Organosilicon Chemistry. Part XIX.[1] Reactions of 1,1,3,3-Tetramethyl- and 1,3-Dimethyl-1,3-diphenyl-1,3-disilacyclobutane with Chlorosilanes in the Presence of Hexachlorophatinic(IV) Acid, Tin(IV) Chloride, Trimethylsilanol, and Triphenylsilanol

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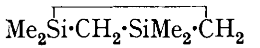
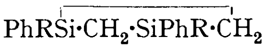
1,1,3,3-Tetramethyl-1,3-disilacyclobutane, (I), reacts with trichlorosilane or dichloro(methyl)silane in the presence of hexachloroplatinic(IV) acid to give the chlorine-exchange adducts, $Me_2SiCl{\cdot}CH_2{\cdot}SiMe_2{\cdot}CH_2{\cdot}SiHCl_2$ (80%) or $Me_2SiCl{\cdot}CH_2{\cdot}SiMe_2{\cdot}CH_2{\cdot}SiMeHCl$ (61%); in the latter reaction the hydrogen-exchange adduct, $Me_2SiH{\cdot}CH_2{\cdot}SiMe_2{\cdot}CH_2{\cdot}SiMeCl_2$ (5%), is also formed. A comparable reaction of 1,3-dimethyl-1,3-diphenyl-1,3-disilacyclobutane, (II), with trichlorosilane gives mainly polymeric material together with the chlorine-exchange adduct (10%). Both silacyclobutanes react with tin(IV) chloride in the absence of catalyst or with trimethylsilanol to afford ring-opened 1 : 1 adducts in high yield. Compound (I) also reacts with triphenylsilanol to afford hexaphenyldisiloxane and 1,1,3,3-tetramethyl-1,3-bis(trimethylsilylmethyl)disiloxane (87%); (II) does not react under comparable conditions.

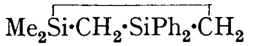
THE preparation and chemistry of 1,3-disilacyclobutanes has been reviewed recently[2] and, in previous papers in this series, the reactions of 1,1,3,3-tetramethyl-1,3-disilacyclobutane, (I),[3] with electrophiles, nucleophiles, and free radicals and the reactions of the phenyl-substituted disilacyclobutanes (II)—(IV)[1] with electrophiles and nucleophiles have been reported. In the present work the reactions of the disilacyclobutanes (I) and (II) with chlorosilanes in the presence of hexachloroplatinic(IV) acid and tin(IV) chloride and of the disilacyclobutanes (I)—(III) with silanols have been investigated.


$Me_2Si{\cdot}CH_2{\cdot}SiMe_2{\cdot}CH_2$

(I)


$PhRSi{\cdot}CH_2{\cdot}SiPhR{\cdot}CH_2$

(II) R = Me; (III) R = Ph


$Me_2Si{\cdot}CH_2{\cdot}SiPh_2{\cdot}CH_2$

(IV)

RESULTS AND DISCUSSION

Reactions with Chlorosilanes and Tin(IV) *Chloride*.—Reactions with the chlorosilanes were carried out at 88 °C, a lower temperature than that used (150 °C) in the reactions of trichlorosilane with alkylsilanes (see later),[4] in order to minimise the known polymerisations of the disilacyclobutanes in the presence of hexachloroplatinic(IV) acid or other platinum catalysts.[5,6] Disilacyclobutane (I) and trichlorosilane gave 1,1,5-trichloro-3,3,5-trimethyl-1,3,5-trisilahexane, (V) (80%), and a polymeric residue, while the reaction with dichloro(methyl)silane gave 2,6-dichloro-2,4,4-trimethyl-2,4,6-trisilaheptane, (VI) (61%), 2,2-dichloro-4,4,6-trimethyl-2,4,6-trisilaheptane, (VII) (5%), and a polymeric residue.

$Me_2SiCl{\cdot}CH_2{\cdot}SiMe_2{\cdot}CH_2{\cdot}SiHCl_2$
(V)

$Me_2SiCl{\cdot}CH_2{\cdot}SiMe_2{\cdot}CH_2{\cdot}SiMeHCl$
(VI)

$Me_2SiH{\cdot}CH_2{\cdot}SiMe_2{\cdot}CH_2{\cdot}SiMeCl_2$
(VII)

$Me_2SiH{\cdot}CH_2{\cdot}SiMe_2{\cdot}CH_2{\cdot}SiCl_3$
(VIII)

