH \longrightarrow R_3SiOR' + H_2$$

A measure of the number of milliliters of gas liberated at STP per gram of compound is called the "hydrogen value" and this procedure constitutes a chemical means for structural determination.

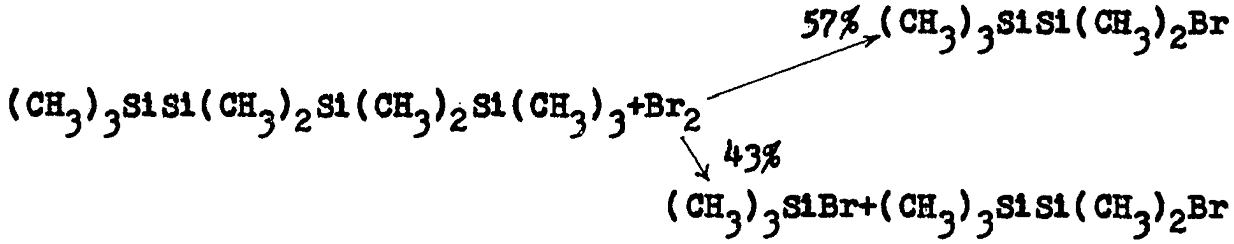
The silicon-silicon bond of hexaaryldisilanes is resistant to cleavage by halogens, whereas the hexaalkyldisilanes are much more reactive (40). With a given silicon-silicon bond, it appears that the relative reactivity of the halogens is: Cl > Br > I (56). This order of reactivity is probably associated with the relative coordinating ability of the halogen with silicon in the pentacovalent state. Hexamethyldisilane has been cleaved by chlorine, bromine and iodine (56, 57):

$$(CH_3)_3SiSi(CH_3)_3 + X_2 \longrightarrow 2(CH_3)_3SiX$$

$$X = Cl, Br, I$$

The silicon-silicon bond of higher straight-chain permethylated polysilane compounds has also been cleaved by halogens (5). Octamethyltrisilane and decamethyltetrasilane was cleaved by bromine in chloroform at -40° (58):

$$(CH_3)_3SiSi(CH_3)_2Si(CH_3)_3 + Br_2 \longrightarrow (CH_3)_3SiBr + (CH_3)_3SiSi(CH_3)_2Br$$



$$(CH_3)_3SiSi(CH_3)_2Si(CH_3)_2Si(CH_3)_3 + Br_2 \begin{cases} \xrightarrow{57\%} (CH_3)_3SiSi(CH_3)_2Br \\ \xrightarrow{43\%} (CH_3)_3SiBr + (CH_3)_3SiSi(CH_3)_2Br \end{cases}$$

A convenient method for the preparation of α,ω-dihalo-permethylated polysilane compounds involves a cleavage reaction of dodecamethylcyclohexasilane by chlorine[1], bromine[2], and iodine (47):

$$\left[\mathrm{Si(CH_3)_2}\right]_6 + X_2 \longrightarrow X-\left[\mathrm{Si(CH_3)_2}\right]_n-X$$

$$n = 2,\ 3,\ 4 \text{ and } 6$$

$$X = \mathrm{Cl},\ \mathrm{Br} \text{ and } \mathrm{I}$$

Dodecamethylcyclohexasilane is also cleaved by phosphorus pentachloride (59). Anhydrous hydrogen chloride and t-butyl chloride were used to hydrohalogenate dodecamethylcyclohexasilane, providing a series of compounds of the general formula $\mathrm{Cl}-\left[\mathrm{Si(CH_3)_2}\right]_n-Y$, where $n = 1\text{-}6$ and Y = hydrogen or chlorine (60, 61):

$$\left[\mathrm{Si(CH_3)_2}\right]_6 + \mathrm{RCl} \longrightarrow \mathrm{Cl}-\left[\mathrm{Si(CH_3)_2}\right]_n-Y$$

$$R = \mathrm{(CH_3)_3C} \text{ or H} \qquad Y = \mathrm{Cl} \text{ or H}, \quad n = 1\text{-}6$$

The reaction of dodecamethylcyclohexasilane was carried out in a stainless steel autoclave at pressures of 400 to 600 psi and temperatures of 50 to 70°. A mixture of t-butyl chloride and dodecamethylcyclohexasilane reacts smoothly when heated at 140-150° in a stainless steel autoclave at 140 psi pressure, but no apparent reaction occurred in o-dichlorobenzene at 155 to 180° after 48 hours.

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[1] Dr. P. K. Sen, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the reaction between dodecamethylcyclohexasilane and chlorine. Private communication. 1964.

[2] Dr. S. El. Mawaziny, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the reaction between dodecamethylcyclohexasilane and bromine. Private communication. 1964.

Permethylated organopolysilane compounds undergo a wide variety of reactions without cleavage of the silicon-silicon bond. Removal of one or two methyl groups of hexamethyldisilane by means of sulphuric acid and subsequent treatment with ammonium halides serves to introduce a functional group onto one or both silicon atoms (62):

$$(CH_3)_3SiSi(CH_3)_3 \xrightarrow[2.\ NH_4X]{1.\ H_2SO_4} (CH_3)_3SiSi(CH_3)_2X$$

$$X = Cl,\ F$$

$$(CH_3)_3SiSi(CH_3)_3 \xrightarrow[2.\ NH_4X]{1.\ H_2SO_4} X(CH_3)_2SiSi(CH_3)_2X$$

$$X = Cl,\ F$$

The procedure is also applicable to higher polysilane compounds (63):

$$CH_3[Si(CH_3)_2]_3CH_3 \xrightarrow[2.\ NH_4Cl]{1.\ H_2SO_4} [Cl\,[Si(CH_3)_2]_3Cl$$

The removal of the first methyl group, which involves a heterogeneous system, is fast, while the removal of the second methyl group is slow in spite of involving a homogeneous system (62). Treatment of these silicon halide compounds with Grignard reagents[1] (59, 64), lithium aluminum hydride[2] (58),

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[1] Dr. P. K. Sen, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the reactions between Grignard reagents and chlorosilanes. Private communication. 1963.

[2] Dr. J. M. Holmes, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the reactions between lithium aluminum hydride and chlorosilanes. Private communication. 1965.

inorganic salts (64) and water (58, 65) gave good yields of the respective derivative without silicon-silicon bond cleavage:

$$(CH_3)_3SiSi(CH_3)_2Cl + RMgX \longrightarrow (CH_3)_3SiSi(CH_3)_2R$$

$$R = CH_2 = CH\text{-},\ CH_2 = CH\text{-}CH_2\text{-},\ C_6H_5\text{-},\ \underline{p}\text{-}BrC_6H_4\text{-},\ \underline{p}\text{-}ClC_6H_4\text{-},\ \text{etc.}$$

$$(CH_3)_3SiSi(CH_3)_2Cl \xrightarrow[Et_2O]{LiAlH_4} (CH_3)_3SiSi(CH_3)_2H$$

$$Cl\left[Si(CH_3)_2\right]_nCl \xrightarrow[Et_2O]{LiAlH_4} H\left[Si(CH_3)_2\right]_nH$$

$$n = 4,\ 6$$

$$(CH_3)_3SiSi(CH_3)_2Cl + AgCN \longrightarrow (CH_3)_3SiSi(CH_3)_2CN$$

$$(CH_3)_3SiSi(CH_3)_2Br \xrightarrow{H_2O} (CH_3)_3SiSi(CH_3)_2OH \text{ and/or}$$

$$(CH_3)_3SiSi(CH_3)_2\ {}_2O$$

Although arylsubstituted silylmetallic compounds are prepared in excellent yields, a number of unsuccessful attempts to synthesize stable solutions of trialkylsilylmetallic compounds have been described (40, 50, 51). Only starting material was obtained from the reaction of 1, 1, 1-trimethyl-2, 2, 2-triphenyldisilane and lithium in THF (66). The formation of trimethylsilylpotassium was indicated by the isolation of trimethylphenylsilane in low yield, in addition to tetraphenylsilane, upon derivatization of the cleavage products of a reaction between 1, 1, 1-trimethyl-2, 2, 2-triphenyldisilane and sodium-potassium alloy with bromobenzene (67):

$$(CH_3)_3SiSiPh_3 + Na/K \longrightarrow (CH_3)_3SiK + Ph_3SiK \xrightarrow{PhBr} (CH_3)_3SiPh + Ph_4Si$$

It was possible to characterize phenylpotassium but not trimethylsilylpotassium from a reaction between trimethylphenylsilane and sodium-potassium alloy, followed by derivatization with chlorotriphenylsilane (68). No reaction was observed between phenylisopropylmethyltriphenylsilane and sodium-potassium alloy in diethyl ether (69), and hexamethyldisilane resisted metal clevage entirely (40, 50, 51).

Evidence for the existence of a transient trialkylsilylmetallic compound is afforded by the cleavage reaction of 1, 1, 1-triethyl-2, 2, 2-triphenyldisilane by lithium (66). The products isolated from this reaction were, after acid hydrolysis, triphenylsilane (92%), triethylsilane (11%) and hexaethyldisilane (14%). Isolation of the last compound clearly indicates the formation of triethylsilyllithium, which by cleavage of 1, 1, 1-triethyl-2, 2, 2-triphenyldisilane, gives hexaethyldisilane:

$$Ph_3SiSiEt_3 + 2Li \longrightarrow Ph_3SiLi + Et_3SiLi$$

$$Ph_3SiSiEt_3 + Et_3SiLi \longrightarrow Et_3SiSiEt_3 + Ph_3SiLi$$

Kraus and Nelson (27) described the preparation of triethylsilyllithium by the cleavage reaction of triphenylgermyltriethylsilane with lithium in ethylamine.. However, it has been shown that silylmetallic compounds are instantly ammonolyzed by amines (70, 71). No reaction was observed between triethylphenylsilane and sodium in liquid ammonia (27).

Attempted cleavage of hexaethyldisilane by sodium-potassium alloy in diethyl ether (67) or lithium in THF (68) was unsuccessful. Gilman et al. (72, 73), in an attempt to prepare triethylsilyllithium, treated triethylsilane with RLi compounds. The product, Et_3SiR was formed instead of the desired triethylsilyllithium compound:

$$Et_3SiH + RLi \longrightarrow Et_3SiR + LiH$$

Octamethyltrisilane (74), decamethyltetrasilane (74) and dodecamethylcyclohexasilane (47, 74) gave mixtures of silylpotassium compounds when treated with sodium-potassium alloy in THF. The silylpotassium compounds were identified by v.p.c., subsequent to the derivatization of the mixture with chlorotrimethylsilane. To explain the formation of products from a reaction of decamethyltetrasilane and sodium-potassium alloy, followed by derivatization with chlorotrimethylsilane, Stolberg proposed the following sequence of reactions (74):

$$(CH_3)_{10}Si_4 \xrightarrow{Na/K} \left\{\begin{array}{l} 2(CH_3)_5Si_2K \\ \\ (CH_3)_3SiK + (CH_3)_7Si_3K \end{array}\right. \xrightarrow{(CH_3)_3SiCl} \begin{array}{l} (CH_3)_6Si_2 \\ (CH_3)_8Si_3 \\ (CH_3)_{10}Si_4 \end{array}$$

$$(CH_3)_{10}Si_4 + (CH_3)_5Si_2K \longrightarrow \begin{array}{l} (CH_3)_7Si_3K + (CH_3)_8Si_3 \\ (CH_3)_5Si_2K + (CH_3)_{10}Si_4 \\ (CH_3)_3SiK + (CH_3)_{12}Si_5 \end{array}$$

Dodecamethylcyclohexasilane is also cleaved by methyllithium to give mixtures of silanyllithium compounds (75).

Recently, Husk and West (76) reported that the reaction of dodecamethylcyclohexasilane with sodium-potassium alloy at -95° gives a blue-green solution which exhibits strong electron paramagnetic resonance. The electron spin resonance spectrum was explained in terms of an anion radical of the parent cyclosilane, $\left[Si(CH_3)_2\right]_6^{\overset{\bullet}{-}}$, in which the unpaired electron is delocalized over all six silicon atoms. The e.s.r. signal was observed up to about -50°. Above this temperature the signal disappears rapidly and the solution becomes pale yellow. Hexamethyldisilane gave no radical signal and decamethyltetrasilane gave a complex e.s.r. spectrum. The transient existence of silyl radicals is suspected in reactions of some permethylated polysilane compounds such as, dodecamethylcyclohexasilane, tetrakis(trimethylsilyl)silane, tris-(trimethylsilyl)methylsilane and octamethyltrisilane with lithium and biphenyl.[1] For example, Harrell[1] has identified some straight-chain α,ω-dihydro compounds of the type $H\,Si(CH_3)_2{}_n\,H$ (where n = 3-6) by v.p.c., obtained by the reaction between dodecamethylcyclohexasilane, biphenyl and lithium followed by acid hydrolysis:

$$\left[Si(CH_3)_2\right]_6 + Li + C_{12}H_{10} \xrightarrow{H_3O^+} H\left[Si(CH_3)_2\right]_n H$$
$$n = 3\text{-}6$$

Some other products in which n > 6 were also present. When the reaction mixture was derivatized with chlorotrimethyl-

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[1] R. L. Harrell, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the reaction between permethylated polysilane compounds, lithium and biphenyl. Private communication. 1966.

silane, compounds of the type $CH_3[Si(CH_3)_2]_nCH_3$ (where n = 5-10) were identified by v.p.c. and compounds in which n = 10 and 12 were isolated:

$$[Si(CH_3)_2]_6 + Li + C_{12}H_{10} \xrightarrow{(CH_3)_3SiCl} CH_3[Si(CH_3)_2]_nCH_3$$
$$n = 5\text{-}12$$

Products containing more than twelve silicon atoms were isolated. The formation of an anion radical by the transfer of an electron to dodecamethylcyclohexasilane is suspected since an insufficient molar quantity of biphenyl was used:

$$C_{12}H_{10} + Li \longrightarrow C_{12}H_{10}^{\dot{-}}$$
$$C_{12}H_{10}^{\dot{-}} + [Si(CH_3)_2]_6 \longrightarrow [Si(CH_3)_2]_6^{\dot{-}}$$

Fearon has found that hexamethyldisilane is unreactive under similar conditions.

Physical properties

Straight-chain permethylated polysilane compounds with n = 2-6 are liquid, while compounds in which n = 8-12 are solids (5, 49). If the melting points of the permethylated polysilane compounds are plotted against the number of silicon atoms, an alternating effect for odd and even numbers is observed up to the octasilane; but afterwards, the melting points display a regular progression as the molecular weight increases (49). Dodecamethylcyclohexasilane is a sublimable

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[1] Dr. F. W. G. Fearon, department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the reaction between hexamethyldisilane, lithium and biphenyl. Private communication. 1966.

solid (ca. 100°) which melts at 250-252° (41, 45) and undergoes an irreversible change in crystalline form when heated to temperatures greater than 74° (45). In general, all of the permethylated polysilane compounds are resistant to decomposition at their boiling and melting points.

Bonds formed between silicon and electronegative elements are generally thermochemically stronger than analogous bonds involving carbon (40). Limited thermochemical data for the silicon-silicon bond, on the other hand, have given the impression that this bond is considerably weaker than a carbon-carbon bond. A thermochemical bond energy E(Si-Si) of 46.4 kcal. mole^{-1} has been calculated for disilane, and the activation energy for its pyrolysis has been taken to imply a value for the dissociation energy $D(H_3Si-SiH_3)$ of 51 kcal. mole^{-1} (77). By electron impact, Steele and Stone (78) found that the dissociation energy $D(H_3Si-SiH_3)$ for the silicon-silicon bond of disilane to be 81.3 kcal. mole^{-1}, which is comparable to that of the carbon-carbon bond of ethane, $D(H_3C-CH_3)$ = 83 kcal. mole^{-1}. Hess, Lampe and Sommer (79, 80) have reported a dissociation energy $D[(CH_3)_3SiSi(CH_3)_3]$ for the silicon-silicon bond of hexamethyldisilane of 81 kcal. mole^{-1}, whereas Haszeldine et al. (81) report a significantly lower value of 58 kcal. mole^{-1}.

Hague and Prince (82) have reported that the ultraviolet spectra of Group IVB organometallic compounds of the type Ph_3MMPh_3 (where M = Si, Ge, Sn and Pb) exhibits a maximum in the 239-248 mμ region ε = 30,400 to 33,900. The absorptions were attributed to interactions between different phenyl groups on different M atoms through the M-M bond. This unusual type of conjugation was considered to occur through overlap of suitable vacant d-orbitals on the M atom. Recently, Gilman *et al.* (83) reported the ultraviolet spectral properties of a family of permethylated polysilanes of the type $CH_3\left[Si(CH_3)_2\right]_nCH_3$ (where n = 2-8). The observed increase in the absorption maxima (λ max) and the values with an increase in chain length was attributed to the silicon-silicon bonding acting as a chromophore, probably through the use of vacant d-orbitals of the silicon atoms (83). The ultraviolet absorption maxima for a given chain length remained essentially constant upon substitution of a hydrogen for chlorine in compounds of the type, Y-$\left[Si(CH_3)_2\right]_n$-Y where n = 2 to 6 and Y = hydrogen or chlorine (60, 61). An ultraviolet spectral study of some straight-chain cyclic and branched-chain polysilane compounds, both methylated and phenylated, have led to the following conclusions (5).

a. Phenyl-containing monosilanes exhibit only the benzenoid fine-structure of B-bands having low molar absorbtivities (40, 82).

b. With polysilanes, intense absorption maxima are observed and the λ max. increases with increasing chain length.

c. The molar absorbtivities also increase with increasing chain length. These compounds appear to obey Beers-Law.

d. Substituents such as phenyl and vinyl cause an increase in λ max., while chloro-, hydroxyl and H- appear to have little effect on the band position.

e. Cyclic and branched polysilanes absorb at lower wavelengths than their corresponding open-chain analogs.

In general, groups attached to silane compounds exhibit a lower shielding value than groups attached to methane compounds. Webster (84) has studied the proton magnetic resonance spectra of C-H and Si-H protons in a series of methyl-, phenyl-substituted methanes and silanes and noted that in the carbon series, the change is much larger than in the silicon series. He attributed this to possible $d\pi-p\pi$ bonding between silicon and the phenyl rings. However, his measurements on other groups, as well as the phenyl group, are much lower in silane compounds than in methane compounds. For example, if the t value he gives for $(CH_3)_3SiH$, 6.149, is put into the equation $t = t(SiH_4) - \Sigma\sigma_{eff}$, σ_{eff} for the methyl group is approximately 0.21 compared with Shoolery's value of 0.466 for the methyl group in substituted methanes (85). Other examples of this phenomenon are evident with the halosilane (75). Although $d\pi-p\pi$ bonding (84, 86) has been invoked to explain the relative decrease in chemical shift differences for substituted silane compounds as compared to methane compounds, this decrease in effective shielding of a group appears even in compounds where this type of bonding is not possible such as methyl silanes, germanes and stannanes

(85, 87). It appears that the effective shielding for the phenyl group and for the methyl group of Group IVB compounds is in the order of the relative electronegativities of the element to which the group is attached: C >> Ge > Sn > Si (85).

It has also been reported that in a series of straight-chain permethylated polysilane compounds, the internal methyl protons are usually deshielded with respect to the terminal methyl protons (5).

Smith and Angelotti (88) have reported that the Si-H stretching absorption varies with the substituents on silicon in a manner which approximately parallels the sum of their electronegativities. Using the sum of "E-values (characteristic constants assigned to the substituents on silicon"), the Si-H frequencies of numerous monosilane derivatives were accurately predicted (88). Thompson (89) has shown that these values may be correlated with Taft's σ^* values, concluding that the vibration frequency of the Si-H bond is controlled by inductive effects.

EXPERIMENTAL

The apparatus consisted of a three-necked flask of appropriate size with ground glass joints, fitted with a tru-bore stirrer, a Friedrich's condenser and an addition funnel. The condenser and addition funnel were topped with nitrogen inlets when reactions involving organometallic or organosilylmetallic compounds were run. All glassware was oven-dried before use and purged while hot with dry oxygen-free nitrogen before reactants were introduced.

Unless otherwise stated, the tetrahydrofuran (THF) was dried by refluxing at least 24 hours over sodium metal followed by distillation from lithium aluminum hydride immediately before use. Anhydrous ether used for reaction purposes was stored over sodium wire.

The organosilicon halides were purchased from Dow Corning Corporation and used without further purification. Trimethyl phosphate, methyl iodide and bromobenzene were purchased from Columbia Organic Chemicals Co., Inc. and were further purified by distillation. The spectrograde cyclohexane used for ultraviolet spectral studies was obtained from Phillips Petroleum Co. and Matheson Coleman and Bell Co.

Lithium metal (0.1% sodium content) was obtained commercially as wire from Lithium Corporation of America and wiped free of its protective coating and cut into small pieces into a nitrogen filled reaction flask. Magnesium metal was

Grignard grade turnings obtained from Mallinkrodt Chemical Works.

Quantitative titrations of organometallic and silylmetallic compounds were carried out in a manner similar to the published procedure, employing a double titration technique using allyl bromide (90). Color Test I was used as a qualitative test for organometallic and organosilylmetallic reagents (91).

Phenylmagnesium bromide (92), n-butyllithium (93), methyllithium (94) and phenyllithium (94, 95) were prepared in diethyl ether according to published directions. Previously described preparations of triphenylsilyllithium (96) and dimethylphenylsilyllithium (96) were employed, using THF as solvent. Sodium-potassium alloy was prepared and the excess alloy was removed from reaction mixtures by amalgamation with mercury according to the published procedure (97). Tetrakis(trimethylsilyl)silane was routinely identified by vapor phase chromatography (v.p.c.) - column temperature was 175° and the injection port temperature was ca. 250° and its infrared spectrum because of the difficulty of obtaining good, reproducible sealed tube melting points on an analytical sample.

Silicon analyses were carried out by Union Carbide Corporation, Silicones Division, Tonawanda Laboratories, Tonawanda, New York. Carbon and hydrogen analyses were carried out by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, Western Germany (formerly Dr. Ing. A. Schoeller). Infrared spectra were routinely determined using the Perkin-Elmer, Model 21, Spectrophotometer. The proton magnetic resonance spectra were measured with a Varian HR-60 and H-60 spectrometer operating at 60 Mc and the ultraviolet spectra were determined with a Beckman DK 2A spectrometer. V.p.c. analysis were carried out with an F + M Model 500 gas chromatograph using an 18 in. x 1/4 in. column packed with silicone gum rubber SE 30 on Chromosorb W(1:20). Molecular weight determinations were made with a Mechrolab Model 301-A Vapor Pressure Osmometer. Benzil was used as a standard with benzene as the solvent. All melting and boiling points are uncorrected.

A Direct Preparation of Some Tetrasilyl-substituted Organopolysilane Compounds

Tetrakis(trimethylsilyl)silane

From silicon tetrachloride, chlorotrimethylsilane and lithium in THF (general procedure) The general procedure involves the addition of ca. 15% of a solution of silicon tetrachloride dissolved in THF (ca. 1:1 volume ratio) to a vigorously stirred solution of a 20% excess of chlorotrimethylsilane and THF (ca. 1:1 volume ratio) in which a small excess of lithium is suspended. After stirring at room temperature for a few minutes, the reaction mixture usually warms up and turns brown. Once the reaction has started, the addition of silicon tetrachloride dissolved in THF may be rapid without decreasing the yield of tetrakis(trimethylsilyl)silane appreciably. However, to maintain control of the exothermic reaction, moderate to slow addition is preferable. Upon completed addition (ca. two to four hours), the reaction mixture should be stirred at room temperature for more than twenty-four hours. At this time, appreciable amounts of insoluble salts and a small amount of unreacted lithium wire are present. Also, the reaction mixture should be at room temperature. If these criteria are not satisfied, continued stirring of the reaction mixture at room temperature is necessary.

In the work-up of the reaction, unreacted lithium wire and insoluble salts are removed by filtration. Hydrolysis of the homogeneous dark brown solution by the addition to a mixture of crushed ice and hydrochloric acid is followed by the separation of the organic layer. The organic layer is dried over anhydrous sodium sulfate, filtered, and the organic solvents are removed under reduced pressure. Pure tetrakis(trimethylsilyl)silane is obtained by crystillization of the semi-solid from 95% ethanol subsequent to sublimation. When a slight excess of silicon tetrachloride is used and/or when the reaction does not proceed to completion, a white colloidal precipitate is observed upon the hydrolysis of the reaction mixture subsequent to the removal of undissolved salts and lithium metal by filtration. Due to its colloidal nature, sometimes a sharp distinction between the organic and aqueous layer is not observed, even after varying the pH of the mixture or adding more ether. At this stage, a filtering aid is added and the mixture is filtered under reduced pressure. Further work-up is continued in the manner described above.

Run 1 To 3.36 g. (0.48 g.-atom) of lithium was added 10 ml. of a solution of 11.7 g. (0.069 mole) of silicon tetrachloride and 50 ml of THF. After stirring for 30 minutes at room temperature, the reaction mixture turned brown and addition of the silicon tetrachloride solution was continued over a period of 30 minutes. After this time, a solution of 25.9 g. (0.24 mole) of chlorotrimethylsilane in 100 ml. of THF was added dropwise. The reaction mixture became warm and upon completed addition (ca. 1 hour), it was refluxed overnight. Unreacted lithium was removed by filtration and the reaction mixture was acidified by addition to a mixture of ice and 10% hydrochloric acid. The hydrolyzed mixture was extracted with three 100 ml. portions of ether and the combined organics were dried over sodium sulfate. Subsequent to the removal of solvents, the brown oil was chromatographed on neutral alumina. Elution with petroleum ether (b.p. 60-70°) afforded a solid from which 6.0 g. of tetrakis(trimethylsilyl)silane was obtained, after two recrystallizations from 95% ethanol followed by sublimation.

Anal. Calcd. for $C_{12}H_{36}Si_5$: C, 44.91; H, 11.31; Mol. Wt.

321; hydrogen value, 279. Found: C, 45.76; H, 11.22; Mol. Wt. 319; hydrogen value, 277[1].

The infrared spectrum (CS_2) showed prominent absorptions in μ at: 3.40 (m), 3.46 (m), 7.20 (w), 7.70 (m), 8.05 (s), 12.0 (s), 13.5 (w), and 14.6 (w).

The n.m.r. spectrum (in CCl_4) shows a sharp singlet at 9.79 τ. Symmetrically disposed about this peak are ^{13}C-H satellite side bands J(^{13}C-H) = 119 cps, and two peaks attributable to $HC^{29}Si$ spin-spin coupling, J($HC^{29}Si$) = 6.24 cps.

There was no absorption in the ultraviolet spectrum above 210 mμ in cyclohexane as solvent.

<u>Run 2</u> To 28.6 g. (0.26 mole) of chlorotrimethylsilane and 6.72 g. (0.92 g.-atom) of lithium suspended in 200 ml. of THF was added 1.0 ml. of silicon tetrachloride. The reaction mixture immediately warmed up and 6.9 ml. of silicon tetrachloride dissolved in 150 ml. of THF was added dropwise while heating at reflux temperature. Upon complete addition, the reaction mixture was refluxed for 5 hours. At this time, the reaction mixture was filtered prior to acidification by pouring onto a mixture of ice and 10% hydrochloric acid. The hydrolyzed mixture was extracted with three 100 ml. portions of ether, and the combined organics were dried over sodium sulfate. Subsequent to the removal of solvents under reduced pressure, the semi-solid was chromatographed on

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[1] The author is grateful to Dr. J. M. Holmes for the hydrogen value determination.

alumina. Elution with petroleum ether (b.p. 60-70°) gave ca. 13.0 g. of a white solid, from which 12.1 g. (58%) of tetrakis(trimethylsilyl)silane was obtained subsequent to crystallization from 95% ethanol followed by sublimation.

Run 3 To 94.2 g. (0.86 mole) of chlorotrimethylsilane and 150 ml. of THF in which 15.1 g. (2.16 g.-atoms) of lithium was suspended, was added 20 ml. of a solution of 36 g. (0.214 mole) of silicon tetrachloride in 200 ml. of THF. After stirring at room temperature for 1 hour, there was no evidence of a reaction and the reaction mixture was refluxed for 4 hours. Heat was removed and dropwise addition was continued over a period of 30 minutes. After stirring overnight at room temperature, the reaction mixture was filtered prior to acidification by pouring onto a mixture of ice and 10% hydrochloric acid. Extraction of the hydrolyzed mixture with three 100 ml. portions of ether was followed by drying of the organic material over sodium sulfate. The solvents were removed under reduced pressure and the semi-solid residue was crystallized from 95% ethanol followed by sublimation to give 37 g. (54%) of tetrakis(trimethylsilyl)silane.

Run 4 To 188.4 g. (1.73 moles) of chlorotrimethylsilane dissolved in 200 ml. of THF, and 30.3 g. (4.32 g.-atoms) of lithium was added 20 ml. of a solution of 60 g. (0.36 mole) of silicon tetrachloride in 200 ml. of THF. After stirring at room temperature for 2 hours, the reaction mixture turned brown and warmed up. Dropwise addition of the silicon tetrachloride solution was continued over a period of *ca.* 3 hours after which the reaction mixture was stirred at room temperature for 14 days. Work-up in the manner described in Run 3 gave 91 g. (65.5%) of tetrakis(trimethylsilyl)silane.

Run 5 To 94.2 g. (0.86 mole) of chlorotrimethylsilane dissolved in 200 ml. of THF, and 15.1 g. (2.15 g.-atoms) of lithium was added 20 ml. of a solution of 30 g. (0.18 mole) of silicon tetrachloride dissolved in 150 ml. of THF. After stirring for 4 hours at room temperature, the reaction mixture warmed up and turned brown. Dropwise addition of the silicon tetrachloride solution was continued and upon complete addition (*ca.* 4 hours), the reaction mixture was stirred overnight at room temperature. Work-up in the same manner described in Run 3 gave 40.5 g. (70%) of tetrakis(trimethylsilyl)silane.

Run 6 To 95 g. (0.88 mole) of chlorotrimethylsilane dissolved in 150 ml. of THF, and 13 g. (1.9 g.-atoms) of lithium was added 20 ml. of a solution of 36 g. (0.21 mole) of silicon tetrachloride in 200 ml. of THF. In less than 5 minutes, the reaction mixture warmed up and turned brown. Dropwise addition of the silicon tetrachloride solution was continued over a period of 2 hours after which the reaction mixture was stirred overnight at room temperature. Work-up in the manner described in Run 3 gave 45 g. (67%) of tetrakis(trimethylsilyl)silane.

Run 7 To 238 g. (2.2 moles) of chlorotrimethylsilane dissolved in 300 ml. of THF, and 30.8 g. (4.4 g.-atoms) of lithium was added 50 ml. of a solution of 85 g. (0.5 mole) of silicon tetrachloride in 200 ml. of THF. After stirring at room temperature for ca. 5 minutes, the reaction mixture warmed up and turned brown. Dropwise addition of the silicon tetrachloride solution was continued over a period of 2 hours after which the reaction mixture was stirred for 36 hours at room temperature. Work-up in the manner described in Run 3 gave 98 g. (61%) of tetrakis(trimethylsilyl)silane.

Seven repeat runs of this reaction gave yields of 57-65%.

Run 8 To 284 g. (2.6 moles) of chlorotrimethylsilane and 37 g. (5.3 g.-atoms) of lithium suspended in 330 ml. of THF was added 25 ml. of a solution of 102 g. (0.6 mole) of silicon tetrachloride and 100 ml of THF. The reaction mixture warmed up and turned brown after ca. 10 minutes of stirring at room temperature. Dropwise addition of the silicon tetrachloride solution was continued and upon complete addition (ca. 2 hours), the reaction was stirred at room temperature for 48 hours. Work-up of the reaction mixture as described in Run 3 gave 124 g. (65%) of tetrakis(trimethylsilyl)silane.

Five repeat runs gave yields of 60-63%.

Run 9 To 218 g. (2.0 moles) of chlorotrimethylsilane dissolved in 200 ml. of THF, and 28 g. (4.0 g.-atoms) of lithium was added 85 g. (0.5 mole) of silicon tetrachloride dissolved in 200 ml. of THF. The reaction mixture turned brown and warmed-up after 20 minutes of stirring at room temperature, after which the reaction mixture was stirred overnight at room temperature. A white colloidal precipitate was observed subsequent to filtration and acid hydrolysis of the reaction mixture. A small quantity of Celite was added and the mixture was filtered under reduced pressure. Work-up of the filtrate in the manner described in Run 3 gave 83.4 g. (52%) of tetrakis(trimethylsilyl)silane.

A repeat run gave 48% of tetrakis(trimethylsilyl)silane.

From silicon tetrachloride, chlorotrimethylsilane and magnesium in THF (attempted) A mixture of 13.6 g. (0.56 g.-atom) of magnesium and 25 ml. of a solution of 11.7 g. (0.069 mole) of silicon tetrachloride in 100 ml. of THF was stirred at room temperature for 3 hours and refluxed for 1 hour. Color Test I was negative and addition of the remainder of the silicon tetrachloride solution was followed by the addition of a solution of 25.9 g. (0.24 mole) of chlorotrimethylsilane in 100 ml. of THF. Color Test I was negative and the unreacted magnesium metal was separated from the reaction mixture. Upon acid hydrolysis of the decanted solution, a white gummy mass precipitated. An infrared spectrum of this

Table 4. Preparations of tetrakis(trimethylsilyl)silane (XLIX)[*]

Run	Lithium (Li)	Silicon tetrachloride $SiCl_4$	Chlorotrimethylsilane $(CH_3)_3SiCl$	Pot contents a reacti
1[a, b]	3.36 g. (0.48 g.-atom)	11.7 g. (0.069 mole)	25.9 g. (0.24 mole)	3.36 g. of Li, solution of 11 in 50 ml. of T
2[a]	6.72 g. (0.96 g.-atom)	"	28.6 g. (0.26 mole)	28.6 g. of (CH g. of Li, 1.0 and 200 ml. of
3[a]	15.1 g. (2.16 g.-atom)	36 g. (0.214 mole)	94.2 g. (0.86 mole)	94.2 g. of (CH ml. of THF, 15 20 ml. of a so of $SiCl_4$ in 20
4	30.3 g. (4.32 g.-atom)	60 g. (0.36 mole)	188.4 g. (1.73 mole)	188.4 g. of (C g. of Li, 200 20 ml. of a so of $SiCl_4$ in 20
5[a]	35.1 g. (2.15 g.atom)	30 g. (0.18 mole)	94.2 g. (0.86 mole)	94.2 g. of (CH g. of Li, 200 20 ml. of a so $SiCl_4$ in 150 m
6	13 g. (1.9 g.-atom)	13 g. (0.21 mole)	95 g. (0.88 mole)	95 g. of (CH_3) Li, 150 ml. of of a solution $SiCl_4$ in 200 m
7[c]	30.8 g. (4.4 g.-atom)	85 g. (0.5 mole)	238 g. (2.2 mole)	238 g. of $(CH_3$ of Li, 300 ml. 50 ml. of a so of $SiCl_4$ in 20

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[*] The THF was freed from moisture and peroxides before use by storag specified.

[a] THF was freed from peroxides and moisture before use by refluxing hydride immediately before use.

[b] The reaction mixture was refluxed.

[c] Seven repeat runs of this reaction gave yields of 57-65%.

ne (XLIX)*

Pot contents at start of reaction	Addition time(min)	Reaction time(hr)	Yield %
3.36 g. of Li, 10 ml. of a solution of 11.7 g. of $SiCl_4$ in 50 ml. of THF	30	overnight[b]	31.6
28.6 g. of $(CH_3)_3SiCl$, 6.72 g. of Li, 1.0 ml. of $SiCl_4$ and 200 ml. of THF	300[b]	5[b]	58.0
94.2 g. of $(CH_3)_3SiCl$ in 200 ml. of THF, 15.1 g. of Li and 20 ml. of a solution of 36 g. of $SiCl_4$ in 200 ml. THF	30	overnight	54.0
188.4 g. of $(CH_3)_3SiCl$, 30.3 g. of Li, 200 ml. of THF, and 20 ml. of a solution of 60 g. of $SiCl_4$ in 200 ml. of THF	180	336	66.5
94.2 g. of $(CH_3)_3SiCl$, 15.13 g. of Li, 200 ml. of THF, and 20 ml. of a solution of 30 g. $SiCl_4$ in 150 ml. of THF	240	overnight	70.0
95 g. of $(CH_3)_3SiCl$, 13 g. of Li, 150 ml. of THF, and 20 ml. of a solution of 36 g. of $SiCl_4$ in 200 ml. of THF	120	overnight	67.0
238 g. of $(CH_3)_3SiCl$, 30.8 g. of Li, 300 ml. of THF, and 50 ml. of a solution of 85 g. of $SiCl_4$ in 200 ml. of THF	120	36	61.0

fore use by storage over sodium wire for 24 hours, unless otherwise

use by refluxing over sodium, followed by distillation from lithium

f 57-65%.

Table 6. Home origins of staff

Zone no.	District no.	Use car pool to job	Duties require use of car on campus	No. of employees
	11	3	13	38
	12	6	13	43
	13	2	11	34
	14	2	6	23
1		13	43	138
	21	2	12	26
	22	3	17	45
	23	9	16	66
	24	2	12	44
	25	6	12	32
2		22	69	213
	31	3	16	34
	32	7	32	88
	33	8	32	81
	34	9	18	62
	35	9	23	63
3		36	121	328
	40	0	8	33
	41	0	12	65
	42	1	39	149
	43	2	18	80
4		3	77	327
	51	1	28	100
	52	6	43	126
	53	6	44	120
	54	3	57	100
	55	1	17	43
5		17	189	489
	61	6	13	69
	62	4	10	26
	63	7	19	52
6		17	42	147
	71	3	48	201
	72	3	24	67
	73	4	27	73
7		10	99	341
	81	0	4	11
	82	5	8	28
	83	0	1	6
8		5	13	45

material showed absorptions for Si-OH and Si-O-Si. No tetrakis(trimethylsilyl)silane was isolated.

From silicon tetrachloride, chlorotrimethylsilane and lithium in 1, 2, 3, 4-tetramethyltetrahydrofuran (attempted)[1]

In this experiment 1, 2, 3, 4-tetramethyltetrahydrofuran was used in place of tetrahydrofuran. An infrared spectrum of the white gummy material obtained after work-up showed absorptions for Si-OH and Si-O-Si. No tetrakis(trimethylsilyl)silane was isolated.

Tetrakis(dimethylphenylsilyl)silane

From chlorodimethylphenylsilane, silicon tetrachloride and lithium in THF To 81.6 g. (0.48 mole) of chlorodimethylphenylsilane, 6.72 g. (0.96 g.-atom) of lithium and 200 ml. of THF was added dropwise 20 g. (0.12 mole) of silicon tetrachloride dissolved in 50 ml. of THF over a period of 3 hours. Upon complete addition, the reaction mixture was stirred for 20 hours at room temperature prior to filtration through glass wool. The organic layer was separated and dried over sodium sulfate subsequent to acid hydrolysis. Removal of the organic solvents under reduced pressure gave an oil which was chromatographed on neutral alumina. Elution with petroleum ether (b.p. 60-70°) gave a liquid which had the same retention time (v.p.c.) as a known sample of 1, 1, 2, 2-

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[1] The author is grateful to Dr. J. B. Dickey for this material.

tetramethyl-1, 2-diphenyldisilane. Purification of this liquid by distillation afforded 25.9 g. (63.6%) of pure 1, 1, 2, 2-tetramethyl-1, 2-diphenyldisilane, b.p. 125-128°/1.8 mm, m.p. 34-35° (mixed m.p.) (Lit. (67) b.p.128-130°/1.8 mm, m.p. 34-35°). Further elution with benzene gave 2.4 g. (3.5%) of tetrakis(dimethylphenylsilyl)silane, m.p. 133-135°, subsequent to purification by crystallization from benzene.

Anal. Calcd. for $C_{32}H_{44}Si_5$: Si, 24.6; Mol. Wt. 507. Found: 24.5; Mol. Wt. 506 (vapor pressure osmometer).

The infrared spectrum (CCl_4) showed prominent absorptions in μ at: 3.26 (m), 3.38 (m), 3.45 (m), 7.0 (s), 7.12 (w), 8.06 (s) and 9.06 (s).

The n.m.r. spectrum (CS_2) shows a sharp singlet at 9.72 τ for the silicon-methyl protons and a multiplet for the silicon-phenyl protons centered at 2.91 τ (aliphatic/aromatic proton ratio = 1.2; calcd. 1.2), and its ultraviolet spectrum consisted of a band at $\lambda_{max}^{cyclohexane}$ 242 mμ (ε 38,600).

From dimethylphenylsilyllithium and silicon tetrachloride To 280 ml. of a THF:ether (1:2) solution of 0.12 mole of freshly prepared dimethylphenylsilyllithium prepared by the cleavage of 1, 1, 2, 2-tetramethyl-1, 2-diphenyldisilane with lithium in THF (96) , cooled to -40° was added dropwise 5.1 g. (0.03 mole) of silicon tetrachloride dissolved in 20 ml. of ether. Color Test I was negative upon complete addition and the reaction mixture was stirred at room temperature for ca. 1 hour. Hydrolysis of the reaction mixture with 200 ml. of a saturated ammonium chloride solution followed by the usual work-up afforded on oil which was chromatographed on neutral alumina. Elution with petroleum ether (b.p. 60-70°) gave 3 g. (60%) of 1, 1, 2, 2-tetramethyl-1, 2-diphenyldisilane, b.p. 126-127°/1.8 mm, m.p. 34-35° (mixed m.p.) after purification by distillation. Further elution with benzene gave, after crystallization from acetone, 2.5 g. (14.6%) of tetrakis(dimethylphenylsilyl)silane, m.p. 133-134° (mixed m.p.).

Tetrakis(triphenylsilyl)silane

From chlorotriphenylsilane, silicon tetrachloride and lithium (attempted) A solution of 70.8 g. (0.24 mole) of chlorotriphenylsilane, 10.0 g. (0.06 mole) of silicon tetrachloride and 250 ml. of THF was added dropwise to 3.36 g. (0.48 g.-atom) of lithium and 20 ml. of THF. The reaction mixture immediately became exothermic and, after complete addition, the reaction was stirred overnight at room temperature. Subsequent to filtration through glass wool, the reaction mixture was hydrolyzed with 200 ml. of 1N hydrochloric acid. Hexaphenyldisilane, 41 g. (66.5%), m.p. 355-358° (mixed m.p.), was removed by filtration. The organic layer of the filtrate was separated and dried over sodium sulfate. Removal of the solvents gave an oil which was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave a solid compound after crystallization from ethyl acetate did not melt when heated above 500°.

A Direct Preparation of Some Trisilyl-substituted Organopolysilane Compounds

Tris(trimethylsilyl)methylsilane

From methyltrichlorosilane, chlorotrimethylsilane and lithium in THF (Run 1) To 105.2 g. (0.96 mole) of chlorotrimethylsilane dissolved in 125 ml. of THF and 16.9 g. (2.4 g.-atoms) of lithium was added 25 ml. of a solution of 40 g. (0.27 mole) of methyltrichlorosilane in 100 ml. of THF. After vigorous stirring for 2 hours, the reaction mixture became exothermic. At this stage, the remainder of the methyltrichlorosilane solution was added dropwise. Upon complete addition (ca. 2 hours), the reaction mixture was stirred overnight at room temperature. The reaction mixture was decanted from the excess lithium upon crushed ice acidified with 10% hydrochloric acid. Work-up of the organic layer in the usual manner gave an oil which was chromatographed on alumina. Elution of the column with petroleum ether (b.p. 60-70°) gave 24.5 g. of a liquid which was distilled to give 22.9 g. (32%) of tris(trimethylsilyl)methylsilane, b.p. 94-97°/7 mm, m.p. 57-59° (mixed m.p.) [see Reaction of Tris(trimethylsilyl)silyllithium with Trimethyl Phosphate].

Run 2 To a very vigorously stirred mixture of 326 g. (3 moles) of chlorotrimethylsilane dissolved in 300 ml. of

THF and 47.2 g. (6.6 g.-atoms) of lithium was added 25 ml. of a solution of 149.5 g. (1 mole) of methyltrichlorosilane in 200 ml. of THF. After *ca.* 1.5 hours of stirring at room temperature, the reaction mixture turned brown and became exothermic. At this stage, the remainder of the methyltrichlorosilane solution was added dropwise over a period of 4 hours and, upon complete addition, the reaction mixture was stirred for 48 hours at room temperature. Work-up in the usual manner gave 105 g. (40%) of tris(trimethylsilyl)methylsilane, b.p. 97-100°/8 mm, m.p. 57-59° (mixed m.p.). The residue from distillation was chromatographed on alumina. Elution of the column with petroleum ether (b.p. 60-70°) afforded a solid product which was purified by crystallization from acetone to give 40.1 g. (21.6%) of *sym*-tetrakis(trimethylsilyl)-dimethyldisilane, m.p. 147-149° (mixed m.p.).

Tris[trimethylsilyl][3, 4, 5, 6-tetrakis(trimethylsilyl)-cyclohexen-1-yl] silane

From phenyltrichlorosilane, chlorotrimethylsilane and lithium To 17 g. (0.16 mole) of chlorotrimethylsilane in 50 ml. of THF and 4.0 g. (0.57 g.-atom) of lithium was added 20 ml. of a solution of 10 g. (0.05 mole) of phenyltrichlorosilane in 100 ml. of THF. A reaction was initiated by refluxing for 15 minutes subsequent to the addition of 1 ml. of triphenylsilyllithium. At this stage, external heat was removed and the remainder of the phenyltrichlorosilane:THF solution was added dropwise with external cooling. Upon complete addition, the reaction mixture was stirred overnight at room temperature. After this time, the red reaction mixture was derivatized by addition to 40 ml. of chlorotrimethylsilane in 50 ml. of THF. Color Test I was negative and the reaction mixture was filtered prior to hydrolysis with 1*N* hydrochloric acid. The organic layer was separated and dried over sodium sulfate. Subsequent to the removal of solvents under reduced pressure, a semi-solid was obtained which was crystallized from ethyl acetate:ethanol to give 15 g. of a solid, m.p. 207-211°. Recrystallization from ethyl acetate gave 14 g. of compound, m.p. 215-218°. Although this compound was not rigorously identified, the spectral properties indicate that it might be tris[trimethylsilyl][3, 4, 5, 6-tetrakis(trimethylsilyl)cyclohexen-1-yl]silane. For the spectral properties, see the Discussion part of this thesis.

Another run of this reaction, employing the same molar quantities of reactants, afforded 12 g. of product, m.p. 215-218° (mixed m.p.).

Tris(dimethylphenylsilyl)methylsilane

From dimethylphenylsilyllithium and methyltrichlorosilane in THF To 360 ml. of a THF:ether (1:2) solution of 0.18 mole of dimethylphenylsilyllithium (prepared in THF), cooled to -40° was added rapidly 9.0 g. (0.06 mole) of methyltrichlorosilane in 30 ml. of ether. Upon complete addition, Color Test I was negative and the reaction mixture was stirred to room temperature. Subsequent to hydrolysis by addition to a mixture of ice and 1N hydrochloric acid, the organic layer was separated and dried over sodium sulfate. The solvents were removed under reduced pressure and the residue was distilled, affording 3.8 g. (15.6%) of 1, 1, 2, 2-tetramethyl-1, 2-diphenyldisilane, b.p. 126-128°/1.8 mm, m.p. 34-35° (mixed m.p.)- Lit. (67) b.p. 128-130/1.8 mm, m.p. 34-35° . The residue from the distillation was chromatographed on a column of alumina. Elution with petroleum ether (b.p. 60-70°) afforded 8.1 g. (30.2%) of tris(dimethylphenylsilyl)methylsilane, m.p. 53-54°, subsequent to purification by crystallization from ethanol.

Anal. Calcd. for $C_{25}H_{36}Si_4$: Si, 24.6; Mol. Wt., 449. Found: Si, 23.9, 24.5; Mol. Wt., 452.

The infrared spectrum (CS_2) showed prominent absorptions in μ at: 3.27 (w), 3.38 (m), 3.45 (w), 7.17 (w), 8.05 (s), 9.05 (s), 12.00 (s), 12.34 (s), 12.82 (s), 13.15 (m), 13.68 (s) and 14.35 (s).

The ultraviolet spectrum consisted of a band at $\lambda_{max}^{cyclohexane}$ 242.5 mμ (ε 39,200).

Tris(trimethylsilyl)silane

From trichlorosilane, chlorotrimethylsilane and lithium in THF (attempted) A solution of 20 g. (0.15 mole) of trichlorosilane, 53 g. (0.49 mole) of chlorotrimethylsilane and 200 ml. of THF was added to 6.2 g. (0.87 g.-atom) of lithium.

The reaction mixture became exothermic after ca. 10 minutes of stirring at room temperature. Upon complete addition (ca. 2 hours), the reaction mixture was stirred overnight and decanted away from the excess lithium on to a mixture of crushed ice acidified with 10% hydrochloric acid. The organic layer was separated and dried over sodium sulfate. Subsequent to the removal of the solvents under reduced pressure, an oil was obtained which was chromatographed on alumina. Elution of the column with petroleum ether (b.p. 60-70°) gave, after two recrystallizations from acetone, 9.3 g. (59.6%) of tetrakis(trimethylsilyl)silane.

Tris(trimethylsilyl)chlorosilane (attempted)

From silicon tetrachloride, chlorotrimethylsilane and lithium A solution of 30 g. (0.18 mole) of silicon tetrachloride and 70 g. (0.64 mole) of chlorotrimethylsilane in 150 ml. of THF was added to 8.6 g. (1.1 g.-atoms) of lithium suspended in 200 ml. of THF. After ca. 15 minutes of stirring at room temperature, the reaction mixture became exothermic. The mixture was stirred overnight at room temperature, subsequent to filtration under a nitrogen atmosphere. The brown solution was derivatized by the addition of phenylmagnesium bromide (100% excess), followed by stirring at reflux temperature overnight. Color Test I was positive and the reaction mixture was worked-up in the usual manner to give 28 g. (54.5%) of tetrakis(trimethylsilyl)silane.

Another run of this reaction yielded 23 g. (46.7%) of tetrakis(trimethylsilyl)silane.

The yields are based on the amount of starting chlorotrimethylsilane.

Reactions of Tetrakis(trimethylsilyl)silane

Tetrakis(trimethylsilyl)silane with sulfuric acid

A mixture of 20 g. (0.06 mole) of tetrakis(trimethylsilyl)silane and 97 g. of concentrated sulfuric acid was stirred at room temperature for 4 hours. There was no evidence of the evolution of a gas and the reaction mixture was heated at 80° for 20 minutes. After this time, there was no evidence of the evolution of a gas. When heated at 130°, a very slow evolution of a gas was observed. External heat was removed and the evolution of a gas, presumably methane, increased rapidly to an "explosive rate".

Tetrakis(trimethylsilyl)silane with aqueous piperidine

A solution of 20 g. (0.06 mole) of tetrakis(trimethylsilyl)silane and 4.5 ml of water in 104 ml. of piperidine was refluxed for 4 days prior to acidification and work-up in the usual manner. Distillation of the residue afforded 11 g. of a liquid which consisted of two compounds (by v.p.c.), b.p. 109-110°/22 mm, n_D^{20} 1.4190. An infrared spectrum showed a strong absorption at 9.55 u and a weak band at 2.9 u, indicative of Si-O and Si-OH, respectively. No starting material, tetrakis(trimethylsilyl)silane, was recovered.

Tetrakis(trimethylsilyl)silane with sodium methoxide in methanol

Sodium metal (0.4 g.) was dissolved in 150 ml. of methanol. To this solution was added 15 g. (0.05 mole) of tetrakis(trimethylsilyl)silane and the reaction mixture was stirred for two days at room temperature prior to acidification and work-up in the usual manner. V.p.c. of the liquid indicated no starting material and the presence of three compounds; and an infrared spectrum showed a strong absorption band at 9.4 μ, indicative of Si-O.

Tetrakis(trimethylsilyl)silane with bromine

To 20 g. (0.06 mole) of tetrakis(trimethylsilyl)silane in 150 ml. of benzene was added dropwise at 4° a solution of 11.2 g. (0.06 mole) of bromine in 80 ml. of benzene. The bromine color was discharged instantaneously and, upon complete addition (ca. 20 min), the reaction mixture was stirred for 1 hour at room temperature. The solvent and volatile products were removed by distillation, affording a brown semi-solid. An excess (100%) of phenylmagnesium bromide was added and the reaction mixture was heated at reflux temperature overnight. After this time Color Test I was positive. A semi-solid was obtained on work-up, and from this was recovered 12.1 g. (60.5%) of tetrakis(trimethylsilyl)silane.

Another run using 8 g. (0.03 mole) of tetrakis(trimethylsilyl)silane, 4 g. (0.03 mole) of bromine and 120 ml. of carbon tetrachloride gave a 6 g. (63%) recovery of tetrakis(trimethylsilyl)silane.

<u>Tetrakis(trimethylsilyl)silane with phosphorus pentachloride</u>

A solution of 20 g. (0.06 mole) of tetrakis(trimethylsilyl)silane and 12.4 g. (0.06 mole) of phosphorus pentachloride in 200 ml. of benzene was refluxed overnight. Subsequent to the addition of an excess (<u>ca</u>. 100%) of phenylmagnesium bromide, the reaction mixture was refluxed overnight. Acid hydrolysis of the reaction mixture gave a 6.1 g. (63%) recovery of tetrakis(trimethylsilyl)silane.

Another run employing 10 g. (0.03 mole) of tetrakis(trimethylsilyl)silane and 6.2 g. (0.03 mole) of phosphorus pentachloride in 200 ml. of carbon tetrachloride afforded 5.8 g. (60%) of unreacted tetrakis(trimethylsilyl)silane. Using 150 ml. of <u>sym</u>.-tetrachloroethane instead of 200 ml. of carbon tetrachloride, 6.1 g. (63%) of tetrakis(trimethylsilyl)silane was recovered.

<u>Tetrakis(trimethylsilyl)silane with methyllithium</u>

<u>In THF:ether (4:1) (Run 1)</u> After stirring a THF:ether (4:1) solution of 0.07 mole of methyllithium and 20 g. (0.06 mole) of tetrakis(trimethylsilyl)silane for 10 minutes at room temperature, a greenish-yellow solution was observed. The solution was refluxed for 5 hours followed by stirring overnight at room temperature. Color Test I was negative and the pale greenish-yellow solution was hydrolyzed by ad-

dition to 120 ml. of 1N hydrochloric acid. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layers were dried over sodium sulfate. Subsequent to the removal of the solvents under reduced pressure, an oil was obtained which was distilled to give 13.4 g. (87%) of tris(trimethylsilyl)silane, b.p. 80-83°/8 mm, n_D^{20} 1.4891, d_4^{20} 0.8092.

Anal Calcd. for $C_9H_{28}Si_4$: Si, 45.13; Mol. Wt., 248; MR_D, 88.95. Found: Si, 44.6; Mol. Wt., 257; MR_D, 88.70.

The infrared spectrum (carbon disulfide) showed absorption bands in μ at: 3.38 (m), 3.45 (w), 4.86 (m), 6.90 (w), 7.15 (w), 8.04 (s), 12.0 (s), 13.35 (m) and 14.55 (m).

The n.m.r. spectrum (carbon disulfide) contained a singlet at 9.77 τ ($Si-CH_3$) and 7.73 τ (Si-H). The ratio of $Si-CH_3$:Si-H protons was found to be 27:1 (calcd 27:1).

The ultraviolet spectrum, determined in cyclohexane, showed no absorptions above 210 mμ.