The structures of the products were determined by consideration of their ^1H n.m.r. and mass spectra. The n.m.r. spectrum of compound (V) contained absorptions at τ 9·10 (2H, d, J 3·1 Hz) and 4·16 (1H, t, J 3·1 Hz), as expected for a CH_2 and a SiH group, respectively, in the grouping $CH_2{\cdot}SiHCl_2$; if the product had been isomer (VIII) a nonet at *ca.* τ 6·0 would have been expected for the SiH absorption in the $Me_2SiH{\cdot}CH_2$ group [$J(HMe) \simeq J(HCH_2)$]. The mass spectrum of the product showed a weak parent peak and a base peak at *m/e* 167 and 165 $(M - CH_2{\cdot}SiHCl_2)^+$ thus showing conclusively the presence of the $Me_2SiCl{\cdot}CH_2{\cdot}SiMe_2$ grouping. Similarly the n.m.r. spectrum of product (VI) showed absorptions at τ 9·50 (2H, d, CH_2, J 3·4 Hz), 9·29 (3H, d, SiMe, J 3·4 Hz), and 4·85 (1H, sextet, SiH, J 3·4 Hz), as expected for a $CH_2{\cdot}SiMeHCl$ grouping, and the mass spectrum contained a base peak at *m/e* 167 and 165 $(M - CH_2{\cdot}SiMeHCl)^+$. The n.m.r. spectrum of product (VII) showed absorptions at τ 9·87 (2H, d, CH_2, J 4·0 Hz), 9·69 (12H, complex, 2 $SiMe_2$), and 5·78 (1H, nonet, SiH, J 4·0 Hz), as expected for the grouping $Me_2SiH{\cdot}CH_2{\cdot}SiMe_2$, and the mass spectrum exhibited peaks at *m/e* 247, 245, and 243 [38%, $(M - Me)^+$] and 188 [100%, $(M - Cl_2)^+$]. The polymeric material from both reactions showed

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[1] Part XVIII, A. M. Devine, P. A. Griffin, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, preceding paper.

[2] R. Damrauer, *Organometallic Chem. Rev. A*, 1972, **8**, 67.

[3] A. M. Devine, P. A. Griffin, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, *J.C.S. Dalton*, in the press.

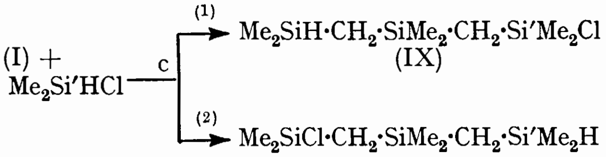
[4] K. R. Beck and R. A. Benkeser, *J. Organometallic Chem.*, 1970, **21**, 35.

[5] D. R. Weyenberg and L. E. Nelson, *J. Org. Chem.*, 1965, **30**, 2618.

[6] W. R. Bamford, J. C. Lovie, and J. A. C. Watt, *J. Chem. Soc.* (*C*), 1966, 1137.

strong bands in their i.r. spectra at 1 000—1 070 cm^{-1} indicative of linear silmethylene chains.

It has been reported[5] previously that monosilacyclobutanes and 1,3-disilacyclobutanes in the presence of platinum catalysts form 1 : 1 adducts with silicon hydrides, but the only chlorohydrosilane used in this investigation was chlorodimethylsilane and it was not possible from its reaction with disilacyclobutane (I) to determine if the product (IX) arose *via* hydrogen exchange [route (1)] or chlorine exchange [route (2)], although the former route was proposed. More recently



$$\text{(I)} + \text{Me}_2\text{Si}'\text{HCl} \xrightarrow{\text{c}} \begin{cases} \xrightarrow{(1)} \text{Me}_2\text{SiH}{\cdot}\text{CH}_2{\cdot}\text{SiMe}_2{\cdot}\text{CH}_2{\cdot}\text{Si}'\text{Me}_2\text{Cl} \quad \text{(IX)} \\ \xrightarrow{(2)} \text{Me}_2\text{SiCl}{\cdot}\text{CH}_2{\cdot}\text{SiMe}_2{\cdot}\text{CH}_2{\cdot}\text{Si}'\text{Me}_2\text{H} \end{cases}$$

it has been reported[4] that trichlorosilane reacts with alkylsilanes in the presence of hexachloroplatinic(IV) acid at *ca.* 150 °C to give products resulting from chlorine exchange with an alkyl group, *e.g.* equation (3).

$$\text{R}_3\text{SiMe} + \text{HSiCl}_3 \xrightarrow[150\ ^\circ\text{C}]{\text{H}_2\text{PtCl}_6} \text{R}_3\text{SiCl} + \text{MeSiHCl}_2 \quad (3)$$

The results obtained in the present work show clearly that in the reactions of disilacyclobutane (I) with the silanes $HSiCl_3$ and $MeSiHCl_2$ chlorine exchange is favored over hydrogen exchange in the presence of hexachloroplatinic(IV) acid. The replacement of an electron-withdrawing chlorine atom in trichlorosilane by an electron-releasing methyl group, however, allows the hydrogen-exchange reaction to compete to some extent with the chlorine-exchange reaction. It is therefore likely that in the reaction of disilacyclobutane (I) with chlorodimethylsilane[5] the product (IX) was formed *via* both chlorine exchange and hydrogen exchange with the former exchange predominating.