Run 2 An ethereal solution of methyllithium (0.13 mole; 85 ml. of 1.5 N) was added to 20 g. (0.06 mole) of tetrakis(trimethylsilyl)silane in 400 ml. of THF. After stirring overnight at room temperature, the greenish-yellow solution was hydrolyzed with 1N hydrochloric acid. Work-up in the usual manner and distillation of the residual oil afforded 12.2 g. (78.4%) of tris(trimethylsilyl)silane, b.p. 81-85°/8 mm, $n_D^{20.3}$ 1.4895.

Tetramethylsilane was collected in a Dry Ice-acetone trap and was identified by v.p.c. (the column was at room temperature and the injection port temperature was 50°).

In ether (attempted) After stirring an ethereal solution of methyllithium (0.03 mole) and 10 g. (0.03 mole) of tetrakis(trimethylsilyl)silane overnight at room temperature, 9.5 g. (95%) of tetrakis(trimethylsilyl)silane was recovered subsequent to acid hydrolysis and work-up in the usual manner.

In ether at reflux (attempted) After refluxing an ethereal solution of methyllithium (0.02 mole) and 5 g. (0.02 mole) of tetrakis(trimethylsilyl)silane for 24 hours, 4.2 g. (84%) of tetrakis(trimethylsilyl)silane was recovered subsequent to acid hydrolysis and work-up in the usual manner.

With two equivalents of methyllithium in THF:ether (3:1)

A solution of 20 g. (0.06 mole) of tetrakis(trimethylsilyl)silane and 0.13 mole of methyllithium in 285 ml. of THF:ether (3:1) was stirred overnight at room temperature. The yellow solution was hydrolyzed by addition to a mixture of ice and 10% hydrochloric acid. Work-up in the usual manner gave 12.2 g. (78.4%) of tris(trimethylsilyl)silane, b.p. 81-85°/8 mm, $n_D^{20.3}$ 1.4895.

Tetrakis(trimethylsilyl)silane with phenyllithium

In THF:ether (4:1) A solution of 0.09 mole of phenyllithium and 26 g. (0.08 mole) of tetrakis(trimethylsilyl)silane in 500 ml. of THF:ether (4:1) was stirred overnight at temperature. Work-up of the red reaction mixture in the usual manner, subsequent to acid hydrolysis, gave an oil which was distilled to give 10.5 g. (84.5%) of trimethylphenylsilane, b.p. 172-173°, $n_D^{20.3}$ 1.4880 (Lit. (40) b.p. 171.5°, n_D^{20} 1.4904) and 10.7 g. (51.5%) of tris(trimethylsilyl)silane, b.p. 95-100°/17 mm, $n_D^{20.3}$ 1.4935. From the residue of distillation, there was obtained 4 g. (15.1%) of recovered tetrakis(trimethylsilyl)silane, subsequent to crystallization from acetone.

Tetrakis(trimethylsilyl)silane with triphenylsilyllithium

To 10 g. (0.03 mole) of tetrakis(trimethylsilyl)silane in 150 ml. of THF was added triphenylsilyllithium (0.03 mole) and the reaction mixture was stirred for 18 hours at room temperature. After this time v.p.c. of a hydrolyzed aliquot of the purple-colored solution indicated an area ratio for tris(trimethylsilyl)silane:tetrakis(trimethylsilyl)silane of 9:1. There appeared to be no change in this ratio after stirring for an additional 20 hours. The reaction mixture was hydrolyzed by addition to a mixture of ice and 1<u>N</u> hydrochloric acid. Work-up of the organic layer in the usual manner gave an oil from which 8 g. of impure 1, 1, 1-trimethyl-2, 2, 2-triphenyldisilane crystallized. Purification by crystallization from 95% ethanol gave 6.5 g. (70%) of the pure compound, m.p. 107-109° (mixed m.p.).

Distillation of the residue afforded 3.1 g. (45%) of tris(trimethylsilyl)silane, b.p. 90-95°/10 mm, n_D^{20} 1.4901 and a viscuous liquid. V.p.c. of the liquid showed only the presence of tetrakis(trimethylsilyl)silane and tris(trimethylsilyl)silane (area ratio of 10:7). There was no evidence for triphenylsilane, triphenylsilanol or hexaphenyldisiloxane.

The yields were based on the amount of unrecovered tetrakis(trimethylsilyl)silane.

Another experiment was carried out, using a procedure identical to that above, but the reaction mixture was stirred overnight. From the reaction mixture there was obtained 51% of 1, 1, 1-trimethyl-2, 2, 2-triphenyldisilane, m.p. 107-109° (mixed m.p.) and 52% of tris(trimethylsilyl)silane, b.p. 94-96°/10 mm, n_D^{20} 1.4891. Some unreacted tetrakis(trimethylsilyl)silane was detected by v.p.c.

Reactions of Tris(trimethylsilyl)silyllithium

General procedure for the preparation of tris(trimethylsilyllithium

Methyllithium was freshly prepared in ether and the solution was decanted from the excess lithium under nitrogen into an addition funnel. Double titration using allyl bromide gave the concentration of the silyllithium compound and the alkoxide base. Only solutions in which the amount of alkoxide base was relatively low (ca. 2 equivalents or less per 15 equivalents of total base) were considered satisfactory for synthetic purposes.

Tris(trimethylsilyl)silyllithium was prepared by stirring a THF:ether (4:1) solution of tetrakis(trimethylsilyl)silane and a 10% molar excess of methyllithium at room temperature until v.p.c. of a hydrolyzed aliquot indicated a ratio of tris(trimethylsilyl)silane:tetrakis(trimethylsilyl)silane of at least 100:1. In general, this condition was satisfied within 24 hours; but if not, a 10% molar excess of methyllithium was added and the reaction mixture was continuously stirred at room temperature. The pale greenish-yellow colored solution was transferred to an addition funnel under nitrogen and the concentration was determined by double titration using allyl bromide. The silyllithium solution was used within one or two days.

Tris(trimethylsilyl)silyllithium with trimethyl phosphate

To a stirred solution of 16.8 g. (0.12 mole) of trimethyl phosphate in 40 ml. of THF was added dropwise a THF:ether (4:1) solution of tris(trimethylsilyl)silyllithium. Upon complete addition (ca. 1 hour), Color Test I was negative. The white reaction mixture was hydrolyzed by addition to a mixture of ice and 10% hydrochloric acid. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layers were dried over sodium sulfate and the solvents were removed under reduced pressure. Distillation of the residue gave 20.1 g. (76.5%) of tris(trimethylsilyl)methylsilane, b.p. 94-96°/7 mm, m.p. 57-59°.

Anal Calcd. for $C_{10}H_{30}Si_4$: Si, 42.8; Mol. Wt., 263. Found: Si, 42.8; Mol. Wt., 267.

The infrared spectrum (carbon disulfide) showed absorption bands in μ at: 3.38 (m), 3.45 (m), 6.95 (w), 7.17 (w), 7.66 (w), 8.06 (s), 8.43 (w), 12.00 (s), 12.83 (s), 13.46 (w), 14.75 (w) and 14.60 (m).

The n.m.r. spectrum, determined in acetone at 80°, consisted of a singlet at 9.90 t (3 protons) and 9.83 t (27 protons) for the silicon-methyl protons at a sweep width of 50 cps. An integrated area was found to be 6:1 (calcd. 9:1) see Discussion part . Tetramethylsilane was used as the internal standard.

The ultraviolet spectrum consisted of the following bands: $\lambda_{max}^{cyclohexane}$ 207.5 mu (ε 13,100, shoulder), 231.5 mu (ε 2,935, shoulder) and 277.5 mu (ε 1,945).

Tris(trimethylsilyl)silyllithium with chlorodimethylphenylsilane

To a solution of 19.6 g. (0.12 mole) of chlorodimethylphenylsilane in 40 ml. of ether was added dropwise a THF: ether solution of tris(trimethylsilyl)silylithium (0.12 mole; 200 ml. of 0.58 N) at room temperature. Upon complete addition, the white reaction mixture was stirred for an additional hour at room temperature. Work-up in the usual manner gave a semi-solid from which 30.7 g. (70%) of tris(trimethylsilyl)-(dimethylphenylsilyl)silane m.p. 190-190.5° was obtained, subsequent to crystallization and sublimation. The transition and solidification points (see Discussion part) were found to be 185° and 184°, respectively.

Anal. Calcd. for $C_{17}H_{38}Si_5$: Si, 36.7; Mol. Wt., 383. Found: Si, 36.7, 36.7; Mol. Wt., 381.

The infrared spectrum (carbon disulfide) showed absorption bands in μ at: 3.27 (m, shoulder), 3.38 (m), 3.45 (m), 7.2 (m), 7.7 (w), 8.06 (s), 9.06 (s), 11.1 (m, shoulder), 12.2 (s), 13.22 (s), 13.42 (m), 13.70 (s), 14.37 (s) and 14.65 (s).

The n.m.r. spectrum (carbon disulfide) consisted of a singlet at 9.75 τ (27 protons) and 9.41 τ (6 protons) for the silicon-methyl protons, and a multiplet centered at 2.91 τ (5 protons) for the silicon-phenyl protons. The area ratio was found to be 5:6:27.05 (calcd. 5:6:27).

The ultraviolet spectrum consisted of a band at $\lambda_{max}^{cyclohexane}$ 239 mμ (ε 16,130).

Tris(trimethylsilyl)silyllithium with chlorodiphenylmethylsilane

To 23.3 g. (0.1 mole) of chlorodiphenylmethylsilane in 50 ml. of ether was added dropwise a THF:ether solution of tris(trimethylsilyl)silyllithium (0.1 mole) at room temperature. Upon complete addition (ca. 2 hours), the mixture was stirred for an additional hour. Work-up of the reaction in the usual manner gave an oil which was chromatographed on alumina. Elution of the column with petroleum ether (b.p. 60-70°) gave, after two recrystallizations from acetone, 26 g. (64.4%) of tris(trimethylsilyl)(diphenylmethylsilyl)-silane, m.p. 187-187.5°. The transition and solidification points (see Discussion part) were found to be 185°.

<u>Anal</u> Calcd for $C_{22}H_{40}Si_5$: Si, 31.7; Mol. Wt., 444. Found: Si, 31.5, 31.7; Mol. Wt. 444.

The infrared spectrum (carbon disulfide) showed absorption bands in μ at: 3.26 (m, shoulder), 3.38 (m), 3.45 (m), 7.2 (w), 7.7 (w), 8.06 (s), 8.43 (w), 9.08 (s), 9.74 (w), 10.1 (w), 11.15 (m, shoulder), 12.15 (s), 12.88 (s), 13.68 (s), 14.15 (s), 14.35 (s), 14.63 (s) and 15.06 (w).

The n.m.r. spectrum (carbon disulfide) consisted of a singlet at 9.83 τ (27 protons) and 9.20 τ (3 protons) for the silicon-methyl protons, and a multiplet centered at 2.55 τ (10 protons) for the aromatic protons. The aliphatic:aromatic ratio was found to be 30:10.1 (calcd. 30:10).

The ultraviolet spectrum consisted of a band with a $\lambda_{max}^{cyclohexane}$ 238 mμ (ε 18,815).

<u>Tris(trimethylsilyl)silyllithium with chlorotriphenylsilane</u>

To 30 g. (0.1 mole) of chlorotriphenylsilane in 50 ml. of ether was added dropwise a THF:ether solution of tris(trimethylsilyl)silyllithium (0.1 mole) at room temperature. Upon complete addition, the white colored reaction mixture was stirred for an additional hour at room temperature. Acid hydrolysis of the reaction mixture followed by the usual work-up gave 39 g. (78%) of crude tris(trimethylsilyl)(triphenylsilyl)silane, m.p. 248-252°. Recrystallization from ethyl acetate gave 35.1 g. (70%) of pure compound, m.p. 287-189°. The transition and solidification points (see Discussion part) were found to be 280 and 287°, respectively.

Anal Calcd. for $C_{27}H_{42}Si_5$: Si, 27.7; Mol. Wt., 507. Found: Si, 27.4, 27.6; Mol. Wt., 506.

The infrared spectrum (carbon disulfide) showed absorption bands in u at: 3.27 (m, shoulder), 3.39 (m), 3.45 (w), 7.2 (w), 7.7 (w), 8.07 (s), 8.46 (w), 9.11 (s), 9.73 (w), 10.2 (w), 11.66 (m, shoulder), 12.1 (s), 13.62 (s), 14.35 (s), and 14.65 (s).

The n.m.r. spectrum (carbon disulfide) consisted of a singlet at 9.78 t for the silicon-methyl protons and a multiplet for the aromatic protons centered at 2.48 t. The aliphatic:aromatic proton ratio was found to be 27:15 (calcd. 27:15).

The ultraviolet spectrum consisted of a shoulder at $\lambda_{max}^{cyclohexane}$ 235 mu (23,200).

Tris(trimethylsilyl)silyllithium with chlorodimethylsilane

To 5.3 g. (0.06 mole) of chlorodimethylsilylsilane dissolved in 250 ml. of ether, cooled to 0°, was added a THF: ether solution of tris(trimethylsilyl)silyllithium (0.06 mole). Upon complete addition, the reaction mixture was stirred for an additional hour at room temperature. Acid hydrolysis of the reaction mixture followed by the usual work-up gave 6.3 g.

(36.8%) of tris(trimethylsilyl)(dimethylsilyl)silane, subsequent to crystallization from absolute ethanol followed by sublimation. This compound sublimes completely at 200°.

Anal Calcd. for $C_{11}H_{34}Si_5$: Mol. Wt., 307; Found: Mol. Wt., 334.

The infrared spectrum (carbon disulfide) absorption bands in µ at: 3.39 (m), 3.45 (w), 7.20 (w), 8.05 (s), 11.35 (w), 12.00 (s), 13.40 (w), and 14.08 (w). The weak absorption band at 9.3 µ (Si-O) indicates that the sample contains a small amount of some siloxane.

Tris(trimethylsilyl)silyllithium with carbon dioxide

Tris(trimethylsilyl)silyllithium (0.1 mole) was added slowly to a Dry Ice-ether slurry. The mixture was allowed to warm to 0° subsequent to hydrolysis by addition to a saturated aqueous solution of ammonium chloride. The organic layer was separated and dried over sodium sulfate. Subsequent to the removal of solvents under reduced pressure, a semi-solid compound was obtained. From this material, 20.5 g. (72%) of tris(trimethylsilyl)silanecarboxylic acid was obtained, subsequent to crystallization from cold petroleum ether (b.p. 60-70°). The acid turned to a cloudy liquid at 131° and this liquid became clear at 136°. Decomposition with the evolution of carbon monoxide, as determined by the procedure of Nowicki (98) was observed at 214°.

An infrared spectrum (CS_2) showed absorption bands in µ at: 3.37 (m), 3.45 (w), 5.95 (m), 6.13 (s), 8.05 (s), 8.45 (w), 8.50 (w), 9.45 (w), 12.00 (s), 13.35 (w) and 14.50 (m). There was also present a broad absorption band (3.07-3.65 µ), assigned to the -OH group of -COOH.

The n.m.r. spectrum consisted of a singlet at 9.72 t for the silicon-methyl protons and at -0.02 t for the carboxylic acid proton. An integration of the areas was found to be 35 (calcd. 27).

Another run employing 0.01 mole of tris(trimethylsilyl)-silyllithium afforded 26 g. (89%) of the acid subsequent to crystallization from cold acetone. A mixture melting point was not depressed.

Tris(trimethylsilyl)silyllithium with fluorene

To 13.5 g. (0.08 mole) of fluorene in 50 ml. of THF was added at one time 525 ml. of 0.15 M solution of tris(trimethylsilyl)silyllithium (0.08 mole). The reaction mixture immediately turned orange and was stirred overnight at room temperature. Color Test I was positive and the reaction mixture was carbonated by pouring onto a Dry Ice-ether slurry. After allowing the mixture to warm to 0°, dilute hydrochloric acid was added. The organic layer was separated and the aqueous layer extracted several times with ether. The combined ethereal layers were extracted with 400 ml. of 5% sodium hydroxide in several portions. The basic extract was boiled to remove traces of THF, then acidified with 10%

hydrochloric acid. Filtration afforded a solid product which was recrystallized from glacial acetic acid to give 12.3 g. of crude fluorene-9-carboxylic acid, m.p. 223-226°. A second recrystallization from the same solvent gave 11.9 g. (70%) of pure acid, m.p. 228-230° (mixed m.p.). In addition, about 2 g. of an insoluble solid was obtained.

The organic layer was dried over sodium sulfate subsequent to the removal of solvents under reduced pressure. The residual oil was chromatographed on a column of alumina. Elution with petroleum ether (b.p. 60-70°) afforded 10.9 g. (81.5%) of tetrakis(trimethylsilyl)silane, subsequent to crystallization from acetone.

A repeat of this reaction gave an 83% yield of the acid, m.p. 228-230° (mixed m.p.).

<u>General procedure for comparative metalation reactions of fluorene</u> To 8.3 g. (0.05 mole) of fluorene in 380 ml. of THF, cooled to 0° with an ice-salt bath, was added at one time 140 ml. of a 0.35 M solution of tris(trimethylsilyl)-silyllithium (0.05 mole). The solution was stirred for 1.5 hours with the temperature maintained between 0° and 5°, prior to carbonation by addition to a Dry Ice-ether slurry. After allowing the mixture to warm to 0°, dilute hydrochloric acid was added. The organic layer was separated and the aqueous layer extracted several times with ether. The combined ethereal layers were extracted with 400 ml. of 5%

sodium hydroxide in several portions. The basic extract was boiled to remove traces of THF, and acidified with 10% hydrochloric acid. Filtration afforded a solid product which, after two recrystallizations from glacial acetic acid, gave 5.2 g. (51%) of fluorene-9-carboxylic acid, m.p. 228-230° (mixed m.p.).

Another experiment was carried out employing 150 ml. of a 0.28 M solution of tris(trimethylsilyl)silyllithium (0.04 mole) and 6.9 g. (0.04 mole) of fluorene. After three recrystallizations from glacial acetic acid, 3.9 g. (44.4%) of fluorene-9-carboxylic acid, m.p. 229-231° (mixed m.p.) was obtained.

Tris(trimethylsilyl)silyllithium with THF

A solution of tris(trimethylsilyl)silyllithium in 275 ml. of THF was heated at reflux temperature for 4 days. After this time, the reaction mixture was hydrolyzed by addition to a mixture of crushed ice acidified with 1N hydrochloric acid. The organic layer was separated and dried over sodium sulfate. Subsequent to the removal of solvents under reduced pressure, the residual oil was chromatographed on a column of alumina. Elution with petroleum ether (b.p. 60-70°) gave a small amount of a solid, identified by v.p.c. as tetrakis(trimethylsilyl)silane. Further elution with ethyl acetate followed by distillation of the combined fractions afforded a liquid, b.p. 175-180°/13 mm. V.p.c. chromatography indicated the presence of two compounds in approximately equal amounts. An i.r. spectrum of the liquid mixture showed the following absorptions in μ: 3.40 (m), 3.45 (m), 5.75 (s), 6.95 (w), 7.2 (w), 7.32 (w), 8.05 (s), 9,45 (m), 9.70 (m), 12.00 (s), and 13.40 (w).

The rate of reaction of tris(trimethylsilyl)silyllithium with THF The rate of reaction of tris(trimethylsilyl)silyllithium with THF was determined at room time by periodically withdrawing a 5 ml. aliquot of the solution and determining the concentration by double titration using allyl bromide. The change in molarity as a function of time and the first-order rate contant for each consecutive determination are given in Table 5.

Table 5. The rate of reaction of tris(trimethylsilyl)silyllithium with THF

Determination No.	Time (hours)	Molarity (mole/liter)	$k_1 \times 10^{-3}$ hours^{-1}
1.	0	0.198	----[a]
2.	23	0.200	----
3.	71	0.196	0.41
4.	99	0.189	1.3
5.	124	0.183	1.3
6.	148	0.177	1.3
7.	171	0.172	1.3
8.	242	0.162	0.82
9.	650	0.100	1.2
10.	1202	0.020	0.3

[a] No rate constant was calculated because the concentration apparently increased.

The rate of reaction of tris(trimethylsilyl)silyllithium with THF was found to follow pseudo first-order kinetics from 0.196 to 0.100 M (see Figure 1). The low value, 0.82 x 10^{-3} hours^{-1}, for determination No. 8 is probably due to an experimental error. The average rate constant was calculated to be 1.3 x 10^{-3} hours^{-1} (using k values for determinations 4, 5, 6, 7 and 9).

Tris(trimethylsilyl)silyllithium with 1, 1, 1-trimethyl-2, 2, 2-triphenyldisilane

Tris(trimethylsilyl)silyllithium (0.02 mole) and 5.6 g. (0.02 mole) of 1, 1, 1-trimethyl-2, 2, 2-triphenyldisilane dissolved in 125 ml. of THF were stirred overnight at room temperature. After this time, the reaction mixture was hydrolyzed by addition to a mixture of ice and 1*N* hydrochloric acid. The organic layer was separated and dried over sodium sulfate prior to the removal of solvents under reduced pressure. The residual oil was distilled to give 3 g. (73%) of tris(trimethylsilyl)silane, b.p. 99-103°/17 mm, n_D^{20} 1.4889.

The residual solid was chromatographed on a column of alumina. Elution with petroleum ether (b.p. 60-70°) gave 4 g. (75%) of unreacted 1, 1, 1-trimethyl-2, 2, 2-triphenyldisilane, m.p. 107-109° (mixed m.p.) and 1 g. (19%) of tetrakis(trimethylsilyl)silane. There was no evidence for triphenylsilane, triphenylsilanol or hexaphenyldisiloxane.

Tris(trimethylsilyl)silyllithium with bromobenzene

To 10.7 g. (0.07 mole) of bromobenzene dissolved in 50 ml. of THF was added dropwise a THF:ether solution of tris-(trimethylsilyl)silyllithium (0.07 mole). Upon complete addition (ca. 1.5 hours), the reaction mixture was stirred overnight at room temperature. Color Test I was negative and the reaction mixture was hydrolyzed by addition to a mixture of ice and 10% hydrochloric acid. Subsequent to work-up in the usual manner, 11.2 g. (55%) of starting material was recovered.

Spectral Determination of Tris(trimethylsilyl)silyllithium

Ultraviolet

Tris(trimethylsilyl)silyllithium was prepared in the usual manner by the reaction of tetrakis(trimethylsilyl)silane and methyllithium. Subsequent to a complete reaction, ether was removed by distillation and the silyllithium solution was transferred under nitrogen to an addition funnel. V.p.c. of a hydrolyzed aliquot indicated an area ratio of tris(trimethylsilyl)silane:tetrakis(trimethylsilyl)silane of ca. 150:1. A few milliliters of the silyllithium solution was diluted to the desired concentration with THF in a nitrogen-filled dry box. The quartz ultraviolet cell was filled with the silyllithium solution and sealed with paraffin wax. The spectrum of this solution showed bands at λ_{max} 370 mu

($\varepsilon \sim 10{,}000$), 295 mμ ($\varepsilon \sim 22{,}000$) and a shoulder at 236 mμ ($\varepsilon \sim 6{,}000$).

N.m.r.

Tris(trimethylsilyl)silyllithium was prepared in the usual manner. The silyllithium solution was concentrated by distillation to *ca.* 2 M (determined by double titration using allyl bromide). This solution was transferred under nitrogen to an n.m.r. capillary tube and sealed. The n.m.r. spectrum of the THF solution of tris(trimethylsilyl)silyllithium, using cyclohexane as the internal standard, contained a singlet at 9.93 τ. Except for the expected multiplets due to THF (99), there were no other absorptions present.

Color Test I of Tris(trimethylsilyl)silyllithium

General procedure

About 1 ml. of tris(trimethylsilyl)silyllithium was added to an equal volume of a 1% solution of Michler's ketone in dry benzene at room temperature. The solution was shaken and hydrolyzed by the addition of *ca.* 1 ml. of water. The hydrolyzed solution was oxidized with a solution of iodine in glacial acetic acid. A positive test was determined by the development of a green colored organic phase. The results of this test are summarized in Table 6.

Table 6. Color Test I of tris(trimethylsilyl)silyllithium

% iodine in glacial acetic acid	Amount of iodine-acetic acid solution used (drops)	Color of organic layer	Color of aqueous layer	Conclusion
0.2	20	reddish-brown	violet	negative
10.0	20	reddish-brown	greenish-blue	negative
20.0	6	green	greenish-yellow	positive
30.0	3	green	greenish-yellow	positive

Preparation of Methyl Tris(trimethylsilyl)silanecarboxylate

From tris(trimethylsilyl)silanecarboxylic acid and diazomethane

Diazomethane (ca. 0.03 mole) was generated by a reaction between N, N'-dinitroso-N, N'-dimethyl terephthalamide and sodium hydroxide in ether. To this yellow ethereal solution of diazomethane was added very slowly 5 g. (0.02 mole) of tris-(trimethylsilyl)silanecarboxylic acid at 0° to 5°. There was evolution of nitrogen, and upon complete addition, the yellow solution was allowed to stand for 1 hour at 0° to 5°. On removal of the excess diazomethane and ether, 4.4 g. (84.5%) of impure methyl tris(trimethylsilyl)silanecarboxylate was obtained subsequent to crystallization of the solid residue from cold petroleum ether (b.p. 60-70°). When inserted in the melting point block at 84°, the ester changed to a cloudy liquid at 91° and the liquid became clear at 96°. The rate of heating was ca. 1°/min.

An infrared spectrum (carbon disulfide) showed absorption bands in u at: 3.37 (m), 3.45 (m), 6.00 (s), 6.13 (s), 9.05 (s), 8.35 (w), 8.50 (w), 9.13 (s), 9.45 (w), 12.00 (s), 12.75 (w) and 14.50 (s).

The n.m.r. spectrum (carbon disulfide) contained singlets at 9.78 t and 9.72 t for the silicon-methyl protons and at 6.43 t for the methoxy protons. An integration of the areas was found to be 18 (calcd. 9)(See Discussion part).

Preparation of Bis(trimethylsilyl)methylsilane

From tris(trimethylsilyl)methylsilane and methyllithium

To 15.8 g. (0.06 mole) of tris(trimethylsilyl)methylsilane dissolved in 200 ml. of THF was added an ethereal solution of methyllithium (0.07 mole). Ether was removed by distillation and the reaction was stirred for ca. 36 hours at room temperature. After this time the pale greenish-yellow solution was hydrolyzed by addition to 120 ml. of 1N-hydrochloric acid. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layers were dried over sodium sulfate. Subsequent to the removal of the solvents under reduced pressure, an oil was obtained which was distilled to give 10.6 g. (83%) of bis(trimethylsilyl)methylsilane, b.p. 64-66°/23 mm, $n_D^{20.3}$ 1.4610 Lit. (100), 59°/21 mm, n_D^{20} 1.4616.

Reactions of Bis(trimethylsilyl)methylsilyllithium

General procedure for the preparation of bis(trimethylsilyl)methylsilyllithium

A 10% molar excess of methyllithium was added to a THF solution of tris(trimethylsilyl)methylsilane. The ether was removed by distillation and the reaction mixture was stirred at room temperature until v.p.c. of a hydrolyzed aliquot indicated a ratio of bis(trimethylsilyl)methylsilane:tris(trimethylsilyl)methylsilane of at least 100:1. In general, this condition was satisfied within 48 hours; but if not, a 10%

molar excess of methyllithium was added and the reaction mixture was continuously stirred at room temperature. The pale greenish-yellow solution was transferred to an addition funnel under nitrogen and the concentration was determined by double titration using allyl bromide. The silyllithium solution was used within one or two days.

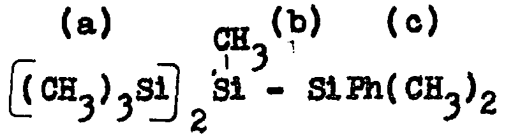
Bis(trimethylsilyl)methylsilyllithium with chlorodimethylphenylsilane

A THF solution of bis(trimethylsilyl)methylsilyllithium (0.039 mole) was added dropwise to 6.8 g. (0.04 mole) of chlorodimethylphenylsilane dissolved in 50 ml. of ether. The greenish-yellow color of the silyllithium solution was discharged instantaneously and upon complete addition, the reaction mixture was stirred for an additional hour at room temperature. Work-up of the reaction mixture in the usual manner afforded a liquid which was distilled to give 6.5 g. (51%) of impure bis(trimethylsilyl)(dimethylphenylsilyl)-methylsilane, b.p. 128-130°/3.7 mm, $n_D^{20.3}$ 1.5370. The compound was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) afforded, subsequent to distillation, 5.9 g. (47%) of pure bis(trimethylsilyl)(dimethylphenylsilyl)-methylsilane, b.p. 138-139°/3.5 mm, $n_D^{20.3}$ 1.5382, $d_4^{20.3}$ 0.8740.

Anal Calcd. for $C_{15}H_{32}Si_4$: Mol. Wt., 325; MR_D, 113.2. Found: Mol. Wt., 328; MR_D, 113.6.

The infrared spectrum (neat) showed absorption bands in μ at: 3.25 (w), 3.37 (m), 3.45 (w), 7.0 (w), 8.03 (s), 9.04 (m), 12.00 (s), 12.83 (s), 13.13 (w), 13.68 (m) and 14.34 (m).

The m.m.r. spectrum (carbon disulfide) consisted of singlets at 9.99 t, 9.88 t and 9.59 t for silicon-methyl protons a, b and c, respectively:



$$\overset{(a)}{[(CH_3)_3Si]_2}\overset{\overset{(b)}{CH_3}}{Si}-\overset{(c)}{SiPh(CH_3)_2}$$

The multiplet, centered at 2.73 t was assigned to the aromatic protons. An integration of the areas gave a ratio of 5 (aromatic):5.9 (protons c):20.5 (protons a and b) calcd. 5:6:21 . It was not possible to integrate areas for the ratio of protons a and b separately, because of their close resonance frequencies (see Discussion part).

The ultraviolet spectrum consisted of a band at $\lambda_{max}^{cyclohexane}$ 237.5 mμ (ε 13,500).

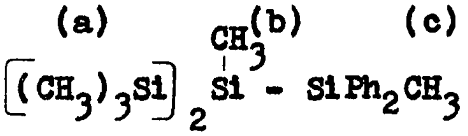
Bis(trimethylsilyl)methylsilyllithium with chlorodiphenylmethylsilane

A THF solution of bis(trimethylsilyl)methylsilyllithium (0.04 mole) was added dropwise to 9.3 g. (0.04 mole) of chlorodiphenylmethylsilane dissolved in 50 ml. of ether at room temperature. The greenish-yellow color of the silyllithium solution was discharged instantaneously and, upon complete addition (ca. 1.5 hours), the reaction mixture was stirred for 1 hour at room temperature. At this stage, the reaction mixture was hydrolyzed by addition to a mixture of ice and 10% hydrochloric acid. Work-up of the organic layer in the usual manner afforded a liquid. Distillation of this material gave 10.3 g. (76%) of bis(trimethylsilyl)(diphenylmethylsilyl)methylsilane, b.p. 148-151°/0.8 mm, $n_D^{20.3}$ 1.5750, $d_4^{20.3}$ 0.9516.

Anal. Calcd. for $C_{20}H_{34}Si_4$: Mol. Wt., 387; MR_D, 133.9. Found: Mol. Wt., 387; MR_D, 133.4.

An infrared spectrum (neat) showed absorption bands in μ at: 3.25 (w), 3.38 (m), 3.45 (w), 7.00 (m), 8.03 (s), 9.05 (s), 11.99 (s), 12.77 (s), 12.90 (s), 13.66 (s), 14.08 (m) and 14.34 (s).

The n.m.r. (carbon disulfide) consisted of singlets at 9.99 τ, 9.76 τ and 9.30 τ for the silicon-methyl protons a, b and c, respectively:



$$\overset{(a)}{[(CH_3)_3Si]_2}\overset{CH_3^{(b)}}{Si}-\overset{(c)}{SiPh_2CH_3}$$

The multiplet, centered at 2.68 τ, was assigned to the aromatic protons. An integration of the areas gave a ratio of 10.5:3:3:18.03 (calcd. 10:3:3:18). Cyclohexane was used as the internal standard.

The ultraviolet spectrum consisted of a band at $\lambda_{max}^{cyclohexane}$ 238.5 mμ (ε 17,400).

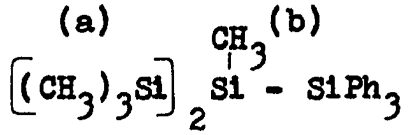
Bis(trimethylsilyl)methylsilyllithium with chlorotriphenylsilane

A THF solution of bis(trimethylsilyl)methylsilyllithium (0.04 mole) was added dropwise to 12.4 g. (0.04 mole) of chlorotriphenylsilane dissolved in 50 ml. of ether at room temperature. The greenish-yellow color of the silyllithium solution was discharged instantaneously and, upon complete addition, the reaction mixture was stirred for 1 hour at room temperature. At this stage, the reaction mixture was hydrolyzed by addition to a mixture of ice and 10% hydrochloric acid. Work-up in the usual manner afforded a liquid which was chromatographed on alumina. Elution of the column with petroleum ether (b.p. 60-70°) gave 12.5 g. (72%) of bis(trimethylsilyl)(triphenylsilyl)methylsilane, m.p. 66-67°, subsequent to crystallization from acetone.

Anal. Calcd. for $C_{25}H_{36}Si_4$: Mol. Wt., 449. Found: Mol. Wt., 448.

The infrared spectrum (carbon disulfide) showed absorption bands in μ at: 3.26 (w), 3.38 (m), 3.45 (w), 7.18 (w), 7.97 (m), 8.06 (s), 8.45 (w), 9.08 (s), 9.74 (w), 10.03 (w), 12.00 (s), 12.76 (s), 13.6 (s) and 14.35 (s).

The n.m.r. spectrum (carbon disulfide) consisted of singlets at 10.00 t and 9.72 t for the silicon-methyl protons a and b, respectively:



$$\overset{(a)}{\left[(CH_3)_3Si\right]_2}\overset{CH_3\,(b)}{\overset{|}{Si}} - SiPh_3$$

The multiplet, centered at 2.7 t, was assigned to the aromatic protons. An integration of the areas gave a ratio of 18:14.9:3 (calcd. 18:15:3). Cyclohexane was used as the internal standard.

The ultraviolet spectrum consisted of shoulders at $\lambda_{max}^{cyclohexane}$ 238 mμ (ε 22,000), 266.5 mμ (ε 5,890) and 273.5 mμ (ε 2,815).

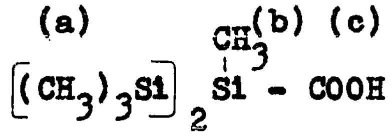
Bis(trimethylsilyl)methylsilyllithium with carbon dioxide

Run 1 (base extraction) A THF solution of bis(trimethylsilyl)methylsilyllithium (0.08 mole) was added slowly to a Dry Ice-ether slurry. The mixture was allowed to warm to *ca.* 0° prior to acidification with 10% hydrochloric acid. The organic layer was separated and extracted very rapidly with 400 ml. of cold 5% sodium hydroxide. Acidification of the basic extracts was followed by ether extraction. Subsequent to drying of the combined organic layer over sodium sulfate, the solvents were removed under reduced pressure to give 7 g. of crude bis(trimethylsilyl)methylsilanecarboxylic acid, m.p. 88-91°. Crystallization from cold petroleum ether (b.p. 60-70°) afforded 6.3 g. (50.4%) of pure compound, m.p. 90-92°. This compound did not decompose at its melting point. However, when heated to *ca.* 170°, evolution of carbon monoxide was observed, as determined by the procedure of Nowicki (98).

Anal. Calcd. for $C_8H_{22}Si_3O_2$: Mol. Wt., 235; Found: Mol. Wt., 237.

An infrared spectrum (CS_2) showed absorption bands in μ at: 3.39 (m), 5.95 (w), 6.11 (s), 8.06 (s), 8.33 (m), 8.5 (w), 9.4 (w), 11.96 (s), 12.75 (s), 13.40 (w) and 14.38 (m). There was also present a broad absorption band (3.05-3.7 μ) for the -OH group of the -COOH.

The n.m.r. spectrum (CS_2) showed singlets at 9.83 t and 9.79 t for the silicon-methyl protons a and b, at a sweep width of 50 cps:



$$\overset{(a)}{\left[(CH_3)_3Si\right]_2}\overset{\overset{(b)}{CH_3}}{\underset{}{Si}} - \overset{(c)}{COOH}$$

An integration of the areas gave a ratio of 18:3 (calcd: 18:3). At a 500 cps sweep width, the singlets at 9.82 t, 9.78 t and -1.95 t were assigned to protons a, b and c, respectively. An integration of the areas gave a ratio of 20.6 (protons a and b):1 (proton c) calcd: 21:1 . It was not possible to integrate the areas for the ratio of protons a and b, at a sweep width of 500 cps, because of their close resonance frequencies (see Discussion part). Cyclohexane was used as the internal standard.

Run 2 (without base extraction) A THF solution of bis(trimethylsilyl)methylsilyllithium (0.14 mole) was added to a Dry Ice-ether slurry. The mixture was allowed to warm to 0°, prior to acidification with 10% hydrochloric acid. The organic layer was separated and the aqueous layer was extracted several times with ether. The combined organic layers were dried over sodium sulfate prior to the removal of the solvents under reduced pressure to yield 26 g. (82%) of crude bis(trimethylsilyl)methylsilanecarboxylic acid, m.p. 82-86°. Purification by crystallization from petroleum ether (b.p. 60-70°) afforded 21.6 g. (67.8%) of pure acid, m.p. 91-92° (mixed m.p.).

Bis(trimethylsilyl)methylsilyllithium with fluorene

General procedure for comparative metalation reactions of fluorene To 7.6 g. (0.05 mole) of fluorene in 380 ml. of THF, cooled to 0° with an ice-salt bath, was added at one time 66 ml. of 0.7 N solution of bis(trimethylsilyl)methylsilyllithium (0.05 mole). The solution was stirred for 1.5 hours at a temperature between 0° and 5°, then carbonated by pouring on to a Dry Ice-ether slurry. After allowing the mixture to warm to 0°, dilute hydrochloric acid was added, followed by several extractions with ether. The combined ether layers were extracted with 400 ml. of 5% sodium hydroxide in several portions. The basic extracts were boiled, then acidified with 10% hydrochloric acid. Filtration afforded a solid product which was recrystallized from glacial acetic acid to give 6.3 g. of crude fluorene-9-carboxylic acid, m.p. 226-232°. A second recrystallization from glacial acetic acid gave 6 g. (63%) of pure acid, m.p. 228-230° (mixed m.p.).

Another experiment was carried out employing the same molar quantities of reactants. After two recrystallizations from glacial acetic acid, 6.8 g. (70.5%) of fluorene-9-carboxylic acid, m.p. 229-231° (mixed m.p.) was obtained.

Reactions of Bis(trimethylsilyl)methylsilaneoarboxylic Acid

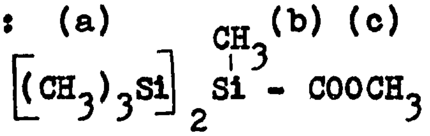
Bis(trimethylsilyl)methylsilanecarboxylic acid with diazomethane

Diazomethane (ca. 0.03 mole) was generated by a reaction between N, N'-dinitroso-N, N'-dimethyl terephthalamide and sodium hydroxide in ether. To this yellow ethereal solution of diazomethane was added very slowly 4.6 g. (0.02 mole) of bis(trimethylsilyl)methylsilanecarboxylic acid at 0° to 5°. There was observed the evolution of a gas (nitrogen) and, upon complete addition, the yellow solution was allowed to stand for 1 hour at 0° to 5°. The excess diazomethane and ether was removed under reduced pressure to give an oil. Distillation of the oil afforded 3.7 g. (75.5%) of methyl bis(trimethylsilyl)methylsilanecarboxylate, b.p. 91-92°/ 7 mm, $n_D^{20.3}$ 1.4728, $d_4^{20.3}$ 0.8758.

Anal. Calcd. for $C_9H_{24}Si_3O_2$: Mol. Wt., 249; MR_D, 79.21. Found: Mol. Wt., 254; MR_D, 79.44.

An infrared spectrum (neat) showed abosrption bands in u at: 3.39 (m), 3.45 (w), 5.97 (s), 8.04 (s), 8.50 (w), 8.99 (s), 10.58 (w), 11.95 (s), 12.75 (s), 13.49 (w) and 14.35 (m).

The n.m.r. spectrum (CS_2) showed singlets at 9.86 t and 9.78 t for the silicon-methyl protons a and b, at a sweep width of 50 cps:



$$\overset{(a)}{\left[(CH_3)_3Si\right]_2}\overset{\overset{(b)\ (c)}{CH_3}}{\underset{|}{}Si} - COOCH_3$$

At a sweep width of 500 cps, the singlets at 9.87 t, 9.79 t and 6.5 t were assigned to protons a, b and c, respectively.

An integration of the areas gave a ratio of 21.1 (protons a and b):3 (protons c) calcd: 21:3 . It was not possible to integrate the areas for the ratio of protons a and b separately at a sweep width of 500 cps, because of their close resonance frequencies (see Discussion part). Cyclohexane was used as the internal standard.

Pyrolysis of bis(trimethylsilyl)methylsilanecarboxylic acid

Five grams (0.02 mole) of bis(trimethylsilyl)methylsilanecarboxylic acid was heated at 200° for 40 minutes. There was observed an evolution of a gas, which was found to be carbon monoxide by the procedure of Nowicki (98). No precipitate was observed when the gas was bubbled through a barium hydroxide solution, indicating the absence of carbon dioxide. The residual liquid was distilled, affording 2.4 g. (81%) of tetrakis(trimethylsilyl)dimethyldisiloxane, b.p. 103-108°/ 1.3 mm, n_D^{20} 1.4815 (b.p. 110/1.0 mm, $n_D^{20.3}$ 1.4841)[1].

Bis(trimethylsilyl)methylsilanecarboxylic acid with 95% ethanol

Ten grams (0.03 mole) of bis(trimethylsilyl)methylsilanecarboxylic acid was heated at reflux in 95% ethanol overnight. The solvent were removed under reduced pressure to give 9.1 g. of recovered bis(trimethylsilyl)methylsilanecarboxylic acid, m.p. 84-86°. Recrystallization from methanol gave 8.8 g.

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[1] R. L. Harrell, Department of Chemistry, Iowa State University of Science and Technology, Ames Iowa. Information on the physical constants of tetrakis(trimethylsilyl)dimethyldisiloxane. Private communication. 1966.

(88%) of pure acid, m.p. 90-92 (mixed m.p.).

Reactions of Tris(trimethylsilyl)silane

Tris(trimethylsilyl)silane with *n*-butyllithium

To 20 g. (0.07 mole) of tris(trimethylsilyl)silane dissolved in 100 ml. THF was added 0.07 mole of *n*-butyllithium (prepared in ether). The reaction mixture instantaneously turned greenish-yellow and the evolution of a gas was observed. After stirring the reaction mixture for 2 hours at room temperature, Color Test I was negative, indicating that all of the *n*-butyllithium had reacted. The concentration of the greenish-yellow solution was determined by double titration using allyl bromide, subsequent to derivatization by addition to 22.7 g. (0.08 mole) of chlorotriphenylsilane dissolved in 100 ml. of ether. The yellow color of the silyllithium solution was discharged instantaneously and upon complete addition (*ca.* 5 minutes), the reaction mixture was hydrolyzed by addition to a mixture of ice and 10% hydrochloric acid. Work-up in the usual manner gave an oil from which 15.1 g. (43.7%) of tris(trimethylsilyl)(triphenylsilyl)silane, m.p. 287° (mixed m.p.), subsequent to crystallization from petroleum ether (b.p. 60-70°). This compound was also identified by its infrared spectrum.

The mother liquor was chromatographed on a column of alumina. Elution with petroleum ether (b.p. 60-70°) afforded 1.8 g. (16%) of tetrakis(trimethylsilyl)silane, subsequent to crystallization of the solid from acetone.

<u>Tris(trimethylsilyl)silane with methyllithium in ether</u>

An ethereal solution of methyllithium (0.03 mole) and 8 g. (0.03 mole) of tris(trimethylsilyl)silane was stirred at reflux temperature overnight. After this time, v.p.c. of a hydrolyzed aliquot of the white reaction mixture showed only tris(trimethylsilyl)silane; and there was no peak with the same retention time as tris(trimethylsilyl)methylsilane.

The reaction mixture was derivatized by the addition to a mixture of 8 g. (0.03 mole) of chlorotriphenylsilane in 50 ml. of ether, followed by refluxing of the resulting reaction mixture for 1 hour. After this time, the reaction mixture was hydrolyzed by the addition to a mixture of ice and 1*N* hydrochloric acid. The organic layer was separated and dried over sodium sulfate. A liquid was obtained subsequent to the removal of solvents under reduced pressure. Subsequent to crystallization from 95% ethanol, 3.6 g. (44.6%) of methyltriphenylsilane, m.p. 67-69° (mixed m.p.), was obtained. The mother liquor was distilled, affording 3.5 g. (31%) of tris(trimethylsilyl)silane, b.p. 90-93°/10 mm, n_D^{20} 1.4880. The residue from the distillation was chromatographed on alumina. Elution with 95% ethanol afforded 1 g. of a solid, m.p. 131-138°.

Tris(trimethylsilyl)silane with phenyllithium in ether

An ethereal solution of 8 g. (0.03 mole) of tris(trimethylsilyl)silane and phenyllithium (0.03 mole) was stirred at reflux temperature overnight. After this time, Color Test I was positive and the reaction mixture was derivatized by addition to an excess (*ca.* 10%) of trimethyl phosphate. The resulting reaction mixture was stirred for 1 hour at room temperature, subsequent to hydrolysis by addition to a mixture of ice and 1*N* hydrochloric acid. Work-up in the usual manner afforded an oil. V.p.c. of this oil indicated the presence of tris(trimethylsilyl)silane, tris(trimethylsilyl)methylsilane and tris(trimethylsilyl)phenylsilane. An unidentified peak with a retention time between that of tris(trimethylsilyl)methylsilane and tris(trimethylsilyl)-phenylsilane was also present.

Miscellaneous Reactions

Triphenylsilane and *n*-butyllithium in THF:ether

To 10 g. (0.037 mole) of triphenylsilane dissolved in 100 ml. of THF was added 40 ml. of 1.1 *n*-butyllithium (0.04 mole, prepared in ether). A white precipitate was observed and the reaction mixture was stirred for 2 hours at room temperature. After this time, the reaction mixture was hydrolyzed by addition to a mixture of ice and 10% hydrochloric acid. Removal of the organic solvents gave a solid from which 9.4 g. (77%) of triphenyl-*n*-butylsilane, m.p. 87-89°

(mixed m.p.) was obtained, subsequent to crystallization from ethanol.

Preparation of bis(trimethylsilyl)diphenylsilane

From diphenyldichlorosilane, chlorotrimethylsilane and lithium A mixture of 3.1 g. (0.44 g.-atom) of lithium and a solution of 25.3 g. (0.1 mole) of diphenyldichlorosilane in 110 ml. of THF was stirred at room temperature. After ca. 10 minutes of stirring, the reaction mixture turned red. At this stage, the remainder of the diphenyldichlorosilane:THF solution was added at such a rate as to maintain the red color. Upon complete addition, (ca. 30 minutes), 21.7 g. (0.2 mole) of chlorotrimethylsilane in 110 ml. of THF was added dropwise at a rate sufficient to maintain the red color. The addition was complete in 1.5 hours and a small amount of unreacted lithium was present. At this stage, enough chlorotrimethylsilane (ca. 25 ml.) was added to consume the unreacted lithium and give a negative Color Test I. The white reaction mixture was hydrolyzed by addition to a mixture of ice and 10% hydrochloric acid. Subsequent to separation and drying of the organic layer over sodium sulfate, the solvents were removed under reduced pressure, affording a viscous liquid. Distillation of the liquid gave 8 g. of impure tris(trimethylsilyl)phenylsilane, b.p. 95-105°/0.01 mm, n_D^{20} 1.5540 Lit (5) 118-121°/0.025 mm, n_D^{20} 1.5723. The impure tris(trimethylsilyl)phenylsilane was chromatographed on a column of alumina. Elution with petroleum ether (b.p. 60-70°) gave, after distillation of the liquid residue, 7.5 g. of pure tris(trimethylsilyl)phenylsilane, sublimes at 101-104°/0.01 mm (solidified on standing to a waxy solid). The impure bis(trimethylsilyl)diphenylsilane could not be purified by similar techniques. However, v.p.c. indicated a mixture of tris(trimethylsilyl)phenylsilane and bis(trimethylsilyl)-diphenylsilane.

The residue from the original distillation was chromatographed on a column of alumina. Elution of the column with petroleum ether (b.p. 60-70°) gave, subsequent to crystallization from ethanol-ethyl acetate, 6.6 g. of a white solid, m.p. 113-114°.

The n.m.r. spectrum of this compound is given in the Discussion part.

Preparation of hexamethyl-2, 2, 3, 3-tetraphenyltetrasilane

To 20 g. (0.06 mole) of hexamethyl-2, 2-diphenyltrisilane dissolved in 150 ml. of benzene at 0° was added dropwise 10.7 g. (0.13 mole) of bromine dissolved in 100 ml. of benzene. Upon complete addition (ca. 3 hours), the reaction mixture was allowed to stir to room temperature. Benzene, bromotrimethylsilane and the excess bromine were removed by distillation prior to the addition of 2.8 g. (0.12 g.-atom) of sodium and 150 ml. of xylene. The reaction mixture was refluxed for 30 hours. After cooling the reaction mixture to 0°, the excess sodium was destroyed by the addition of 95% ethanol and the resulting reaction mixture was acidified with 10% hydrochloric acid. The mixture was extracted several times with ether and the ethereal extracts were dried over sodium sulfate. Removal of the solvents afforded a solid from which 11.1 g.(74%) of hexamethyl - 2,2,3,3 - tetraphenyltetrasilane, m.p. 264-267° (mixed m.p.)[1] was obtained, after two recrystallizations ethyl acetate-ethanol solvents.

Preparation of octamethyl - 2,2,4,4 - tetraphenylpentasilane

To 9 g.(0.018 mole) of hexamethyl - 2,2,3,3 - tetraphenyl tetrasilane and 2 g.(0.28 g. - atom) of lithium was added sufficient THF to form a thick paste. After stirring for a few minutes, the reaction had started, as evidenced by the formation of a yellow color. Eighty milliliters of THF was added dropwise over a period of 30 minutes. After stirring the reaction mixture overnight at room temperature, Color Test I was positive. The reaction mixture was decanted away from the excess lithium into an addition funnel. The concentration of the silyllithium compound, $(CH_3)_3SiSiPh_2Li$, was determined by double titration using allyl bromide.

To 0.78 g.(0.06 mole) of dichlorodimethylsilane dissolved

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[1] G. L. Schwebke, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the melting point of hexamethyl - 2,2,3,3 - tetraphenyltetrasilane. Private communication. 1963.

in 160 ml. of ether, cooled to -50°, was added the silyllithium compound (0.012 mole). The reaction mixture was stirred at -50° for 1 hour, subsequent to stirring at room temperature for 1 hour. After this time, Color Test I was negative and the reaction mixture was hydrolyzed by addition to a mixture of ice and 10% hydrochloric acid. The organic layer was separated and dried over sodium sulfate. Removal of the solvents under reduced pressure afforded an oil which was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave 1.4 g.(41%) of octamethyl-2,2,4,4 - tetraphenylpentane, m.p. 97-97.5°, subsequent to crystallization of the solid from ethyl acetate-methanol solvents.

<u>Anal.</u> Calcd. for $C_{32}H_{44}Si_5$: C, 67.51; H, 7.79; Mol. Wt., 569. Found: C, 66.67, 66.86; H, 7.99, 8.19; Mol. Wt., 562.

DISCUSSION

A Direct Preparation of Some Tri- and Tetrasilyl-substituted Organopolysilanes

Trisilyl-substituted compounds

Gilman and Schwebke[1] treated decaphenylcyclopentasilane (XL) with chlorotrimethylsilane and lithium in THF. From this reaction, the following products were isolated: trimethylphenylsilane (XLI), (trimethylsilyl)diphenylsilane (XLII), bis(trimethylsilyl)diphenylsilane (XLIII), tris(trimethylsilyl)phenylsilane (XLIV) and bis(trimethylsilyl)phenylsilane (XLV):

$$\underset{\text{XL}}{[Ph_2Si]_5} + 11(CH_3)_3SiCl + 11Li \xrightarrow{\text{THF}} \underset{\text{XLI}}{(CH_3)_3SiPh} + \underset{\text{XLII}}{(CH_3)_3SiSiPh_2H}$$

$$+ 2\ \underset{\text{XLIII}}{[(CH_3)_3Si]_2SiPh_2} + \underset{\text{XLIV}}{[(CH_3)_3Si]_3SiPh} + \underset{\text{XLV}}{[(CH_3)_3Si]_2SiPhH}$$

Compounds XLIV and XLV, unexpected products of this reaction, were formed by a cleavage reaction of the silicon-phenyl bond of XLIII with lithium followed by derivatization of the silyllithium with chlorotrimethylsilane and by acid hydrolysis, respectively:

$$\begin{tikzcd}
 & & \text{XLIV} + \text{XLI} \\
\text{XLIII} + 2Li \arrow[r, "\text{THF}"] & {[(CH_3)_3Si]_2SiPhLi} \arrow[ur, "(CH_3)_3SiCl"] \arrow[dr, "H_3O^+"'] & \\
 & & \text{XLV} + C_6H_6
\end{tikzcd}$$

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[1] G. L. Schwebke, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the reaction between decaphenylcyclopentasilane, chlorotrimethylsilane and lithium. Private communication. 1963.

Octaphenylcyclotetrasilane[1] reacts with chlorotrimethylsilane, and lithium in a similar manner as XL.

Prompted by these studies, reactions between a polychlorinated silicon compound, chlorotrimethylsilane and lithium were investigated. The reaction between diphenyldichlorosilane, chlorotrimethylsilane and lithium in THF afforded XLIII, XLIV and a solid product:

$$Ph_2SiCl_2 + (CH_3)_3SiCl + Li \xrightarrow{THF} XLIII + XLIV + \text{a solid product}$$

Although the structure of this solid compound has not been elucidated, its n.m.r. spectrum (Figure 1) indicated that one of the aromatic rings of XLIII was reduced by lithium. The n.m.r. spectrum contains what appear to be 5 aromatic protons from 2.72 t to 2.34 t (multiplet), 1 olefinic proton centered at 4.07 t (doublet) and 2 olefinic protons centered at 4.85 t (triplet), 2 aliphatic protons from 9.00 t - 8.12 t (multiplet) and 53 silicon-methyl protons from 10.01 t - 9.61 t (three peaks). However, the presence of a double bond was not substantiated by its infrared spectrum (Figure 1). The reaction between dichlorodiphenylsilane, chlorotrimethylsilane and lithium in THF:ether (1:9) afforded XLIII in a 60% yield[2]:

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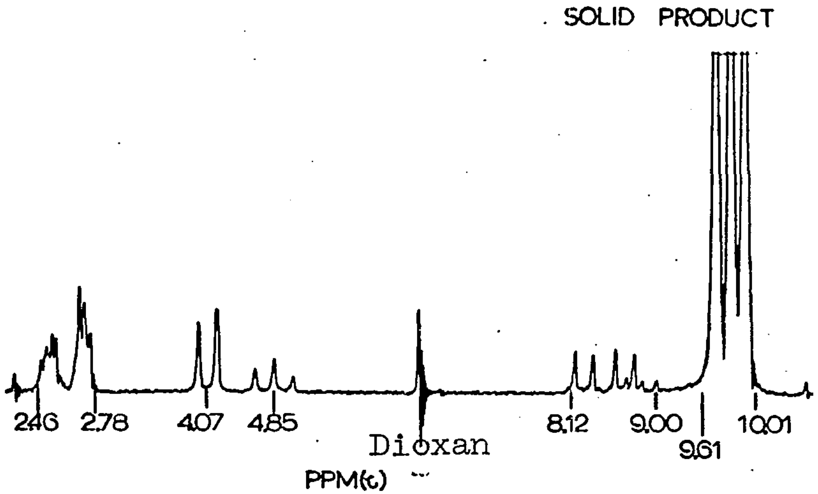
[1] R. L. Harrell, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the reaction between octaphenylcyclotetrasilane, chlorotrimethylsilane and lithium. Private communication. 1963.