The reaction of trichlorosilane with disilacyclobutane (II) in the presence of hexachloroplatinic(IV) acid under comparable conditions [equation (4)] gave mainly polymeric material (strong i.r. bands at 1 000—1 070 cm^{-1} indicative of linear $Si{\cdot}CH_2$ chains), unchanged trichlorosilane (12%), and a high-boiling liquid fraction. A coupled g.l.c.–mass spectrometric examination of the high-boiling material showed that it consisted of four components (ratio 10 : 47 : 5 : 38) and the three major components were identified as biphenyl, dimethyldiphenylsilane (*ca.* 12%) with mass-spectral bands at *m/e* 212 (6%, M^+) and 197 [100%, $(M - \text{Me})^+$], and the chlorine-exchange 1 : 1 adduct 1,1,5-trichloro-3-methyl-3,5-diphenyl-1,3,5-trisilahexane, (X) (*ca.* 10%), with mass-spectral bands at *m/e* 393, 391, 389, and 387 [100%, $(M - \text{Me})^+$], 331, 329, 327, and 325 [50%, $(M - \text{Ph})^+$], 251, 249, and 247 (100%, $\text{SiHCl}_2{\cdot}\text{CH}_2{\cdot}\text{SiMePh}{\cdot}\text{CH}_2^+$), 199 and 197 (25%, $\text{MePhSiCl}{\cdot}\text{CH}_2^+$), and 103, 101, and 99 (50%, SiHCl_2^+). It is probable that the low yield of

$$\text{(II)} + \text{HSiCl}_3 \xrightarrow[88\ ^\circ\text{C}]{\text{H}_2\text{PtCl}_6} \underset{\text{(X)}}{\text{SiHCl}_2{\cdot}\text{CH}_2{\cdot}\text{SiMePh}{\cdot}\text{CH}_2{\cdot}\text{SiMePhCl}} \quad (4)$$

adduct (X) is due to the presence of electron-withdrawing phenyl groups in the disilacyclobutane which retard the exchange reaction thus allowing the polymerisation of the disilacyclobutane to be favoured. A similar retardation of the chlorine-exchange reaction between alkylsilanes and trichlorosilane has been observed[4] when electron-withdrawing substituents, *e.g.* Ph, are present in the alkylsilane. The formation of dimethyldiphenylsilane in the reaction possibly involves hydrogen and chlorine exchange from the trichlorosilane with methyl and phenyl groups in the polymer, but it is not apparent how the biphenyl is formed.

The reaction of disilacyclobutane (I) with silicon tetrachloride at 88 °C in the presence of hexachloroplatinic(IV) acid, which was investigated in order to determine whether chlorine exchange would occur in the absence of a Si–H bond in the reactant silane, gave unchanged silicon tetrachloride (15%) and linear polymeric material (i.r.), which fumed in air and reacted vigorously with water with the evolution of hydrogen chloride. Attempted reactions of disilacyclobutane (I) with silicon tetrachloride and germanium(IV) chloride in the absence of hexachloroplatinic(IV) acid carried out in refluxing nitromethane (5 h) gave quantitative recoveries of reactants.

Redistribution reactions between tetra-alkyltin compounds and tin(IV) chloride often proceed readily under mild conditions,[7,8] *e.g.* the reaction between tetrabutyltin and tin(IV) chloride at room temperature which involves quantitative exchange of one butyl group for chlorine [equation (5)].[8] Such Sn–C cleavage reactions prompted

$$\text{Bu}^n{}_4\text{Sn} + \text{SnCl}_4 \longrightarrow \text{Bu}^n{}_3\text{SnCl} + \text{Bu}^n\text{SnCl}_3 \quad (5)$$

an investigation of the reactions of tin(IV) chloride with the disilacyclobutanes (I) and (II) to determine if the Si–C bonds in these strained ring systems would be cleaved similarly. The reactions were exothermic in nitromethane in the absence of catalyst at room temperature and afforded the adducts (XI) (79%) and (XII) (96%), respectively. The adducts were identified by