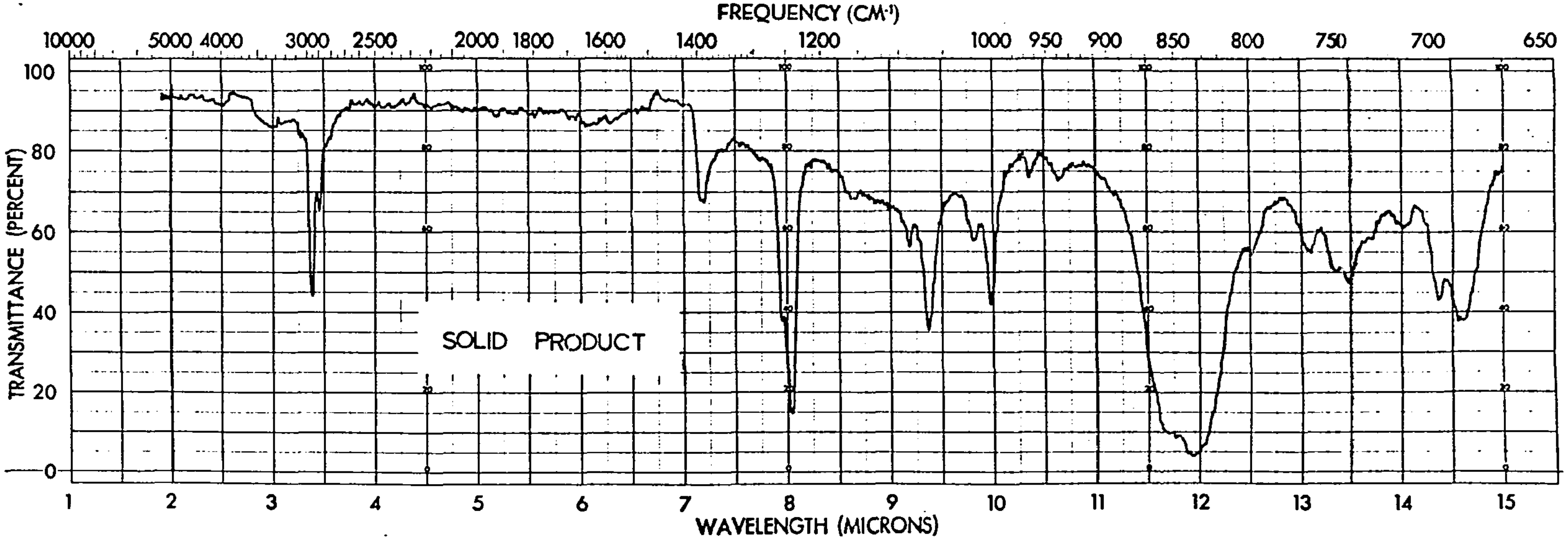
[2] Dr. K. Shiina, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the reaction between dichlorodiphenylsilane, chlorotrimethylsilane and lithium in THF:ether (1:9). Private communication. 1966.

Figure 1. Infrared and nuclear magnetic resonance spectra of the solid product

Top: Infrared spectrum

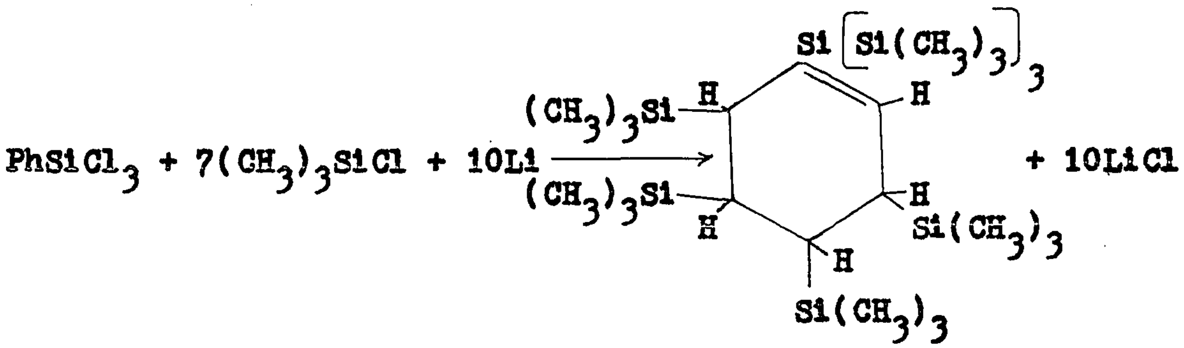
Bottom: Nuclear magnetic resonance spectrum


SOLID PRODUCT
2.46
2.78
4.07
4.85
Dioxan
8.12
9.00
9.61
10.01
PPM(τ)


FREQUENCY (CM⁻¹)
10000
5000
4000
3000
2500
2000
1800
1600
1400
1200
1000
950
900
850
800
750
700
650
TRANSMITTANCE (PERCENT)
100
80
60
40
20
0
SOLID PRODUCT
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
WAVELENGTH (MICRONS)

$$Ph_2SiCl_2 + 2(CH_3)_3SiCl + 4Li \xrightarrow{\text{THF:ether (1:9)}} \text{XLIII}$$

A reaction of phenyltrichlorosilane, chlorotrimethylsilane and lithium in THF afforded a solid product which is probably some geometric isomer of tris [trimethylsilyl] [3, 4, 5, 6-tetrakis(trimethylsilyl)cyclohexen-1-yl] silane (XLVI), instead of the expected XLIV:



XLVI

The n.m.r. spectrum (Figure 2) contains what appear to be an olefinic proton centered at 4.12 t (doublet), the aliphatic protons from 8.86 - 7.88 t (multiplet) and the silicon-methyl protons from 9.91 - 9.75 t (triplet). The integrated area ratio was found to be 1:4.4:61.5 (calcd. 1:4:63). An expansion of the silicon-methyl region (Figure 2) over a sweep width of 50 c.p.s. indicates the presence of five nonequivalent trimethylsilyl groups with absorptions for the silicon-methyl protons at 9.95, 9.90, 9.87, 9.85, and 9.83 t in a ratio of 1:1:1:1:3 (calcd. 1:1:1:1:3). The molecular weight, determined by mass spectrocopy, was found to be 616 (calcd. 616)[1]. The

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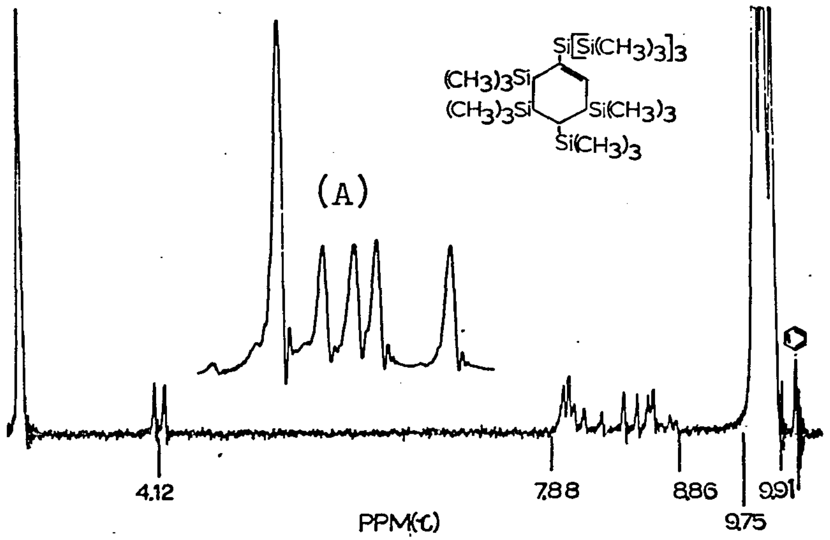
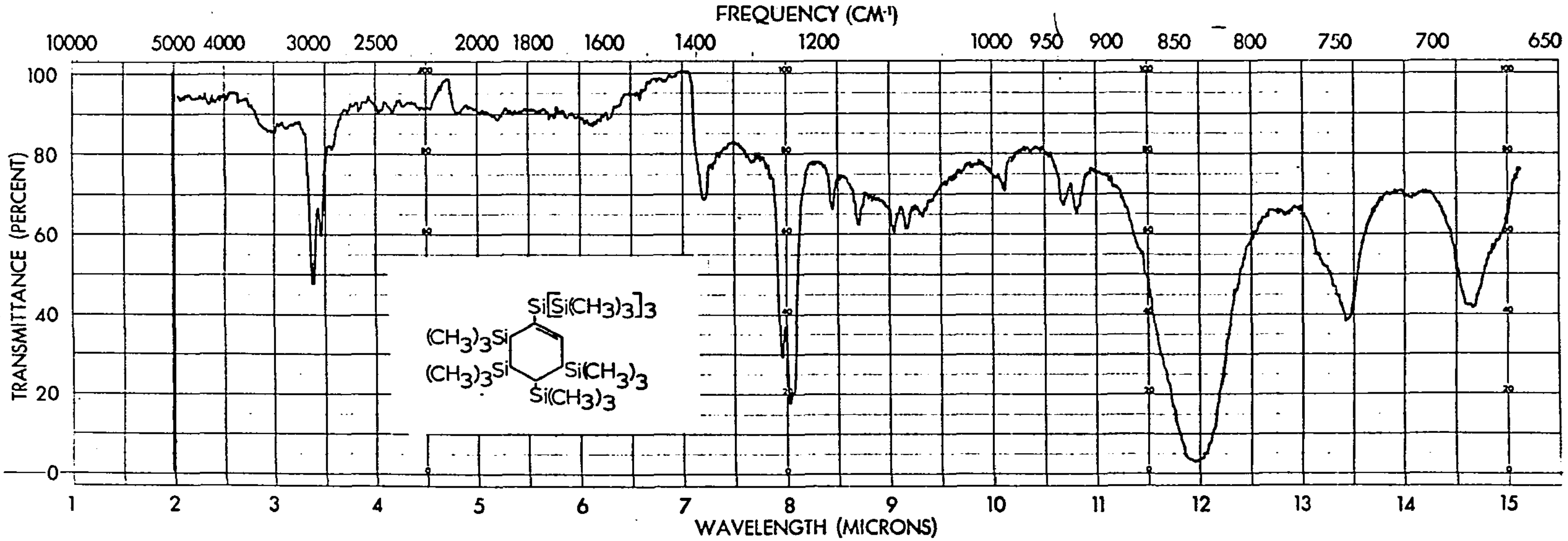
[1] R. L. Harrell, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the mass spectral data. Private communication. 1966.

Figure 2. Infrared and nuclear magnetic resonance spectra of tris-[trimethylsilyl][3, 4, 5, 6-tetrakis(trimethylsilyl)-cyclohexen-1-yl] silane (XLVI)

Top: Infrared spectrum

Bottom: Nuclear magnetic resonance spectrum


Si[Si(CH3)3]3
(CH3)3Si
(CH3)3Si
Si(CH3)3
Si(CH3)3
(A)
4.12
7.88
8.86
9.75
9.91
PPM(τ)


FREQUENCY (CM-1)
10000
5000
4000
3000
2500
2000
1800
1600
1400
1200
1000
950
900
850
800
750
700
650
TRANSMITTANCE (PERCENT)
100
80
60
40
20
0
Si[Si(CH3)3]3
(CH3)3Si
(CH3)3Si
Si(CH3)3
Si(CH3)3
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
WAVELENGTH (MICRONS)

infrared spectrum (Figure 2) agrees with the proposed structure (XLVI), containing an absorption for the double bond at 6.3 μ.

Tris(trimethylsilyl)methylsilane (XLVII), together with sym-tetrakis(trimethylsilyl)dimethyldisilane (XLVIII), was prepared by a reaction between chlorotrimethylsilane, methyltrichlorosilane and lithium in THF:

$$3\ CH_3SiCl_3 + 6(CH_3)_3SiCl + 12Li \xrightarrow{THF} \underset{XLVII}{[(CH_3)_3Si]_3SiCH_3} +$$

$$\underset{XLVIII}{(CH_3)[(CH_3)_3Si]_2Si - Si[Si(CH_3)_3]_2(CH_3)} + 12\ LiCl$$

The reaction appears to be slower and the yields of XLVII (ca. 40%) are lower than that of tetrakis(trimethylsilyl)silane (XLIX) formed under similar conditions from silicon tetrachloride, chlorotrimethylsilane and lithium (see Tetrasilyl-substituted compounds):

$$SiCl_4 + 4(CH_3)_3SiCl + 8Li \xrightarrow{THF} \underset{XLIX}{[(CH_3)_3Si]_4Si} + 8LiCl$$

Unlike the synthesis of XLIX in which none of the higher polysilane, hexakis(trimethylsilyl)disilane could be isolated, compound XLVIII was obtained in ca. 20% yield. It seems unlikely that XLVIII is an important precursor to XLVII since attempts to cleave a silicon-silicon bond of XLVIII with lithium have failed.[1] Thus, in a similar manner as XLIX, com-

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[1] R. L. Harrell, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the reaction of sym-tetrakis(trimethylsilyl)dimethyldisilane with lithium. Private communication. 1966.

pound XLVII may result <u>via</u> a sequence of consecutive formations of silyllithium compounds, followed by a coupling reaction with chlorotrimethylsilane:

$$Cl_3SiCH_3 + Li \longrightarrow LiCl_2SiCH_3 + LiCl$$

$$LiCl_2SiCH_3 + (CH_3)_3SiCl \longrightarrow Cl_2\left[(CH_3)_3Si\right]SiCH_3 + LiCl$$

$$Cl_2\left[(CH_3)_3Si\right]SiCH_3 + Li \longrightarrow LiCl\left[(CH_3)_3Si\right]SiCH_3 + LiCl$$

$$LiCl\left[(CH_3)_3Si\right]SiCH_3 + (CH_3)_3SiCl \longrightarrow Cl\left[(CH_3)_3Si\right]_2SiCH_3 + LiCl$$

$$Cl\left[(CH_3)_3Si\right]_2SiCH_3 + Li \longrightarrow Li\left[(CH_3)_3Si\right]_2SiCH_3 + LiCl$$

$$Li\left[(CH_3)_3Si\right]_2SiCH_3 + (CH_3)_3SiCl \longrightarrow XLVII + LiCl$$

Tris(dimethylphenylsilyl)methylsilane was prepared by a reaction between methyltrichlorosilane and dimethylphenylsilyllithium:

$$CH_3SiCl_3 + 3Ph(CH_3)_2SiLi \longrightarrow \left[Ph(CH_3)_2Si\right]_3SiCH_3 + 6LiCl$$

<u>Tetrasilyl-substituted compounds</u>

Tetrakis(trimethylsilyl)silane (XLIX), the first tetrasilyl-substituted organopolysilane having contiguous silicon atoms, was synthesized in yields of 60-70% (see Table 4) by reactions between silicon tetrachloride, chlorotrimethylsilane and lithium in THF. In general, the yield of XLIX was affected by: (1) the mode of addition and the ratio of reactants; (2) the reaction time; and (3) the method of purification. The highest hields were obtained when silicon tetrachloride was added to an excess of chlorotrimethylsilane and an excess of lithium; and the reaction mixture was very vigorously stirred for more than 24 hours at room temperature prior to work-up and purification of XLIX by sublimation.

Compound XLIX may result <u>via</u> a sequence of consecutive formations of silyllithium compounds, followed by a coupling reaction with chlorotrimethylsilane (Scheme I). When a molecule of silicon tetrachloride comes in contact with the large surface of the lithium metal, in a high concentration of chlorotrimethylsilane, enough energy may be derived to complete the substitution of the remaining silicon-chlorine bonds:

Scheme I

$$SiCl_4 + Li \longrightarrow LiSiCl_3 + LiCl$$

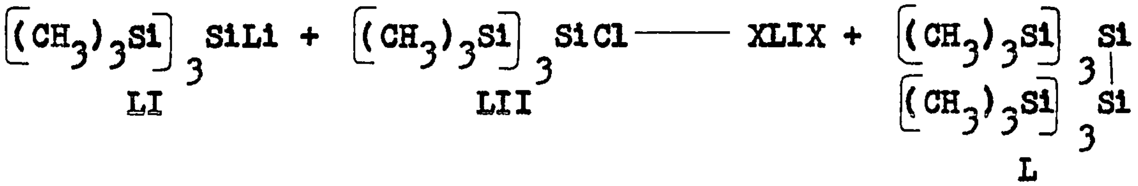
$$LiSiCl_3 + (CH_3)_3SiCl \longrightarrow (CH_3)_3SiSiCl_3 + LiCl$$

$$(CH_3)_3SiSiCl_3 + Li \longrightarrow (CH_3)_3SiSiCl_2Li + LiCl$$

$$(CH_3)_3SiSiCl_2Li + (CH_3)_3SiCl \longrightarrow \left[(CH_3)_3Si\right]_2SiCl_2 + LiCl \text{ etc.}$$

Thus, the mode of formation of XLIX can be explained on the basis of the "heterogeneity (101)" of the system. This mechanism is in agreement with the experimental observations: the highest yields of XLIX were obtained when silicon tetrachloride dissolved in THF was added to chlorotrimethylsilane and lithium in THF. Interestingly, in an attempt to prepare some intermediates postulated in Scheme I, tris(trimethylsilyl)chlorisilane and bis(trimethylsilyl)dichlorosilane, by reactions of silicon tetrachloride, chlorotrimethylsilane and lithium, compound XLIX was the major product.

Another possible route leading to the formation of XLIX might involve the intermediate formation of some higher branched-chain polysilane compounds. An inspection of the intermediates shown in Scheme I reveals the possibility of a variety of silyllithium coupling and/or lithium cleavage reactions, leading to the intermediate formation of hexakis-(trimethylsilyl)disilane (L) and other related branched-chain compounds. For example, tris(trimethylsilyl)silyllithium (LI) reacts with tris(trimethylsilyl)chlorosilane (LII), affording compounds XLIX and L (102):



$$\underset{\text{LI}}{[(CH_3)_3Si]_3SiLi} + \underset{\text{LII}}{[(CH_3)_3Si]_3SiCl} \longrightarrow \text{XLIX} + \underset{\text{L}}{\begin{array}{c}[(CH_3)_3Si]_3Si \\ | \\ [(CH_3)_3Si]_3Si\end{array}}$$

However, in an attempt to prepare L by a reaction between silicon tetrachloride, chlorotrimethylsilane and lithium, the major product was XLIX, and the presence of only a trace of L was indicated by v.p.c. (102). If compound L was formed in these reactions a mechanism based on lithium metal and/or silyllithium cleavage reactions could be invoked to explain its transitory existence. For example, a cleavage reaction of the silicon-silicon bond of L by lithium would give LI which could react with chlorotrimethylsilane, affording XLIX:

Scheme II

$$\text{L} + 2\text{LI} \longrightarrow 2\text{LI}$$

$$\text{LI} + (CH_3)_3SiCl \longrightarrow \text{XLIX} + LiCl$$

Alternatively, a cleavage reaction of the silicon-silicon bond of L by a silyllithium compound would give XLIX or its precursor. For instance, a cleavage reaction of the silicon-

silicon bond of L by LI would give XLIX and pentakis(trimethylsilyl)disilanyllithium: <u>Scheme III</u>

$$\mathrm{L} + \mathrm{LI} \longrightarrow \mathrm{XLIX} + \left[(CH_3)_3Si\right]_3 SiSi\left[Si(CH_3)_3\right]_2 Li$$

The validity of these possibilities was substantiated by separate experiments (102).

There also exists the possibility of the intermediate formation of silirenes and dilithiosilanes of the types $Cl_n\left[(CH_3)_3Si\right]_{2-n}Si:$ and $Cl_n\left[(CH_3)_3Si\right]_{2-n}SiLi_2$, respectively. These intermediates probably have very little or no significance in the formation of XLIX, since there is no definitive evidence for the existence of dilithiosilanes of this nature (30) and the existence of silirenes in reactions of this type is not well documented (103). The formation of silyl radicals is possible.

It is difficult to accurately describe the character and fate of the intermediate species involved because of the complex nature of metal coupling and cleavage reactions in general, and particularly those involving two or more different chlorosilanes. However, of the possible pathways leading to the formation of XLIX, those depicted in Schemes I, II, and III are quite reasonable, and mechanisms involving intermediates such as silirenes, dilithiosilanes and silyl radicals probably have lesser significance. Moreover, as a consequence of steric hindrance involved in the formation of L, Scheme I is a favored pathway.

An inspection of Table 5 reveals that the highest yield of XLIX is 70%. The inability to reproduce this yield using other conditions is probably a reflection on the intrinsic nature of the heterogeneous reaction: four silicon-chlorine bonds may have to be cleaved subsequent to four silyllithium coupling reactions per molecule of XLIX formed. Hence in view of the diversity of reactions involved: namely, lithium cleavage and silyllithium coupling, and the high structural specificity required, it is difficult to establish and maintain ideal conditions. Probably the most significant factors contributing to the high yield of XLIX are the "inertness" of chlorotrimethylsilane to lithium coupling reactions, relative to the other chlorosilanes involved, and of XLIX to lithium cleavage of the silicon-silicon bond.

The related tetrakis compound, tetrakis(dimethylsilyl)-silane (LIII) was prepared by a similar technique involving a reaction between chlorodimethylsilane, silicon tetrachloride and lithium:[1]

$$\mathrm{SiCl_4} + 4\mathrm{H(CH_3)_2SiCl} + 8\mathrm{Li} \longrightarrow \underset{\text{LIII}}{\left[\mathrm{H(CH_3)_2Si}\right]_4\mathrm{Si}} + 8\mathrm{LiCl}$$

Tetrakis(dimethylphenylsilyl)silane (LIV), the first phenylated tetrasilyl-substituted polysilane, was prepared by two independent methods:

<u>Method A</u> the reaction between silicon tetrachloride

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[1] Dr. J. M. Holmes, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the preparation of tetrakis(dimethylsilyl)silane. Private communication. 1964.

chlorodimethylphenylsilane and lithium in THF,

$$\mathrm{SiCl_4} + 4\mathrm{Ph(CH_3)_2SiCl} + 8\mathrm{Li} \xrightarrow{\mathrm{THF}} \underset{\mathrm{LIV}}{\left[\mathrm{Ph(CH_3)_2Si}\right]_4\mathrm{Si}} + \begin{array}{r}\mathrm{Ph(CH_3)_2Si}\\ |\\ \mathrm{Ph(CH_3)_2Si}\end{array}$$

and

Method B the reaction between dimethylphenylsilyllithium and silicon tetrachloride in THF:ether.

$$\mathrm{SiCl_4} + 4\mathrm{Ph(CH_3)_2SiLi} \xrightarrow{\mathrm{THF:ether}} \mathrm{LIV} + \mathrm{Ph(CH_3)_2SiSi(CH_3)_2Ph}$$

Reaction A was carried out at room temperature in THF and the yield of LIV obtained by this procedure was quite low (3.5%). The conditions used in Method B, namely, a low temperature (-40°) and THF:ether as solvents, seemed more favorable for the formation of LIV, giving a 14.6% yield.

It seems that the low yield of LIV might be due to steric crowding of atoms in the molecule imposed by the four bulky phenyl groups, and that a high order of orientation of reactant species is necessary for the formation of the product. The rigorous steric requirement presumably increases the probability of some secondary reactions leading to the formation of the less sterically hindered compound, 1, 1, 2, 2-tetramethyl-1, 2-diphenyldisilane, in high yields (60-65%). Presumably these reactions involve:

(1) cleavage of an intermediate disilane by silyllithium,

$$\mathrm{Ph(CH_3)_2SiLi} + \mathrm{SiCl_4} \longrightarrow \mathrm{Ph(CH_3)_2SiSiCl_3} + \mathrm{LiCl}$$

$$\mathrm{Ph(CH_3)_2SiLi} + \mathrm{Ph(CH_3)_2SiSiCl_3} \longrightarrow \mathrm{Ph(CH_3)_2SiSi(CH_3)_2Ph} + \mathrm{LiSiCl_3}$$

and

(2) direct coupling of chlorodimethylphenylsilane and dimethylphenylsilyllithium.

$Ph(CH_3)_2SiCl + Ph(CH_3)_2SiLi \longrightarrow Ph(CH_3)_2SiSi(CH_3)_2Ph + LiCl$

Dimethylphenylsilyllithium could be formed by Method A from the reaction between chlorodimethylphenylsilane and lithium (104), and a halogen-metal interconversion reaction between chlorodimethylphenylsilane and silicon tetrachloride (Method B) would afford chlorodimethylphenylsilane (96).

Thus, it is not surprising that tris(triphenylsilyl)silane was prepared in a 4.4% yield and attempts to synthesize tetrakis(triphenylsilyl)silane gave only hexaphenyldisilane, triphenylsilane and some polymeric material (30). It is also noteworthy that whereas tetrakis(dimethylsilyl)methane and tetrakis(trimethylsilyl)methane can be prepared by a reaction between a chlorosilane, polyhalo methane and magnesium, application of the technique to the attempted preparation of tetrakis(dimethylphenylsilyl)methane gave good yields of bis-(dimethylphenylsilyl)methane; and no tetrakis compound was isolated (12). It appears that the formation of tetrasilyl-substituted methanes and silanes is limited by the number of large groups bonded to the peripheral silicon atoms.

The linear-chain isomer of LIV, octamethyl-2, 2, 4, 4-tetraphenylpentasilane (LV), was prepared by the following sequence of reactions:

$$\left[(CH_3)_3Si\right]_2SiPh_2 + Br_2 \xrightarrow{\text{benzene}} (CH_3)_3Si\text{-}SiPh_2Br + (CH_3)_3SiBr$$

$$2\ (CH_3)_3Si\text{-}SiPh_2Br + 2Na \xrightarrow{\text{xylene}} (CH_3)_3Si\text{-}SiPh_2SiPh_2\text{-}Si(CH_3)_3 + 2NaBr$$

$$(CH_3)_3Si\text{-}SiPh_2SiPh_2\text{-}Si(CH_3)_3 + 2Li \xrightarrow{\text{THF}} 2(CH_3)_3Si\text{-}SiPh_2Li$$

$$\overset{2}{2}\ (CH_3)_3Si\text{-}SiPh_2Li + (CH_3)_2SiCl_2 \xrightarrow{-40^\circ} \left[(CH_3)_3Si\text{-}SiPh_2\right]_2Si(CH_3)_2 + 2LiCl$$

LV

Reactions of Tetrakis(trimethylsilyl)silane

The silicon-silicon bond of XLIX is cleaved by a wide variety of reagents. When XLIX was treated with sodium-potassium (Na/K) alloy a dark yellowish-green colored solution was observed. It was possible to characterize tris(trimethylsilyl)silylpotassium (LVI), but not any trimethylsilylpotassium, by derivatives:

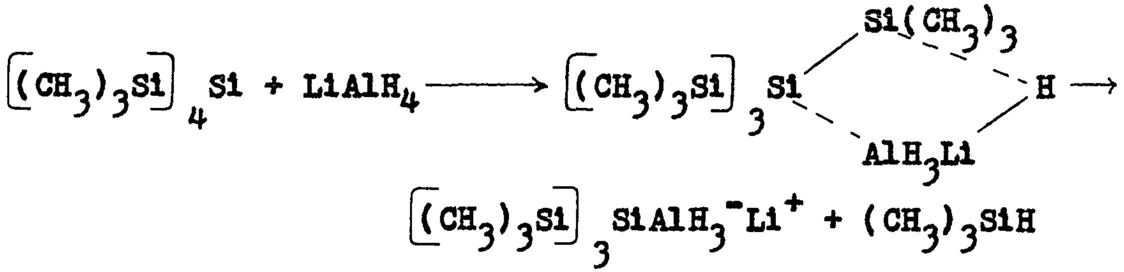
$$\begin{tikzcd}
XLIX + Na/K \arrow[r] & \underset{\text{LVI}}{\left[(CH_3)_3Si\right]_3SiK} \arrow[r, "H_3O^+"] \arrow[d, "Ph(CH_3)_2SiCl"] & \underset{\text{LVII}}{\left[(CH_3)_3Si\right]_3SiH} \\
& \underset{\text{LVIIIb}}{\left[(CH_3)_3Si\right]_3SiSi(CH_3)_2Ph} &
\end{tikzcd}$$

For instance, v.p.c. of a hydrolyzed aliquot of the yellowish-green solution, subsequent to the removal of the excess alloy by amalgamation, showed the presence of only XLIX and tris-(trimethylsilyl)silane (LVII) in a ratio of 3:1. When the solution was derivatized with chlorodimethylphenylsilane, v.p.c. of the hydrolyzed reaction mixture indicated the presence of only XLIX and tris(trimethylsilyl)(dimethylphenylsilyl)silane (LVIIIb) in a ratio of 4:1. From the reaction mixture, it was possible to isolate and characterize a small amount of LVIIIb. If trimethylsilylpotassium were formed, a metalation reaction of the solvent by this presumably reactive compound, giving the volatile trimethylsilane, could be invoked to explain the absence of the expected derivative, pentamethylphenyldisilane. No reaction was observed between XLIX and sodium-potassium alloy in ether.

It is particularly interesting that the silicon-silicon bond of XLIX is cleaved by lithium aluminum hydride ($LiAlH_4$) but not by lithium metal, to give LVII subsequent to acid hydrolysis:

$$\text{XLIX} + LiAlH_4 \xrightarrow{H_3O^+} \text{LVII}$$

Presumably, the mechanism of cleavage by $LiAlH_4$ involves the formation of a pentacovalent intermediate:



It is reasonable to postulate that the silyl-aluminum compound might decompose to give tris(trimethylsilyl)silyllithium (LI) and aluminum hydride:

$$\left[(CH_3)_3Si\right]_3SiAlH_3^-Li^+ \longrightarrow \underset{\text{LI}}{\left[(CH_3)_3Si\right]_3SiLi} + AlH_3$$

However, chemical evidence in a related reaction involving the cleavage of hexaphenyldisilane by $LiAlH_4$ suggests that a silyl-aluminum bond does exist and is favored over a possible decomposition reaction to give a silyllithium compound (75).

While no silyl-Grignard reagent has been isolated, its intermediate formation has been proposed by several workers (105, 106, 107, 108). A transient silyl-Grignard reagent, tris(trimethylsilyl)silylmagnesium chloride, may be responsible for the formation of hexakis(trimethylsilyl)disilane (L) from the reaction of tris(trimethylsilyl)chlorosilane (LII) and magnesium (102):

$$\underset{\text{LII}}{\left[(CH_3)_3Si\right]_3SiCl} + Mg \longrightarrow \left[(CH_3)_3Si\right]_3SiMgCl \xrightarrow{\text{LII}} \text{XLIX}$$

$$+ \underset{\text{L}}{\left[(CH_3)_3Si\right]_3Si-Si\left[Si(CH_3)_3\right]_3}$$

Compound XLIX did not react with phenylmagnesium bromide or methylmagnesium iodide,[1] while the respective organolithium compounds afforded good yields of LI [see Preparation and reactions of tris(trimethylsilyl)silyllithium].

When XLIX was treated with either one mole of bromine in benzene or carbon tetrachloride, or phosphorus pentachloride in benzene, sym-tetrachloroethane or carbon tetrachloride, 60-65% recovery of XLIX was realized; but no other products have so far been isolated. In reactions between

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[1] R. L. Harrell, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the reaction between tetrakis(trimethylsilyl)silane and methylmagnesium iodide. Private communication. 1966.

XLIX and nucleophilic reagents, such as aqueous piperidine or sodium methoxide in methanol, none of XLIX was recovered. The products of these reactions were mixtures of compounds which were not separated; but their infrared spectra indicated the presence of Si-O and Si-OH groups. Presumably, the primary cleavage products of these reactions are more reactive than the tetrakis compound. This could well be a consequence of the highly symmetrical structure of XLIX, a compound which can be envisaged as a sphere of twelve chemically equivalent methyl groups surrounding the silicon skeleton. The less symmetrical compounds, tris(trimethylsilyl)-methylsilane (XLVII), and tris(trimethylsilyl)silane (LVII) undergo cleavage of the silicon-silicon bond by phosphorus pentachloride or chlorine in carbon tetrachloride, affording good yields of chlorinated derivatives (109):

$$\underset{\text{XLVII}}{\left[(CH_3)_3Si\right]_3SiCH_3} + PCl_5 \text{ or } Cl_2 \xrightarrow{CCl_4} \left[(CH_3)_3Si\right]_2Si(CH_3)Cl$$

$$\underset{\text{LVII}}{\left[(CH_3)_3Si\right]_3SiH} + PCl_5 \text{ or } Cl_2 \xrightarrow{CCl_4} \left[(CH_3)_3Si\right]_2SiCl_2$$

Compound XLIX does not react with concentrated sulfuric acid at room temperature, probably because of its insolubility in this solvent. However, at an elevated temperature (ca. 130°), the reaction proceeds at an uncontrollable rate, leading to an explosion.

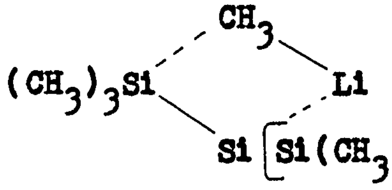
Tris(trimethylsilyl)silyllithium

Preparations and reactions of tris(trimethylsilyl)silyllithium

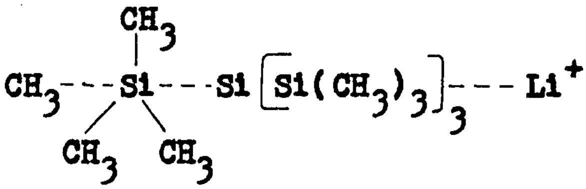
An attractive route to the synthesis of tris(trimethylsilyl)silyllithium (LI) involved a cleavage reaction of a silicon-silicon bond of XLIX by methyllithium in THF:ether (4:1):

$$\text{XLIX} + CH_3Li \xrightarrow{\text{THF:ether (4:1)}} \underset{\text{LI}}{\left[(CH_3)_3Si\right]_3SiLi} + (CH_3)_4Si$$

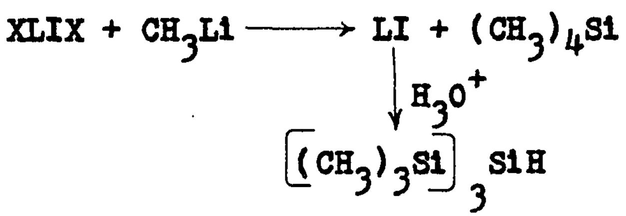
The procedure was suitable for solutions of preparative usefulness since the volatile tetramethylsilane (b.p. 26.6°) was removed by distillation at room temperature and compound LI was obtained in excellent yields (ca. 90%), essentially free of any contaminant. The mechanism of this reaction can be reasonably depicted as one involving a nucleophilic attack by methyllithium on a peripheral silicon atom of XLIX followed by elimination of the tris(trimethylsilyl)silyl group via a pentacovalent intermediate:



and/or



From a reaction between XLIX and methyllithium, tetramethylsilane was collected in a Dry Ice-acetone trap and was identified by v.p.c., prior to acid hydrolysis of the reaction mixture to give tris(trimethylsilyl)silane (LVII):



$$\begin{tikzcd} \mathrm{XLIX} + CH_3Li \arrow[r] & \mathrm{LI} \arrow[d, "H_3O^+"] & + (CH_3)_4Si \\ & {[(CH_3)_3Si]_3SiH} & \end{tikzcd}$$

LVII

An attempted synthesis of LVII by a direct method involving a reaction between chlorotrimethylsilane, trichlorosilane and lithium, lead to the formation of XLIX as the only isolable product. However, the trisilyl-substituted structure of LVII was unequivocally estabilshed by the equivalency of the silicon-methyl protons and an integrated area ratio of its nuclear magnetic resonance spectrum (n.m.r.): the Si-CH_3/Si-H was 27 (calcd. 27). Definitive evidence for the existence of a silicon-lithium bond prior to acid hydrolysis was afforded by derivatization of LI with trimethyl phosphate which gave tris(trimethylsilyl)methylsilane (XLVII):

$$\mathrm{LI} + [CH_3O]_3PO \longrightarrow [(CH_3)_3Si]_3SiCH_3$$

XLVII

The formation of XLVII in a high yield (78%) clearly excludes any significant metalation reactions of the solvent to give LVII prior to derivatization with trimethyl phosphate. Compound XLVII was also prepared directly from a reaction between chlorotrimethylsilane, methyltrichlorosilane and lithium.

$$CH_3SiCl_3 + 3(CH_3)_3SiCl + 6Li \longrightarrow \mathrm{XLVII} + 6LiCl$$

The reaction of LI with chlorodimethylsilane, chlorodimethylphenylsilane, chlorodiphenylmethylsilane, and chlorotriphenylsilane gave tris(trimethylsilyl)(dimethylsilyl)silane (LVIIIa), tris(trimethylsilyl)(dimethylphenylsilyl)silane (LVIIIb), tris(trimethylsilyl)(diphenylmethylsilyl)silane (LVIIIc), and tris(trimethylsilyl)(triphenylsilyl)silane (LVIIId), respectively:

$$\mathrm{LI} + R^1R^2R^3SiCl \longrightarrow \left[(CH_3)_3Si\right]_3SiSiR^1R^2R^3$$

LVIIIa, $R^1 = R^2 = CH_3$; $R^3 = H$
LVIIIb, $R^1 = R^2 = CH_3$; $R^3 = Ph$
LVIIIc, $R^1 = R^2 = Ph$; $R^3 = CH_3$
LVIIId, $R^1 = R^2 = R^3 = Ph$

With the exception of LVIIIa, which decomposes on standing, all of the derivatives are stable in air. The formation of compounds, LVIIIa, LVIIIc and LVIIId, in excellent yields substantiates the novel structure of LI.

The reaction between compounds LI and bromobenzene afforded a 55% yield of XLIX and none of the expected derivative, tris(trimethylsilyl)phenylsilane, was isolated:

$$\mathrm{LI} + PhBr \longrightarrow \mathrm{XLIX}$$

Presumably, the bromosilane, tris(trimethylsilyl)bromosilane (LIX), and phenyllithium were formed by a halogen-metal interconversion reaction:

$$\mathrm{LI} + PhBr \longrightarrow \underset{\mathrm{LIX}}{\left[(CH_3)_3Si\right]_3SiBr} + PhLi$$

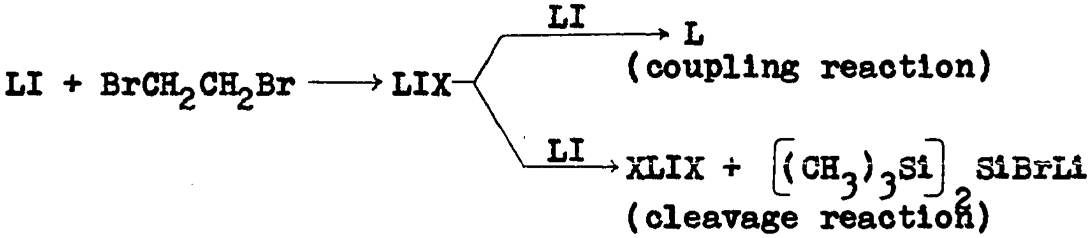
A cleavage reaction of the silicon-silicon bond of LIX or products formed in coupling reactions, L and tris(trimethylsilyl)phenylsilane, by LI would give XLIX:

$$\mathrm{LI + LIX \longrightarrow XLIX + \left[(CH_3)_3Si\right]_2SiBrLi}$$

$$\mathrm{LI + LIX \longrightarrow L \xrightarrow{LI} XLIX + LiSi\left[Si(CH_3)_3\right]_2Si\left[Si(CH_3)_3\right]_3}$$

$$\mathrm{PhLi + LIX \longrightarrow \left[(CH_3)_3Si\right]_3SiPh \xrightarrow{LI} XLIX + \left[(CH_3)_3Si\right]_2SiPhLi}$$

Convincing evidence for a halogen-metal interconversion reaction, leading to the formation of LIX, is afforded by the reaction between LI and 1,2-dibromoethane, giving XLIX and L (102).



Derivatization of LI with carbon dioxide afforded a white crystalline solid which appears to be tris(trimethylsilyl)-silanecarboxylic acid (LX):

$$\mathrm{LI + CO_2 \xrightarrow{H_3O^+} \underset{LX}{\left[(CH_3)_3Si\right]_3SiCOOH}}$$

Difficulties in the purification of this compound were expected since all known organosilicon compounds, in which the silicon atom is attached directly to a carboxylic acid or ester group, undergo decomposition under a variety of conditions, such as heat, base and polar solvents, with the elimination of the carbonyl as carbon monoxide (110, 111). Compound LX could not be isolated by base extraction because it was decomposed by base, with the elimination of carbon monoxide, affording a mixture of products. Work-up without base extraction afforded a compound which turned to a cloudy liquid at 131° and liquid truned clear at 136°. Decomposition with the evolution of carbon monoxide was observed at 214°. The infrared spectrum (Figure 3) shows absorptions at 5.95 μ and 6.13 μ for c = 0, and a broad absorption at 3.07-3.65 μ for the carboxylic-OH group. There are no absorptions indicative of Si-H or Si-O. The n.m.r. spectrum (Figure 3) indicates that this compound is impure. Despite the presence of only two peaks, a singlet for the silicon-methyl protons at 9.72 t and for the carboxylic acid proton at -0.02 t, an integrated area ratio for $Si-CH_3/COOH$ was 35 (calcd. 27). Treatment of this compound LX with diazomethane afforded methyl tris(trimethylsilyl)silanecarboxylate (LXI):

$$\mathrm{LX} + CH_2N_2 \longrightarrow \underset{\mathrm{LXI}}{\left[(CH_3)_3Si\right]_3SiCOOCH_3} + N_2$$

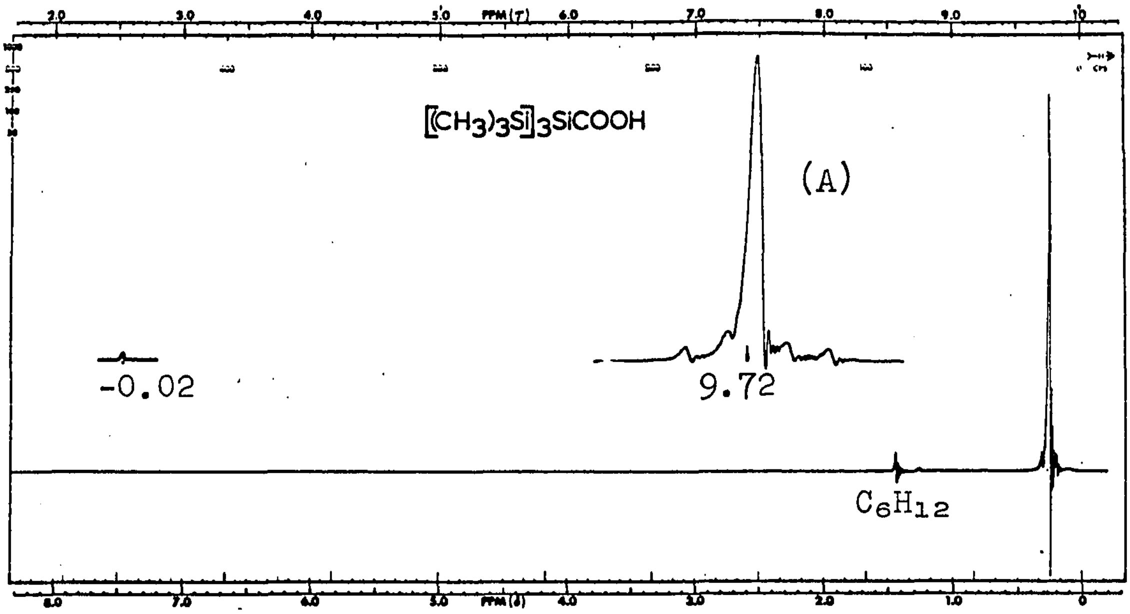
Like LX, compound LXI was shown to be impure by its n.m.r. spectrum (Figure 4) which contains a singlet for the methoxy protons at 6.43 t, and singlets for silicon-methyl protons at 9.78 t and 9.72 t. An integrated area ratio for $SiCH_3/-OCH_3$ was 18 (calcd. 9). The infrared spectrum (Figure 3) showed absorptions at 6.0 μ and 6.13 μ for c = 0, and 9.13 μ for c - 0.

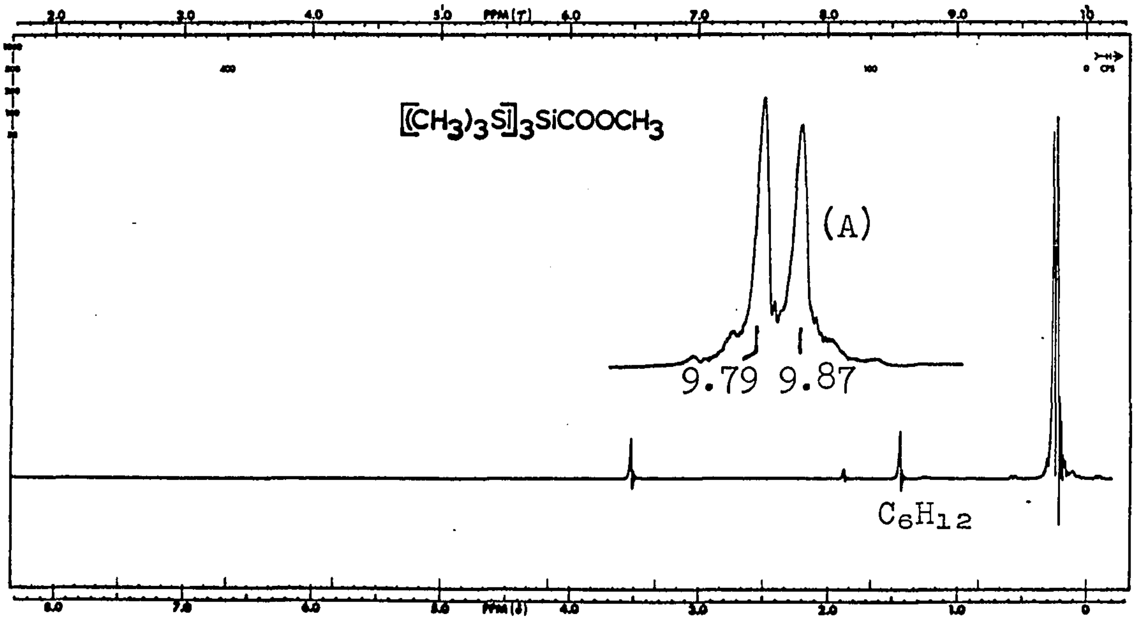
Under similar conditions, an attempt to prepare bis(trimethylsilyl)silylenedilithium (LXII) by the reaction between XLIX and two equivalents of methyllithium gave only LI, subsequent to acid hydrolysis of the reaction mixture. Similarly, diphenylsilylenedilithium (LXIII) was not detected in a

Figure 3. Nuclear magnetic resonance spectra

Top: Tris(trimethylsilyl)silanecarboxylic acid (LX)

Bottom: Methyl tris(trimethylsilyl)silanecarboxylate (LXI)


PPM (τ)
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
[(CH3)3Si]3SiCOOH
(A)
-0.02
9.72
C6H12
PPM (δ)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0


PPM (τ)
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
[(CH3)3Si]3SiCOOCH3
(A)
9.79
9.87
C6H12
PPM (δ)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

reaction between octaphenyltrisilane and lithium (30).

$$\left[(CH_3)_3Si\right]_2SiLi_2 \qquad\qquad Ph_2SiLi_2$$

LXII LXIII

Other approaches to the synthesis of LI involved a cleavage reaction of a silicon-silicon bond of XLIX by phenyllithium in THF:ether (4:1) and triphenylsilyllithium in THF:

$$XLIX + RLi \longrightarrow LI + RSi(CH_3)_3$$

$$R = Ph \text{ or } Ph_3Si$$

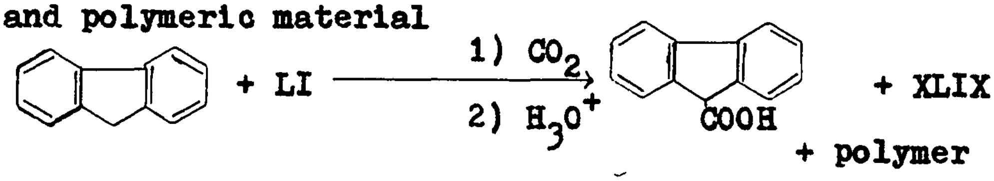
Subsequent to acid hydrolysis of the reaction mixture, characterization of the expected cleavage fragments, LI and $RSi(CH_3)_3$, served to substantiate the proposed mechanism. For synthetic purposes, the preparation of LI by these methods were not attractive because the yields were lower than those obtained by the use of methyllithium and solutions are contaminated with the respective cleavage fragment $\left[RSi(CH_3)_3\right]$.

It is noteworthy, however, that the color of these silyllithium solutions varied markedly with the nature of RLi. For instance, methyllithium gave a pale greenish-yellow colored solution, phenyllithium a red, and triphenylsilyllithium a purple. Presumably, pale greenish-yellow is the true color of THF:ether solutions of LI since methyllithium is grayish-white. Therefore, hues associated with the use of the colored phenyllithium and triphenylsilyllithium might be a consequence of complementary mixing.

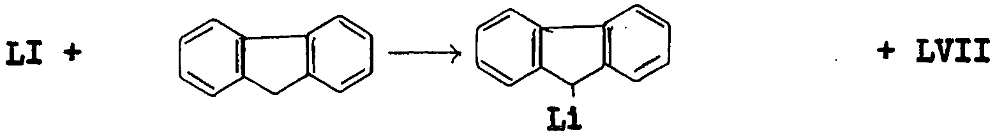
π-Bonding in tris(trimethylsilyl)silyllithium

Comparative metalation reactions (112) and kinetic studies (113) have recently been used to estimate the relative reactivity of Group IVB lithium compounds. The uncommon, symmetrical arrangement of the three trimethylsilyl groups bonded to the silicon-bearing lithium atom, together with failures to prepare stable solutions of trimethylsilyllithium (40, 50, 51), prompted a study to determine the importance of dative π-bonding between contiguous silicon atoms in LI, by these procedures.

Compound LI was prepared in the usual manner by a reaction between XLIX and methyllithium in THF:ether (4:1). In this investigation, the volatile tetramethylsilane and ether were removed by distillation. The high purity of the resulting THF solution of the silyllithium compound was indicated by v.p.c. of a hydrolyzed aliquot and the n.m.r. spectrum of the silyllithium solution. Treatment of LI with fluorene at room temperature in THF afforded, subsequent to carbonation and acid hydrolysis, compound fluorene-9-carboxylic acid, XLIX and polymeric material



The high yield of compound XLIX and the absence of the expected (LVII) can be reasonably explained by the following reactions:



$$\text{LVII} + \text{LI} \longrightarrow \text{XLIX} + \left[(CH_3)_3Si\right]_2SiHLi$$

The reaction of LI ann LVII, affording a ca. 90% yield of XLIX (102), supports this mechanism, and therefore, a yield of greater than 50% of fluorene-9-carboxylic acid suggests that fluorene is also metalated by other lithium species. Although the reaction of LI and fluorene presumably involves cleavage of the silicon-silicon bonds, together with metalation by other lithium species, it was of interest to compare the relative reactivity of a THF solution of this compound with that of other silyllithiums. The results are summarized in Table 7. From the data given in the Table, it appears that the reactivity of pentaphenyldisilanyllithium is about equal to that of triphenylsilyllithium. However, the reaction of this compound, a polysilane, and fluorene is probably similar to that of LI, involving silicon-silicon bond cleavage and metalation by other lithium species. The reaction of tetrakis(dimethylsilyl)silyllithium and fluorene is probably even more complicated because of the reactive Si-H bonds.[1]

A kinetic investigation of the rate of reaction of compound LI with THF at room temperature was also undertaken by periodically titrating an aliquot of the silyllithium solution

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[1] Dr. J. M. Holmes, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the reaction of tris(dimethylsilyl)silyllithium with fluorene. Private communication. 1965.

Table 7. Metalation of fluorene[a]

R_3SiLi	Yield of fluorene-9-carboxylic acid, %		
	Run 1	Run 2	Average
$Ph_3SiSiPh_2Li$[b]	44.6	39.8	42.2
Ph_3SiLi	44.5	37.7	41.1
$[(CH_3)_3Si]_3SiLi$[c]	51.0	44.4	47.7
$[H(CH_3)_2Si]_3SiLi$[d]	54.0	52.4	53.2
$Ph(CH_3)_2SiLi$	61.6	54.7	58.1
$Ph_2(CH_3)SiLi$	65.2	57.4	61.3

[a] The silyllithium compounds were allowed to metalate fluorene under identical conditions of time, temperature, and concentrations of reagents, followed by carbonation to produce fluorene-9-carboxylic acid (112).

[b] A third run with this reagent gave a yield of 20.3% which was not included in the average.

[c] See Experimental.