$$\underset{\text{(XI)}}{\text{Me}_2\text{SiCl}{\cdot}\text{CH}_2{\cdot}\text{SiMe}_2{\cdot}\text{CH}_2{\cdot}\text{SnCl}_3}$$

$$\underset{\text{(XII)}}{\text{MePhSiCl}{\cdot}\text{CH}_2{\cdot}\text{SiMePh}{\cdot}\text{CH}_2{\cdot}\text{SnCl}_3}$$

consideration of their ^{1}H n.m.r. and mass spectra. The n.m.r. spectrum of adduct (XI) showed absorptions at τ 8·48 (2H, s), 9·52 (6H, s), 9·60 (2H, s), and 9·63 (6H, s), assigned to $SnCH_2$, $SiMe_2Cl$, $Si{\cdot}CH_2{\cdot}Si$, and $SiMe_2$ groups, respectively, and that of adduct (XII) showed absorptions at τ 2·56 (10H, complex, 2 SiPh), 8·43—8·52 (2H,

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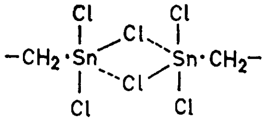
[7] G. J. M. Van der Kerk and J. G. A. Luitjen, *J. Appl. Chem.*, 1957, **7**, 369.

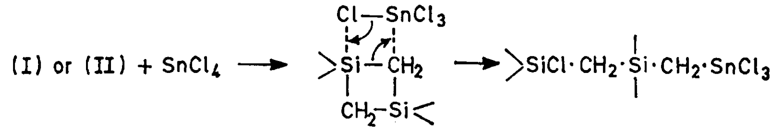
[8] B.P. 739,883/1958.

AB, $\mathrm{Sn{\cdot}CH_2}$), 9·15 (2H, s, $\mathrm{Si{\cdot}CH_2{\cdot}Si}$), and 9·36—9·41 (6H, complex, 2 SiMe). The mass spectra of the two adducts showed bands at *m/e* 391 and 389 [50%, $(M - \mathrm{Me})^+$] and 167 and 165 [100%, $(M - \mathrm{CH_2{\cdot}SnCl_3})^+$] and at *m/e* 515 and 513 [84%, $(M - \mathrm{Me})^+$] and 291 and 289 [100%, $(M - \mathrm{CH_2{\cdot}SnCl_3})^+$], respectively. The molecular weights of both the adducts, determined in benzene, indicated that the adducts are dimeric in this solvent; the dimers are probably of type (XIII) with bridging chlorine atoms.



(XIII)

The reaction of tin(IV) chloride with the disilacyclobutanes probably occurs as in equation (6), *via* a four-centre transition state. An attempted reaction between disilacyclobutane (I) and triphenyltin chloride in refluxing nitromethane (5 h) gave only unchanged reactants.



(6)

With Silanols.—The ring opening of 1,1-dimethyl-1-silacyclobutane, (XIV), on reaction with n-heptanol under reflux has been reported [equation (7)],[9] but in contrast disilacyclobutane (I) did not react with ethanol or n-heptanol under reflux.[3] In order to determine

$$\underset{\text{(XIV)}}{\overline{\mathrm{CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}SiMe_2}}} + \mathrm{n\text{-}C_7H_{15}{\cdot}OH} \longrightarrow \underset{(58\%)}{\mathrm{n\text{-}C_3H_7{\cdot}SiMe_2{\cdot}O{\cdot}C_7H_{15}\text{-}n}} \quad (7)$$

whether more acidic hydroxy-compounds would induce ring opening of disilacyclobutanes the reactions of trimethylsilanol and phenol with the disilacyclobutanes (I)—(III) were investigated.

Trimethylsilanol did not react with disilacyclobutane (I) at room temperature, but in acetonitrile under reflux (3 h) the ring-opened 1 : 1 adduct 2,2,4,4,6,6-hexamethyl-3-oxa-2,4,6-trisilaheptane,[10] (XV) (91%), was formed. A comparable reaction (6 h) with compound (II) gave 2,2,4,6-tetramethyl-4,6-diphenyl-3-oxa-2,4,6-trisilaheptane, (XVI) (83%), but the tetraphenyldisilacyclobutane (III) did not react even on prolonged

$$\mathrm{Me_3Si{\cdot}O{\cdot}SiMe_2{\cdot}CH_2{\cdot}SiMe_3}$$

(XV)

$$\mathrm{Me_3Si{\cdot}O{\cdot}SiMePh{\cdot}CH_2{\cdot}SiMe_2Ph}$$

(XVI)

reflux (30 h). It would appear that these ring-opening reactions are the first successful cleavages of Si–C bonds by a silanol to be reported. An attempted reaction of disilacyclobutane (I) with the carbon analogue t-butyl alcohol gave only unchanged reactants.