[d] Dr. J. M. Holmes, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the relative reactivity of tris(dimethylsilyl)silyllithium. Private communication. 1965.

using the procedure of double titration (90). The results are tabulated in Table 5 and the first-order rate constant is given in Table 7. A plot of time against the logarithm of molarity (Figure 4) reveals that the reaction of LI with THF follows pseudo first-order kinetics up to ca. 900 hours at which time the rate increases considerably. The deviation, observed with all of the compounds listed in Table 8, has been attributed to a possible catalytic effect of one of the

Figure 4. Plot of -molarity against time for tris(trimethylsilyl)-silyllithium (LI)

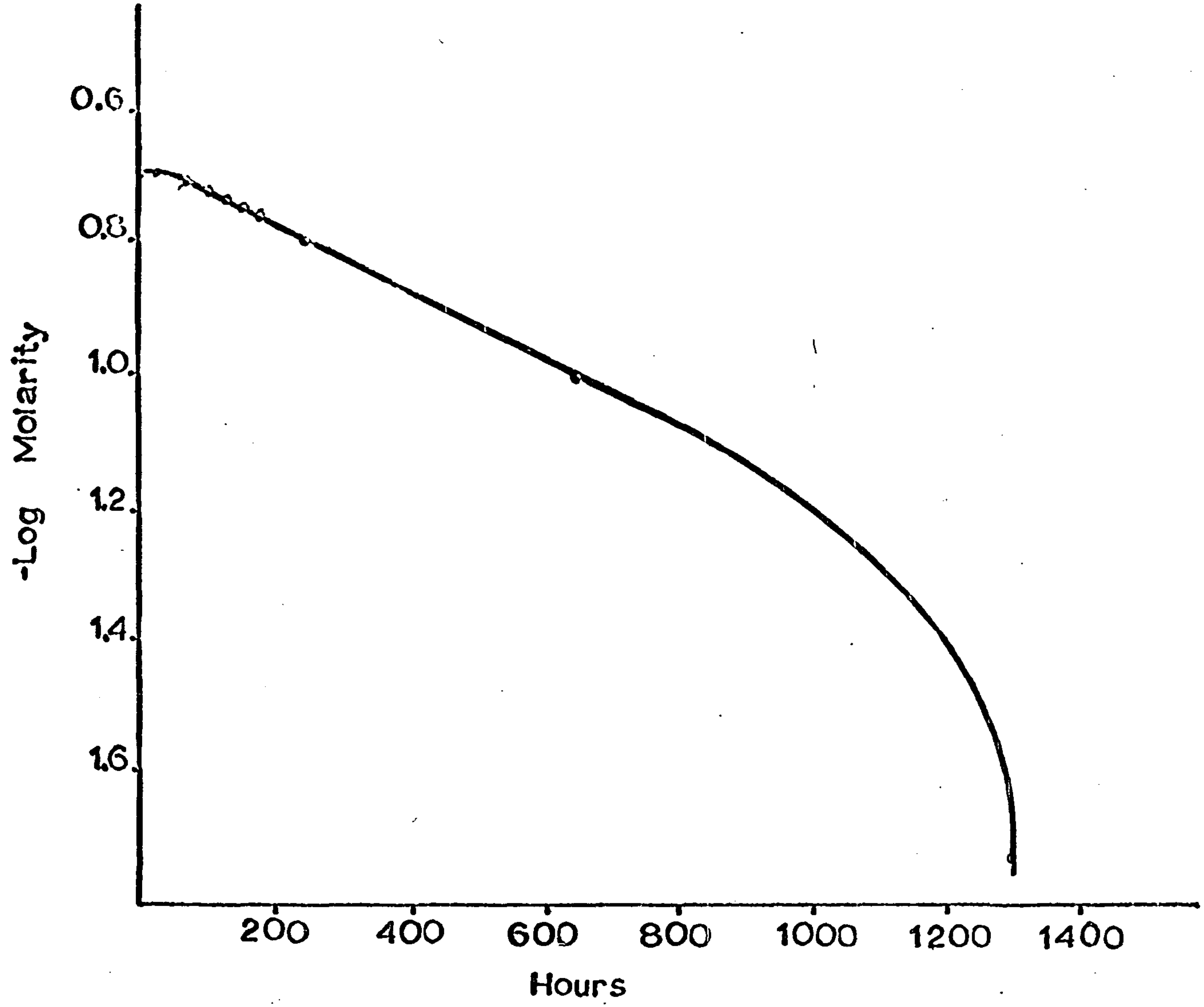

-Log Molarity
0.6
0.8
1.0
1.2
1.4
1.6
200
400
600
800
1000
1200
1400
Hours

Table 8. First-order rate constants for the reactions between some silyllithiums and THF[a]

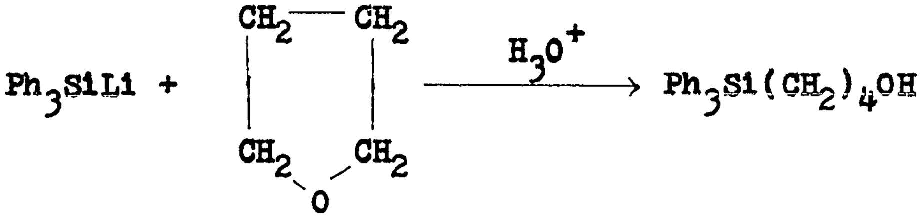
R_3SiLi	$k \times 10^{-3}$ hours^{-1}
$[H(CH_3)_2Si]_3SiLi$[b]	0.0
Ph_3SiLi	0.84
$[(CH_3)_3Si]_3SiLi$[c]	1.3
$Ph(CH_3)_2SiLi$	1.4
$Ph_2(CH_3)SiLi$	2.1

[a] Determinations were made at room temperature by periodic titration of an aliquot of the solution. Double titration using allyl bromide was the technique employed (113).

[b] No decrease in molarity of the active species during 400 hours [Dr. J. M. Holmes, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the reaction of tris(dimethylsilyl)silyllithium with THF. Private communication. 1965].

[c] See the Experimental part.

reaction products (112). In a similar manner as its reaction with fluorene, the treatment of LI with THF probably involves, in addition to ring opening, cleavage of the silicon-silicon bonds to give other lithium species. For instance, the reaction of LI and THF afforded compound XLIX and a liquid mixture of two compounds (determined by v.p.c.). The infrared spectrum of this mixture showed a strong absorption at 5.75 μ (probably c = 0), and medium absorptions at 9.45 μ and 9.7 μ (Si-O): there were no absorptions indicative of C-OH. Moreover, it is not known whether all of the other compounds listed in Table 8 undergo reaction by the same mechanism or afford the same types of products as the reaction of triphenylsilyllithium and THF (114):



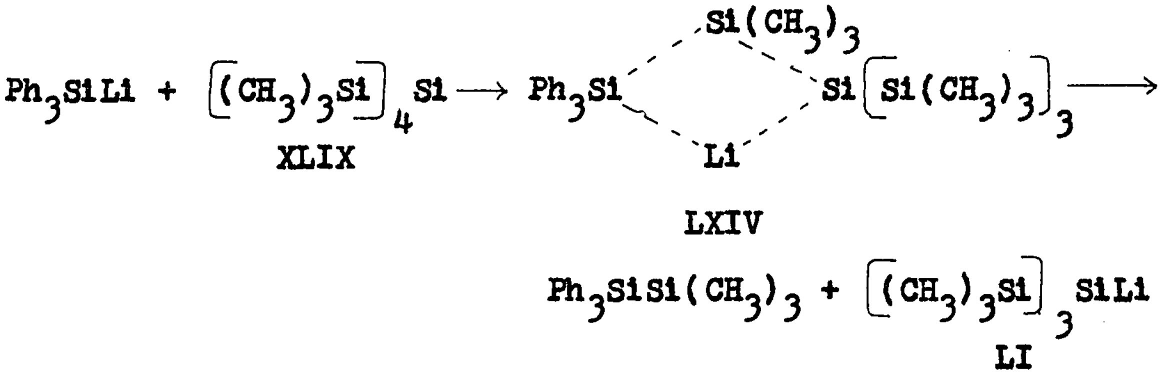
Results obtained by the metalation and kinetic studies indicate the following order of decreasing reactivity:

$$Ph_2(CH_3)SiLi \geqq Ph(CH_3)_2SiLi > [H(CH_3)_2Si]_3SiLi > [(CH_3)_3Si]_3SiLi > Ph_3SiLi \approx Ph_3SiSoPh_2SiLi$$

The greater reactivity observed for diphenylmethylsilyllithium as opposed to dimethylphenylsilyllithium is surprising since the reverse order would be expected on the basis of the electronic effect of the substituents. A sequence based on cleavage reactions of the silicon-silicon bond is in agreement with theoretical expectations (115):

$$Ph(CH_3)_2SiLi > Ph_2(CH_3)SiLi > Ph_3SiLi$$

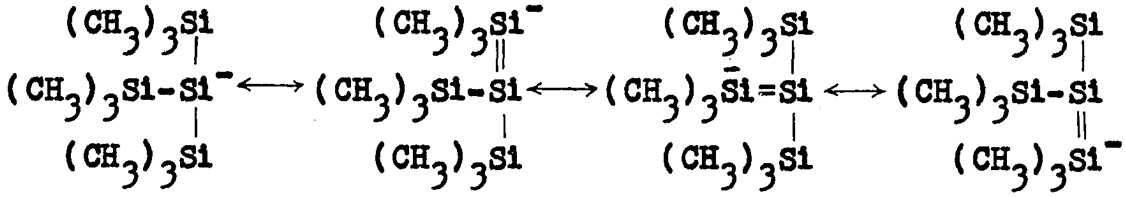
Since different disilanes were involved, the reactivity of the silicon-silicon bond was assumed to be constant with varying substituents. On the basis of this assumption, a similar investigation was undertaken to determine the relative reactivity of triphenylsilyllithium and LI. To achieve this objective, the reaction below seemed suitable for the following reasons: (1) the reactants and products are very soluble and stable in THF; (2) secondary cleavage reactions to give other silyllithium compounds, for example, trimethylsilyllithium and bis(trimethylsilyl)silylenedilithium, are quite unlikely because of their high reactivity; (3) the forward and reverse reactions presumably proceed through the same intermediate, LXIV, and therefore, steric factors involved in these reactions are about the same.



When compound XLIX was treated with triphenylsilyllithium, a 70% yield of 1, 1, 1-trimethyl-2, 2, 2-triphenyldisilane was isolated. The reaction was followed by v.p.c. of a hydrolyzed aliquot of the reaction mixture and there appeared to be no change in the relative ratios of tris(trimethylsilyl)silane (LVII) and XLIX after ca. 36 hours. The reverse reaction, between compound LI and 1, 1, 1-trimethyl-2, 2, 2-triphenyldisilane, afforded a 75% recovery of the disilane. It appears that no appreciable equilibria exist and that triphenylsilyllithium is more reactive than compound LI.

Although the results obtained by these methods are not definitive, they seem to imply, however, that the reactivity of compound LI is comparable to or even less than that of triphenylsilyllithium. Secondary cleavage reactions of the silicon-silicon bond and subsequent reaction by presumably more reactive, less branched species were evident in reactions involving THF and fluorene. Due to their presence, the reactivity of LI is undoubtedly less than the experimental data suggest. In the treatment of triphenylsilyllithium with XLIX, which indicated a lower order of reactivity for LI, the reactivity of the silicon-silicon bonds of the polysilane compounds, XLIX and 1, 1, 1-trimethyl-2, 2, 2-triphenyldisilane, were assumed to be about equal.

The reactivity of triphenyl- and other phenylated silyllithium compounds has been attributed to delocalization of the negative charge over the aromatic ring(s) whereas trialkylsilyllithiums have at most only a transitory existence (40, 50, 51). A reason for the enhanced stability of LI becomes apparent if one compares its structure with that of the reactive trimethylsilyllithium compound. On the basis of inductive effects alone, one would expect trimethylsilyllithium to be less reactive than LI since a trimethylsilyl group is a better electron donor than a methyl group (40). However, a unique type of conjugation is possible for compound LI, but not trimethylsilyllithium, involving delocalization of the negative charge over the vacant d-orbitals on the adjacent silicon atoms (dπ - pπ bonding):

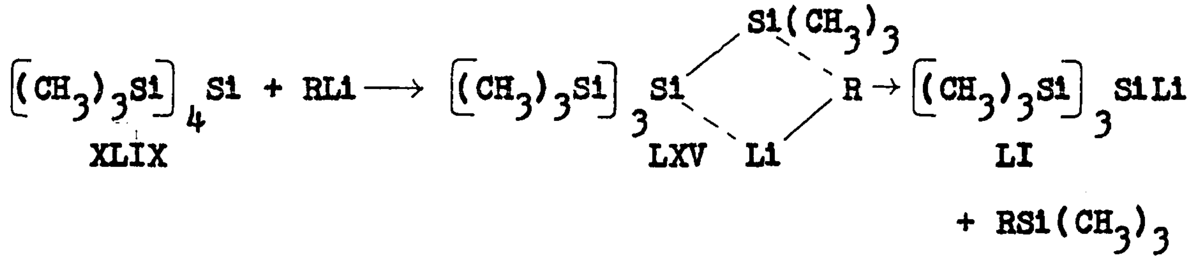


$$\begin{array}{r}(CH_3)_3Si\\ |\;\;\\ (CH_3)_3Si-Si^-\\ |\;\;\\ (CH_3)_3Si\end{array} \longleftrightarrow \begin{array}{r}(CH_3)_3Si^-\\ \|\;\;\\ (CH_3)_3Si-Si\\ |\;\;\\ (CH_3)_3Si\end{array} \longleftrightarrow \begin{array}{r}(CH_3)_3Si\\ |\;\;\\ (CH_3)_3\overset{-}{Si}=Si\\ |\;\;\\ (CH_3)_3Si\end{array} \longleftrightarrow \begin{array}{r}(CH_3)_3Si\\ |\;\;\\ (CH_3)_3Si-Si\\ \|\;\;\\ (CH_3)_3Si^-\end{array}$$

The conjugative (-T) effect requires the multiple bonding of the vacant 3d-orbitals of the peripheral silicon atoms (the electron acceptors) with the 3p-orbital of the lithium-bearing silicon atom (the electron donor). As a consequence, it is not surprising that compound LI cannot be prepared by the reaction between XLIX and lithium metal which would require the formation of the very reactive trimethylsilyllithium (40):

$$\text{XLIX} + \text{Li} \longrightarrow \text{LI} + (CH_3)_3SiLi$$

The formation of LI, on the other hand, by reactions of XLIX with RLi compounds (R = CH_3, Ph and Ph_3Si), probably involves a nucleophilic attack by the R group on a peripheral silicon atom of XLIX, followed by the elimination of the tris(trimethylsilyl)silyl group <u>via</u> a pentacovalent intermediate (LXV) giving stable products:



XLIX LXV LI

The relative ease of formation of some silyllithium compounds by a cleavage reaction of the silicon-silicon bond of the respective polysilane compounds with methyllithium, suggests the following order of decreasing reactivity:

$$(CH_3)_3SiSi(CH_3)_2Li > \left[(CH_3)_3Si\right]_2Si(CH_3)Li > \left[(CH_3)_3Si\right]_3SiLi$$

The parallelism between the number of trimethylsilyl groups bonded to the silicon atom and the reactivity of the silanion is further evidence for dative π-bonding in LI.

The most compelling evidence for π-bonding in compound LI is afforded by the reaction of LVII with n-butyllithium. Since triphenylsilane reacted with n-butyllithium in THF:ether to give n-butyltriphenylsilane, it was expected that LVII would react in a similar manner.

$$Ph_3SiH + \underline{n}\text{-}C_4H_9Li \xrightarrow{\text{THF:ether}} Ph_3SiC_4H_9$$

However, treatment of LVII with n-butyllithium in THF:ether prior to derivatization of the greenish-yellow solution with chlorotriphenylsilane afforded LVIIId and XLIX, indicating the formation of LI.

$$\text{LVII} + \underline{n}\text{-}C_4H_9Li \longrightarrow \text{LI} \xrightarrow{Ph_3SiCl} \text{LVIIId}$$

The reactions of LVII with other RLi compounds (R = CH_3 and Ph) in ether were very slow and it was difficult to determine whether compound LI and/or the product of a coupling reaction, $(CH_3)_3Si\quad {}_3SiR$, was formed. Triphenylsilane reacted readily with RLi compounds (R = CH_3, Ph, or n-C_4H_9) in ether, giving Ph_3SiR and LiH (116), while triphenylgermane (116) and triphenylmethane (116) afforded the respective lithium compounds:

$$Ph_3SiH + RLi \xrightarrow{\text{ether}} Ph_3SiR + LiH$$

$$Ph_3CH + RLi \xrightarrow{\text{ether}} Ph_3CLi + RH$$

$$Ph_3GeH + RLi \xrightarrow{\text{ether}} Ph_3GeLi + RH$$

The formation of LI from a reaction between LVII and n-butyllithium, indicating that the hydrogen atom of LVII is more protonic than the hydrogen atom of triphenylsilane, is probably associated with dative π-bonding in the LI molecule. In other words, the negative charge in compound LI is delocalized to a greater extent than that in triphenylsilyllithium, leading to a more electronegative silicon atom and consequently a more acidic silicon-hydrogen bond. The central silicon atom in LVII is, however, less electronegative than the carbon atom in triphenylmethane or the germanium atom in triphenylgermane, since LVII reacts very slowly with *n*-butyllithium in ether whereas triphenylmethane and triphenylgermane reacts readily. The difference in the mode of reactions of these Group IV hydrogen compounds has been explained in terms of the relative polarizations of the E-H bonds (E = C, Si or Ge)(116). In triphenylsilane, the hydrogen atom has more hydridic character than the hydrogen atoms of triphenylmethane and triphenylgermane, indicating the following polarizations:

$$\overset{\delta+}{Ph_3Si} - \overset{\delta-}{H} \qquad \overset{\delta-}{Ph_3C} - \overset{\delta+}{H} \qquad \overset{\delta-}{Ph_3Ge} - \overset{\delta+}{H}$$

The proposed polarizations are consistent with the relative electronegativities of the E atoms which, in decreasing order, are (116): $C > Ge > Si$.

The ultraviolet and n.m.r. spectra of LI are in agreement with the proposed dative π-bonding. The ultraviolet spectrum (THF) consists of bonds at λ_{max} 295 mμ ($\varepsilon \sim 22{,}000$), 370 mμ ($\varepsilon \sim 10{,}000$) and a shoulder at 236 mμ ($\varepsilon \sim 6{,}000$) whereas its derivatives, compounds XLIX and LVII, showed no absorption (cyclohexane) above 210 mμ. Undoubtedly, this marked bathochromic shift implies considerable resonance stabilization of the excited state (117). Thus, it is suspected that similar resonance also exists, but to a lesser extent, in the ground state (117). The ^{1}H n.m.r. spectrum of LI (THF), consisting of a singlet at 9.93 t, represents a 0.2 ppm upfield chemical shift with respect to LVII (9.93 t). In view of the ultraviolet spectral data, the small diamagnetic shielding of the silicon-methyl protons of LI seems to be associated with this type of conjugation (dπ-pπ bonding). The ultraviolet and n.m.r. spectra of triphenylsilyllithium have been explained in terms of dative (pπ-pπ) bonding involving delocalization of the negative charge over the phenyl rings (118).

Color Test I of tris(trimethylsilyl)silyllithium

In general, organosilylmetallic compounds give a positive Color Test I, indicating that they are sufficiently reactive to add to Michler's ketone (50). The reaction product is hydrolyzed with water prior to oxidation with a few drops of 0.2% solution of iodine in glacial acetic acid to give a blue or green color. If the main product is a reducing agent, a larger amount of iodine must be added before the leuco-base is oxidized to the dye (a substituted Malachite green). Using this procedure, compound LI gave a negative test. It is reasonable to assume that LI adds to Michler's ketone since its reactivity is comparable to that of triphenylsilyllithium. However, the hydrolysis product of LI, compound

LVII, has been found to reduce carbon tetrachloride at room temperature to give LII and chloroform (109):

$$\mathrm{LVII} + CCl_4 \longrightarrow \mathrm{LII} + CHCl_3$$

Thus, a study was undertaken to determine the applicability of Color Test I to detect the presence of LI using more concentrated solutions of iodine in glacial acetic acid. It was found that LI gave a positive test when a few drops of a 20 to 30% solution of iodine in glacial acetic acid was used as the oxidizing agent.

Bis(trimethylsilyl)methylsilyllithium

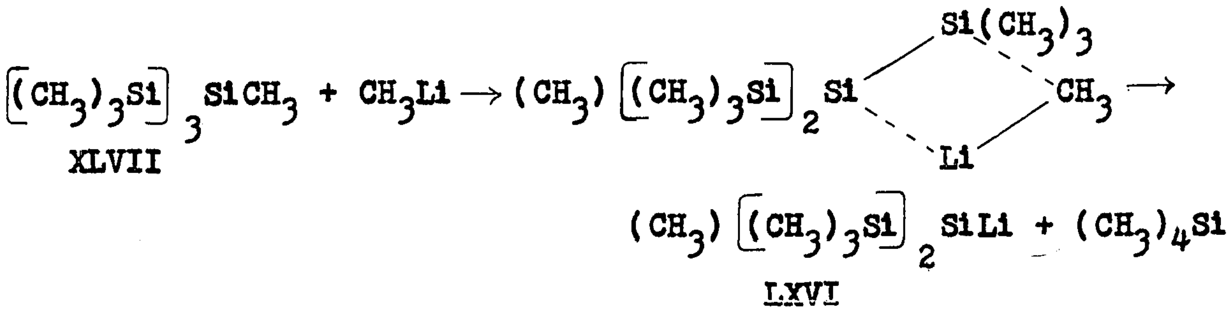
Preparation and reactions of bis(trimethylsilyl)methylsilyllithium

Encouraged by the successful preparation of LI in high yields and its usefulness as a precursor to other novel tetrasilyl-substituted compounds, a similar study was undertaken with bis(trimethylsilyl)methylsilyllithium (LXVI).

Compound LXVI was prepared by a cleavage reaction of a silicon-silicon bond of XLVII by methyllithium in THF:

$$\underset{\mathrm{XLVII}}{\left[(CH_3)_3Si\right]_3SiCH_3} + CH_3Li \xrightarrow{\mathrm{THF}} \underset{\mathrm{LXVI}}{(CH_3)\left[(CH_3)_3Si\right]_2SiLi} + (CH_3)_4Si$$

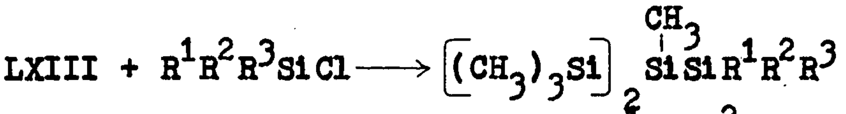
The mechanism of this reaction can be reasonably depicted as one involving a nucleophilic attack by methyllithium on a peripheral silicon atom of XLVII followed by the displacement of the bis(trimethylsilyl)methylsilyl group *via* a pentacovalent intermediate:



In view of the high volatility of bis(trimethylsilyl)methylsilane (LXVII), the hydrolysis product of LXVI and XLVII, the extent of the reaction between XLVII and methyllithium is rapidly and conveniently followed by v.p.c. of hydrolyzed aliquots of the silyllithium solution:

$$\text{XLVII} + CH_3Li \longrightarrow \text{LXVI} \xrightarrow{H_3O^+} \underset{\text{LXVII}}{(CH_3)\left[(CH_3)_3Si\right]_2SiH}$$

Like LI, compound LXVI was found to undergo a variety of reactions, affording derivatives in good yields. The reaction of LXVI with chlorodimethylphenylsilane, chlorodiphenylmethylsilane and chlorotriphenylsilane gave bis(trimethylsilyl)(dimethylphenylsilyl)methylsilane (LXVIIIa), bis(trimethylsilyl)(diphenylmethylsilyl)methylsilane (LXVIIIb), and bis(trimethylsilyl)(triphenylsilyl)methylsilane (LXVIIIc), respectively:



$$\text{LXIII} + R^1R^2R^3SiCl \longrightarrow \left[(CH_3)_3Si\right]_2\overset{CH_3}{\overset{|}{Si}}SiR^1R^2R^3$$

LXVIIIa, $R^1 = R^2 = CH_3$; $R^3 = Ph$
LXVIIIb, $R^1 = R^2 = Ph$; $R^3 = CH_3$
LXVIIIc, $R^1 = R^2 = R^3 = Ph$

The formation of these compounds in high yield served to substantiate the novel structure of LXVI.

Derivatization of LXVI with carbon dioxide afforded bis(trimethylsilyl)methylsilanecarboxylic acid (LXIX):

$$\text{LXVI} + CO_2 \xrightarrow{H_3O^+} (CH_3)\left[(CH_3)_3Si\right]_2SiCOOH$$

LXIX

Compound LXIX, a white crystalline solid, melts at 90-92° and decomposes above 170° to give sym-tetrakis(trimethylsilyl)dimethyldisiloxane (LXX) and carbon monoxide:

$$\text{LXIX} \longrightarrow (CH_3)\left[(CH_3)_3Si\right]_2Si\text{-}O\text{-}Si\left[Si(CH_3)_3\right]_2(CH_3) + CO$$

LXX

Unlike tris(trimethylsilyl)silanecarboxylic acid (LX), compound LXIX was found to be considerably more stable and could be purified by crystallization. Work-up of the reaction mixture without base extraction gave a 68% yield of pure LXIX, whereas work-up involving base extraction gave a 50% yield. Treatment of LXIX with diazomethane afforded methyl bis(trimethylsilyl)methylsilanecarboxylate (LXXI):

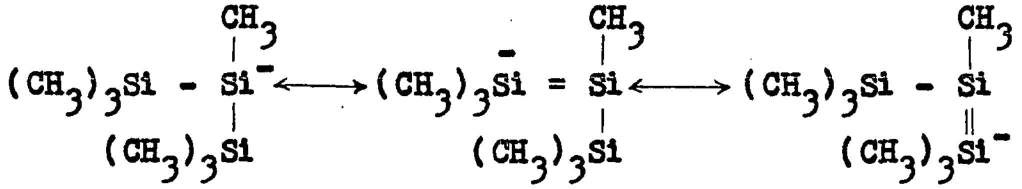
$$\text{LXIX} + CH_2N_2 \longrightarrow (CH_3)\left[(CH_3)_3Si\right]_2SiCOOCH_3$$

LXXI

Compound LXXI, a liquid was purified by distillation under reduced pressure without decomposition. No reaction was observed between LXIX and 95% ethanol.

π-Bonding in bis(trimethylsilyl)methylsilyllithium

The relative reactivity of LXVI, based on the metalation of fluorene (112), appears to be greater than that of diphenylmethylsilyllithium: compound LXVI gave an average yield of 66.5% of fluorene-9-carboxylic acid whereas diphenylmethylsilyllithium gave a 61.3% yield of the acid.[1] The results are not definitive since secondary reactions involving the cleavage of the silicon-silicon bonds are undoubtedly involved, presumably affording more reactive silyllithium compounds which could also methalate fluorene. However, on the basis of the inductive effects alone, one would expect trimethylsilyllithium to be less reactive than LXVI since a trimethylsilyl group is a better electron donor than a methyl group (40). Presumably compound LXVI is stabilized by delocalization of the negative charge over the vacant d-orbitals on the adjacent silicon atoms (dπ-pπ bonding), a type of conjugation that is not possible with the structure of trimethylsilyllithium:



$$(CH_3)_3Si - \underset{\underset{(CH_3)_3Si}{|}}{\overset{\overset{CH_3}{|}}{Si^-}} \longleftrightarrow (CH_3)_3Si = \underset{\underset{(CH_3)_3Si}{|}}{\overset{\overset{CH_3}{|}}{\overset{-}{Si}}} \longleftrightarrow (CH_3)_3Si - \underset{\underset{(CH_3)_3Si^-}{\|}}{\overset{\overset{CH_3}{|}}{Si}}$$

The greater reactivity observed for compound LXVI as compared to tris(trimethylsilyl)silyllithium (LI) presumably reflects the parallelism between the number of trimethylsilyl groups bonded to silicon and the stability of the silanion.

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[1] For a complete tabulation of the relative reactivity of other silyllithiums as determined by this method, see π-bonding in tris(trimethylsilyl)silyllithium.

Physical Properties of Some Tri- and Tetrasilyl-substituted Organopolysilanes

Tetrakis(trimethylsilyl)silane (XLIX) is a white, crystalline, waxy, odorless solid. It crystallizes from organic solvents and sublimes in the form of fern-shaped crystals. Compound XLIX is very soluble in most common organic solvents, sparingly soluble in ethanol and insoluble in methanol.

Unexpected for a permethylated polysilane, compound XLIX is an extraordinarily high melting solid and it exhibits a high degree of volatility. In a sealed tube, it melts at 319-321° without decomposition, and does not melt in an open tube but sublimes readily and completely below 265°. Even upon standing at room temperature and atmospheric pressure, it sublimes very slowly. The uncommonly high melting point of XLIX is associated with its branched-chain and its very high degree of symmetry. Timmerman (119) has suggested that branched-chain molecules of high symmetry can absorb a considerable amount of rotational energy, before their thermal vibration cause a disruption in the crystal lattice. That is, the more symmetrical a molecule, the more rotational freedom it can attain in the solid state before melting. This causes a relatively large gain in entropy in the solid state as the temperature increases and the entropy of fusion correspondingly decreases (120, 121, 122). For example, hexamethylethane melts at 377.1° K and has a liquid interval of only 2.8°. Compound XLIX and adamantane represent extreme examples of the effect of symmetry on the melting point. Like compound XLIX, adamantane does not melt under ordinary conditions but sublimes readily. In a sealed tube, adamantane melts at 268°. The known isomers of XLIX and adamantane have considerably lower melting points: isocyclene, 4, 7, 7-trimethyltricyclo[2.2.0]heptane, an isomer of adamantane, has the next highest melting point of 119° and a boiling point of 150-151°; and dodecamethylpentasilane, the only known isomer of XLIX, has a boiling point of 268° (44). The great disparity between the melting point of adamantane and its isomer, and XLIX and its isomer, is undoubtedly associated with their high symmetry which is best depicted by molecular models as a sphere. It is noteworthy that compound XLIX melts appreciably higher than some of its related highly symmetrical derivatives: namely, tetrakis(dimethylsilyl)silane (LIII) 40-42° [1] and tetrakis(dimethylphenylsilyl)silane (LIV) m.p. 133-135 .

Another interesting thermal property exhibited by XLIX is that it appears to undergo a phase transition to another solid form at 170-180°. Similar behavior is displayed by other highly symmetrical molecules; for example, adamantane undergoes a phase transition at 208.62° K (123) and tetrakis(trimethylsilyl)methane (IX) at 195-210° (12). The

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[1] Dr. J. M. Holmes, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the melting point of tetrakis(dimethylsilyl)silane. Private communication. 1965.

transition is probably of the pseudo-rotational-reorientation type (123). That is, the transition presumably involves an increase in molecular freedom in which the molecules rotate more freely, or assume different, random orientation on the lattice sites of the high temperature form.

Compound XLIX also possesses extra thermal stability: it is stable above 400°.

The melting point behavior of some tetrasilyl-substituted derivatives of LI are particularly noteworthy. For example, tris(trimethylsilyl)(dimethylphenylsilyl)silane (LVIIIb), tris(trimethylsilyl)(diphenylmethylsilyl)silane (LVIIIc), and tris(trimethylsilyl)(triphenylsilyl)silane (LVIIId) appear to have melting point ranges instead of sharp melting points, and thus seem to resemble the melting behavior of liquid crystals (124). That is, these compounds form a turbid liquid which appears to be a mixture of liquid and solid at some temperature just before the liquid becomes clear. The appearance of a turbid liquid was recorded as the transition point and the melting point was the development of a clear liquid. Presumably, the transition point represents the temperature at which the solid and crystalline-liquid phases are in equilibrium at a pressure of one atmosphere, and the melting point is the temperature at which crystalline-liquid and isotropic liquid phases are in equilibrium (124).[1]

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[1] For the melting, transition and solidification points of these compounds, see the Experimental part.

The tri- and other tetrasilyl-substituted compounds have normal boiling and melting points.

The relative volatilities of some tri- and tetrasilyl-substituted compounds have been determined. The order of decreasing volatility as determined by their ease of sublimation and v.p.c. is as follows:

$\left[(CH_3)_3Si\right]_3SiH > \left[(CH_3)_3Si\right]_3SiCH_3 > \left[H(CH_3)_2Si\right]_3SiSi(CH_3)_2H >$
$\left[(CH_3)_3Si\right]_3SiSi(CH_3)_2H > \left[(CH_3)_3Si\right]_3SiSiCH_3)_3 >$
$\left[(CH_3)_3Si\right]_3SiSi(CH_3)_2Ph > \left[(CH_3)_3Si\right]_3SiSi(CH_3)\ Ph_2 >$
$\left[(CH_3)_3Si\right]_3SiSiPh_3 > \left[Ph(CH_3)_2Si\right]_4Si$

The replacement of a hydrogen in the organic group by a heavier atom decreases the volatility of the organometallic compound (125). Thus, the trisilyl-substituted compounds are more volatile than the tetrasilyl-substituted derivatives. It has also been reported that substitution of branched-chain groups for straight-chain increases the volatility of the compound (125). The above scheme elegantly illustrates these observations. Indeed, in view of their high molecular weights and melting points, these compounds exhibit a surprisingly high degree of volatility. In addition to their ease of sublimation, the purity of these compounds is conveniently ascertained by v.p.c.

Spectral Properties of Some Tri- and Tetrasilyl-substituted Organopolysilanes

Infrared spectral properties

The infrared spectrum of the tri- and tetrasilyl-substituted polysilanes shows the expected prominent peaks below 12 u, and above this region each compound exhibits a characteristic absorption pattern.

A stretching abosrption at 4.87 µ for the tertiary Si-H group of tris(trimethylsilyl)silane (LVII) represents a shift to a lower stretching frequency, relative to the usual (4.4-4.8 u) absorption region. This shift appears to be characteristic of tertiary Si-H compounds in general (see Table 9).

Table 9. Spectral data of some polysilanes containing a tertiary Si-H group

Compound	Si-H, u (solvent)	Si-H, t[a] (solvent)
$[Ph_3Si]_3SiH$[b]	4.85 (CCl_4)	5.89 (CCl_4)
$[Ph(CH_3)_2Si]_3SiH$[b]	4.88 (CCl_4)	7.32 (CS_2)
$[H(CH_3)_2Si]_3SiH$	4,75, 4.80 (CCl_4)	7.57 (CS_2)
$[(CH_3)_3Si]_3SiH$[c,d]	4.87 (CCl_4)	7.73 (CS_2)

[a] Good integration values were obtained for all compounds.

[b] Reported in ref. 126.

[c] Spectra must be determined quickly due to reaction with the solvent.

[d] A strong band at 5.53 µ developed during the determination of the spectra, apparently due to the formation of phosgene(127).

If one considers a series of primary, secondary and tertiary Si-H compounds, the shift is even more apparent. The data for such a series formed by successive replacement of phenyl groups by trimethylsilyl groups are summarized in Table 10.

Table 10. Spectral data for a series of primary, secondary and tertiary Si-H compounds

Compound	Si-H, µ (solvent)	Si-H, t (solvent)
$Ph_2[(CH_3)_3Si]SiH$[a]	4.77 (CCl_4)	5.20 (CCl_4)
$Ph[(CH_3)_3Si]_2SiH$[a]	4.83 (CCl_4)	6.40 (CCl_4)
$[(CH_3)_3Si]_3SiH$	4.87 (CCl_4)	7.73 (CS_2)

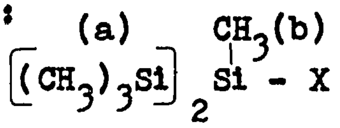
[a] Reported in ref. 126.

N.m.r. spectral properties

The n.m.r chemical shifts for the Si-H have been found to vary with substituents on silicon (88). The marked diamagnetic shift for the Si-H proton of LVII is given in Tables 9 and 10. This shift appears to be general for tertiary Si-H compounds and is probably associated with the electronegativity of the peripheral silicon groups. The n.m.r. spectral data for compounds containing the tertiary Si-H group are given in Table 9. With the highly phenylated derivative, $[Ph_3Si]_3SiH$, this shift appears to be opposed by the paramagnetic shielding properties of the phenyl groups.

The pronounced diamagnetic shielding observed for the Si-H proton, as one proceeds from a primary to a tertiary structure, is illustrated in Table 10. The diamagnetic shifts observed with LVII and $[Ph(CH_3)_2Si]_3SiH$, in particular, together with their facile reaction with carbon tetrachloride suggest an enhanced reactivity of the Si-H group.

The n.m.r. spectra, particularly of the silicon-methyl region, of some trisilyl-substituted polysilane compounds are rather interesting. The area ratio, even after expanding the spectrum over a 50 c.p.s. sweep width, for an analytical sample of tris(trimethylsilyl)methylsilane (XLVII) was found to be 6:1 which is in poor agreement with the calculated value of 9:1 (Figure 5). The poor value is probably due to the very close chemical shift of the two different types of silicon-methyl protons, and therefore the intensity of absorption of one is partially masked by the other. This effect is also observed with some of the other related trisilyl-substituted compounds, and its magnitude appears to be dependent upon the substituent (X) bonded to the central silicon atom:



$$\overset{(a)}{[(CH_3)_3Si]_2}\overset{CH_3(b)}{\overset{|}{Si}} - X$$

where X = $-Si(CH_3)_2Ph$ (LXVIIIa), $-Si(CH_3)Ph_2$ (LXVIIIb), $-SiPh_3$ (LXVIIIc), $-COOH$ (LXIX) or $-COOCH_3$ (LXXI)

For example, at a sweep width of 500 c.p.s it was not possible to integrate the area for protons a or b separately with respect to those of X in LXVIIIa, whereas LXVIIIb and

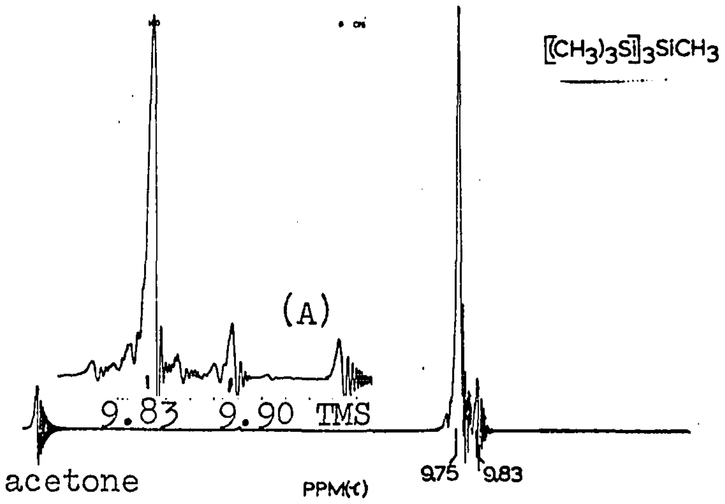
Figure 5. Nuclear magnetic resonance spectra

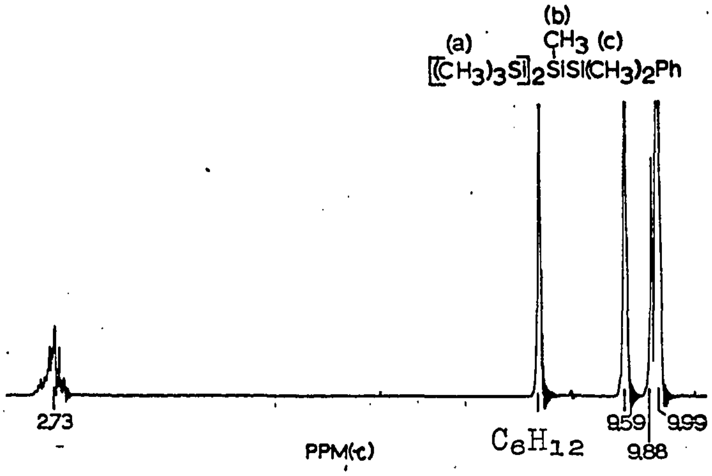
Top: Tris(trimethylsilyl)methylsilane (XLVII) in carbon disulfide as solvent

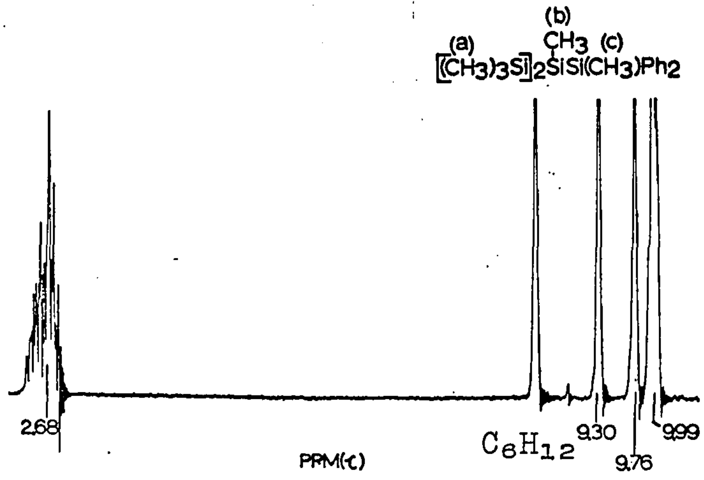
(A) Expansion of the silicon-methyl region over a sweep width of 50 c.p.s. Acetone was used as the solvent

Middle: Bis(trimethylsilyl)(dimethylphenylsilyl)-methylsilane (LXVIIIa)

Bottom: Bis(trimethylsilyl)(diphenylmethylsilyl)-methylsilane (LXVIIIb)


[(CH3)3Si]3SiCH3
(A)
9.83
9.90
TMS
acetone
PPM(τ)
9.75
9.83


(b)
(a)
CH3 (c)
[(CH3)3Si]2SiSi(CH3)2Ph
2.73
PPM(τ)
C6H12
9.59
9.88
9.99


(b)
(a)
CH3 (c)
[(CH3)3Si]2SiSi(CH3)Ph2
2.68
PPM(τ)
C6H12
9.30
9.76
9.99

LXVIIIc gave good values (Figures 5 and 6). Also, at a sweep width of 500 c.p.s., protons a and b of LXIX and LXXI could not be integrated separately with respect to those of X, but at a sweep width of 50 c.p.s. good values were obtained (Figure 6). It is noteworthy that the internal silicon-methyl protons (3 protons at 9.90 t) are shielded relative to the external protons (27 protons at 9,83 t in XLVII. In general, the terminal silicon-methyl protons are deshielded relative to the internal protons (5, 74) and this shielding effect is observed in the spectrum of the other trisilyl-substituted compounds, LXVIIIa, LXVIIIb, LXVIIIc, LXIX and LXXI.

Ultraviolet spectral properties

Recent sutdies have led to the conclusion that the ultraviolet spectra of polysilanes promise to be extremely useful in their characterization (83, 128). An inspection of Table 11 reveals that the branched-chain (B) compounds absorb at lower wavelengths than the related linear-chain (L) derivatives but have higher molar absorptivities. Interestingly, λ_{max} does not increase with successive substitution of the methyl group of LXVIIIa to give LXVIIIb, and LXVIIIc, respectively. However, an increase in the molar absorptivity is observed. A similar phenomenon is observed with the related tetrasilyl-substituted polysilane compounds: LVIIIa, LVIIIb and LVIIIc.

Figure 6. Nuclear magnetic resonance spectra

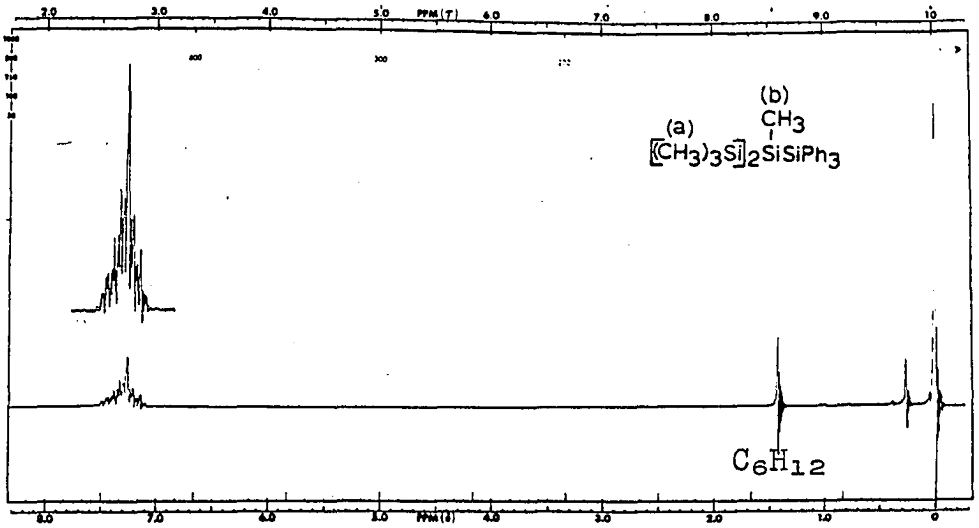
Top: Bis(trimethylsilyl)(triphenylsilyl)methylsilane (LXVIIIc)

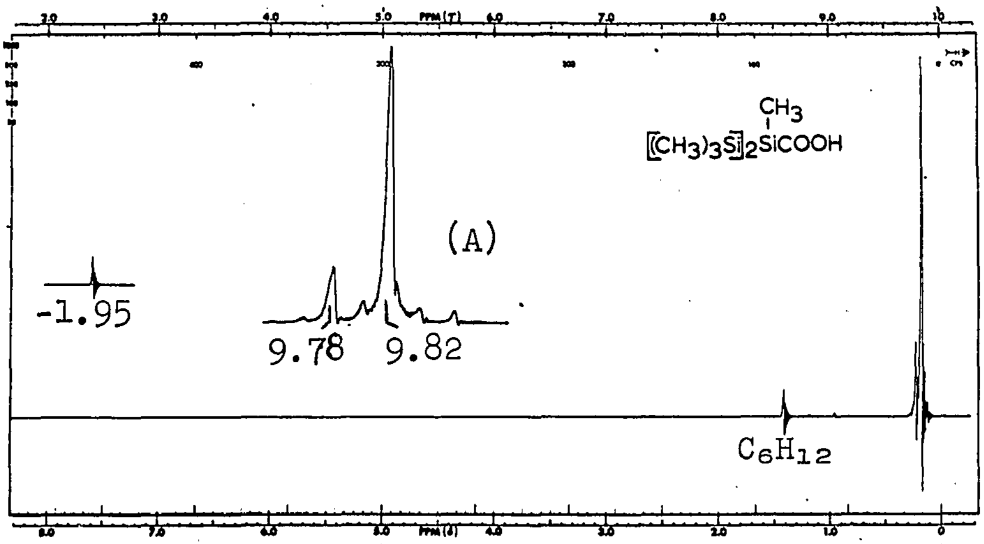
Middle: Bis(trimethylsilyl)methylsilanecarboxylic acid (LXIX)

(A) Expansion of the silicon-methyl region over a sweep width of 50 c.p.s.

Bottom: Methyl bis(trimethylsilyl)methylsilanecarboxylate (LXXI)

(A) expansion of the silicon-methyl region over a sweep width of 50 c.p.s.


2.0 3.0 4.0 5.0 PPM (τ) 6.0 7.0 8.0 9.0 10
(a) (b)
$[(CH_3)_3Si]_2Si(CH_3)SiPh_3$
C₆H₁₂
8.0 7.0 6.0 5.0 PPM (δ) 4.0 3.0 2.0 1.0 0


2.0 3.0 4.0 5.0 PPM (τ) 6.0 7.0 8.0 9.0 10
$[(CH_3)_3Si]_2Si(CH_3)COOH$
(A)
-1.95
9.78
9.82
C₆H₁₂
8.0 7.0 6.0 5.0 PPM (δ) 4.0 3.0 2.0 1.0 0

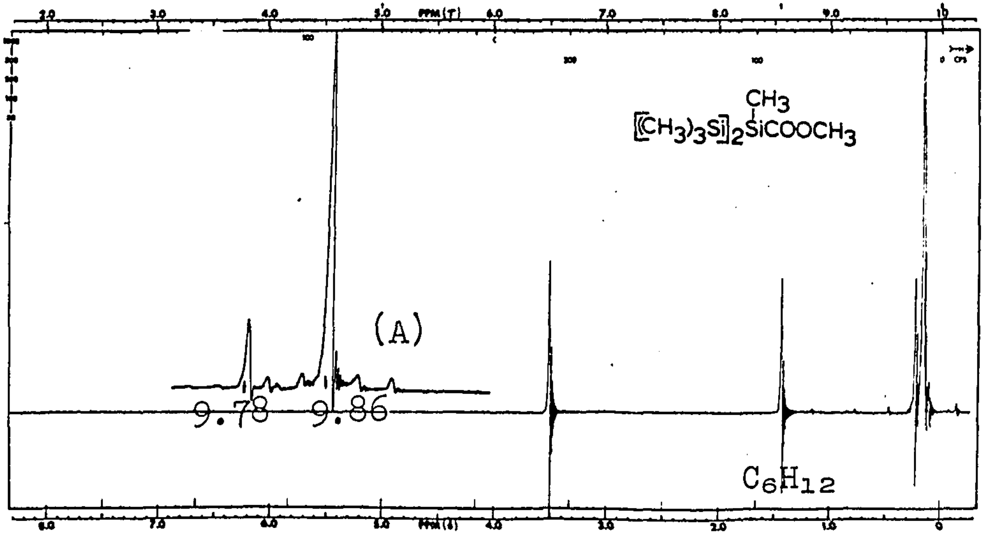

2.0 3.0 4.0 5.0 PPM (τ) 6.0 7.0 8.0 9.0 10
$[(CH_3)_3Si]_2Si(CH_3)COOCH_3$
(A)
9.78
9.86
C₆H₁₂
8.0 7.0 6.0 5.0 PPM (δ) 4.0 3.0 2.0 1.0 0

Table 11. Ultraviolet spectral data of some branched-chain polysilanes and straight-chain derivatives

Compounds	λ_{max}, mμ (cyclohexane)	Molar absorptivity	Reference
A. Trisilyl-substituted compounds			
B $[(CH_3)_3Si]_3SiH$	none above 210		-a
B $[(CH_3)_3Si]_3SiCH_3$	207.5 (shoulder)	13,100	-a
B $[Ph(CH_3)_2Si]_3SiH$	237	30,200	-b
B $[Ph(CH_3)_2Si]_3SiCH_3$	242.5	39,200	-a
B $[Ph_3Si]_3SiH$	240 (shoulder)	41,900	-b
L $Ph(SiPh_2)_3Ph$	254	32,200	-b
B $[(CH_3)_3Si]_3SiPh$	241	13,200	-b
L $(CH_3)_3Si[SiPh(CH_3)]Si(CH_3)_3$	243	11,150	-b
B $(CH_3)[(CH_3)_3Si]_2SiSi(CH_3)_2Ph$	237.5	13,500	-a
B $(CH_3)[(CH_3)_3Si]_2SiSi(CH_3)Ph_2$	238.5	17,400	-a
B $(CH_3)[(CH_3)_3Si]_2SiSiPh_3$	238	22,000	-a
B. Tetrasilyl-substituted compounds			
B $[(CH_3)_3Si]_4Si$	none above 210		-a
L $CH_3[Si(CH_3)_2]_3CH_3$	215	9,020	-b
B $[(CH_3)_3Si]_3SiSi(CH_3)_2Ph$	239	16,130	-a
B $[(CH_3)_3Si]_3SiSi(CH_3)Ph_2$	238	18,815	-a
B $[(CH_3)_3Si]_3SiSiPh_3$	235 (shoulder)	23,200	-a
B $[Ph(CH_3)_2Si]_4Si$	242	38,600	-a
L $Ph[Si(CH_3)_2]_3Ph$	243	18,900	-b

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[a] See the Experimental part.

[b] Reported in ref. 126.

SUMMARY

Details are provided for the preparation of tetrakis(trimethylsilyl)silane, the first tetrasilyl-substituted organopolysilane compound containing contiguous silicons, and a discussion of its properties and mechanisms of formation are presented. This compound was prepared in good yields from a reaction between silicon tetrachloride, chlorotrimethylsilane and lithium. The high melting point and ease of sublimation of the tetrakis compound have been attributed to its high degree of symmetry and its branched-chain structure. Also, unsuccessful efforts to cleave one silicon-silicon bond of tetrakis(trimethylsilyl)silane with base or halogens could well be a consequence of its highly symmetrical structure, a compound which can be envisaged as a sphere of twelve chemically equivalent methyl groups surrounding the silicon skeleton. The cleavage of one silicon-silicon bond was achieved by the reaction of tetrakis(trimethylsilyl)silane with methyllithium, phenyllithium and triphenylsilyllithium to give tris(trimethylsilyl)silyllithium, the first example of a branched-chain silanyllithium compound. Its formation in high yields represents the first stable solution of a silyllithium compound which does not contain an aryl group and is of synthetic utility. Sodium-potassium alloy and lithium aluminum hydride also effected the cleavage of a silicon-silicon bond of tetrakis(trimethylsilyl)silane.

An investigation has been made of the relative reactivity of tris(trimethylsilyl)silyllithium in an attempt to estimate the importance of $(d\pi - p\pi)$ bonding involving two contiguous silicon atoms. The procedures used were: (1) a comparative metalation reaction; (2) a kinetic study; and (3) a cleavage reaction of a silicon-silicon bond. The results are not definitive, although they seem to imply that the reactivity of tris(trimethylsilyl)silyllithium is comparable to or less than that of triphenylsilyllithium. The reactivity of tris(trimethylsilyl)silyllithium, together with its ultraviolet and n.m.r. spectra, has been explained in terms of dative π-bonding. Treatment of tris(trimethylsilyl)silane with *n*-butyllithium, affording tris(trimethylsilyl)silyllithium, seems to imply that π-bonding in the tris(trimethylsilyl)silyllithium silaniom is greater than that of triphenylsilyllithium.

A discussion of the preparation, physical and spectral properties of some derivatives of tris(trimethylsilyl)silyllithium is also presented and the synthesis of the following compounds is reported: tris(trimethylsilyl)silane, tris(trimethylsilyl)methylsilane, tris(trimethylsilyl)(dimethylphenylsilyl)silane, tris(trimethylsilyl)diphenylmethylsilyl)silane, and tris(trimethylsilyl)(triphenylsilyl)silane. Due to their facile reaction with a variety of reagents, tris(trimethylsilyl)(dimethylsilyl)silane, tris(trimethylsilyl)silanecarboxylic acid and methyl tris(trimethylsilyl)-

silanecarboxylate were prepared but not purified.

Tris(trimethylsilyl)methylsilane was prepared by a reaction between methyltrichlorosilane, chlorotrimethylsilane and lithium, and treatment of the tris compound with methyllithium afforded bis(trimethylsilyl)methylsilyllithium in good yields. A discussion of the preparation, physical and spectral properties of some derivatives of bis(trimethylsilyl)methylsilyllithium is also presented and the synthesis of the following compounds is reported: bis(trimethylsilyl)methylsilane, bis(trimethylsilyl)(dimethylphenylsilyl)silane, bis(trimethylsilyl)(dimethylphenylsilyl)silane, bis(trimethylsilyl)(triphenylsilyl)silane, bis(trimethylsilyl)-methylsilanecarboxylic acid and methyl bis(trimethylsilyl)-methylsilanecarboxylate.

Tetrakis(dimethylphenylsilyl)silane, the first phenylated tetrasilyl-substituted compound of this type, was prepared by two independent methods: (1) the reaction between silicon tetrachloride, chlorodimethylphenylsilane and lithium; and (2) the reaction between dimethylphenylsilyllithium and silicon tetrachloride.

SUGGESTIONS FOR FURTHER RESEARCH

The present investigation has opened the area of branched-chained polysilane compounds. The technique described in this work for the preparation of some branched-chain organopolysilanes: namely, tris(trimethylsilyl)methylsilane and tetrakis(trimethylsilyl)silane should be studied more intensively and extensively in terms of its applicability and mechanism. Since the reduction of the phenyl ring(s) is observed when phenylated polysilanes are used, as the polyhalo silane, it would be interesting to investigate the reactivity of some vinyl- and allyl-substituted silicon compounds to determine the nature and degree of substitution on the double bond(s). The preparation of compounds, straight- and branched-chain, in which silicon is bonded to Group III, V and other Group IV elements by this procedure seems promising.

The preparation of a variety of other branched-chain compounds and a comparison of the physical, chemical and spectral properties with those of their straight-chain analogs, to determine the effect of branching, would be of interest.

Although evidence for dative π-bonding involving contiguous silicon atoms has been presented in this work, it would be of value to attempt the preparation of some stable silanion compounds. One route which appears attractive is the reaction of some phenylated trisilyl-substituted organopolysilanes with organolithium compounds under a variety of conditions. For example, the reaction of tris(triphenylsilyl)silane with *n*-butyllithium may lead to the formation of tris(triphenylsilyl)silyllithium. This silyllithium compound should be more stable than tris(trimethylsilyl)-silyllithium because the presence of the phenyl groups provides a more extended conjugative system involving delocalization of the negative charge over the vacant d-orbitals of the silicon atoms and the phenyl rings. The preparation of some related silyl radicals might also be possible in view of the electronic effects of the silyl groups.

Since a limited number of reactions of bis(trimethylsilyl)methylsilyllithium and tris(trimethylsilyl)silyllithium was possible in this study, it would be of value to explore the reactivity of these compounds more thoroughly. Some reactions which should be carried out are: (1) addition to double and triple bonds; (2) metalation of a variety of acidic hydrocarbons; and (3) a comparison of the extent of halogen-metal interconversion with triphenylsilyllithium. For instance, despite the greater electronegativity of carbon as compared to silicon, is the tris(triphenylsilyl)silyl group a better electron acceptor than phenyl? This might be the case because in a tris(triphenylsilyl)silyl-substituted compound, electronic transitions could conceivably occur through the vacant d-orbitals on the silicon atoms and the phenyl rings, whereas in the related phenyl-substituted compound delocalization is only possible through one ring.

The reaction of bis(trimethylsilyl)methyllithium and tris(trimethylsilyl)silyllithium with inorganic salts should also be investigated.

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