The structures of the products were determined by ^{1}H n.m.r. spectroscopy and mass spectrometry. Thus the n.m.r. spectrum of compound (XV) showed absorptions at τ 10·0 (9H, s, $\mathrm{Me_3Si{\cdot}O}$) and 9·89 to 9·91 (17H, complex, $\mathrm{SiMe_2}$, $\mathrm{CH_2}$, and $\mathrm{SiMe_3{\cdot}C}$), while the mass spectrum showed a base peak at *m/e* 219 $(M - \mathrm{Me})^+$ and a peak at *m/e* 147 ($\mathrm{Me_3Si{\cdot}O{\cdot}SiMe_2^+}$). Similarly the n.m.r. spectrum of adduct (XVI) showed absorptions at τ 9·91 (9H, s, $\mathrm{Me_3Si{\cdot}O}$), 9·65—9·73 (11H, complex, SiMe, $\mathrm{SiMe_2}$, and $\mathrm{CH_2}$), and 2·61 (10H, complex, 2SiPh), while the mass spectrum exhibited peaks at *m/e* 358 (M^+), 343 [25%, $(M - \mathrm{Me})^+$], 209 (100%, $\mathrm{Me_3Si{\cdot}O{\cdot}SiMePh^+}$), and 135 (50%, $\mathrm{SiMe_2Ph^+}$).

The ring openings of the disilacyclobutanes (I) and (II) could occur by three distinct mechanisms: (*a*) initial electrophilic attack by the proton of the silanol at a $\mathrm{CH_2}$ group in the disilacyclobutane; (*b*) initial nucleophilic attack by the oxygen atom of the silanol at a silicon atom in the disilacyclobutane; and (*c*) a fully concerted four-centre mechanism. Mechanism (*a*) is considered to be unlikely because the more acidic hydroxy-compound phenol did not react with either of the disilacyclobutanes (I) or (II) under comparable conditions, but it is not possible at the present time to differentiate between mechanisms (*b*) and (*c*). The failure of the disilacyclobutane (III) to react with trimethylsilanol is attributed to steric hindrance by the phenyl groups. The driving force behind the successful reactions of the silanol with the disilacyclobutanes is probably the formation of the stable Si–O–Si grouping, as present in polysiloxane polymers which are thermally stable to relatively high temperatures (>300 °C). In order to extend the reaction and also to determine the effect of electron-withdrawing substituents in the silanol, the reaction of triphenylsilanol with the disilacyclobutanes (I) and (II) was investigated.

Triphenylsilanol and disilacyclobutane (I) did not react at room temperature but in refluxing acetonitrile (2 h) reaction occurred to give 1,1,3,3-tetramethyl-1,3-bis(trimethylsilylmethyl)disiloxane, (XVII) (87%), and hexaphenyldisiloxane contaminated with a small amount of unchanged triphenylsilanol. The disiloxane (XVII),

$$\mathrm{(Me_3Si{\cdot}CH_2{\cdot}SiMe_2)_2O}$$

(XVII)

$$\mathrm{Ph_3Si{\cdot}O{\cdot}SiMe_2{\cdot}CH_2{\cdot}SiMe_3}$$

(XVIII)

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[9] N. S. Nametkin, V. M. Vdovin, and P. L. Grinberg, *Doklady Akad. Nauk S.S.S.R.*, 1964, **155**, 320.

[10] U.S.P. 2,452,895/1949.

together with the silanol $Me_3Si{\cdot}CH_2{\cdot}SiMe_2OH$, has been reported [3] to be formed in the reaction of disilacyclobutane (I) with aqueous ethanolic sodium hydroxide.

It is considered that initial reaction of the silanol affords the 1 : 1 adduct (XVIII) from which the observed products could be formed by a symmetrisation reaction, *i.e.* as in equation (8). However, such redistributions of

$$2(\text{XVIII}) \longrightarrow (Ph_3Si)_2O + (\text{XVII}) \qquad (8)$$

siloxane bonds in the absence of catalysts generally require high temperatures (300—350 °C) [11,12] and it is more likely that the 1 : 1 adduct (XVIII) reacts further with triphenylsilanol [equation (9)]. The silanol (XIX)

$$(\text{XVIII}) + Ph_3SiOH \longrightarrow (Ph_3Si)_2O + \underset{(\text{XIX})}{Me_3Si{\cdot}CH_2{\cdot}SiMe_2OH} \qquad (9)$$

produced in this reaction then reacts with more disilacyclobutane (I) to afford the observed product (XVII) [equation (10)].

$$(\text{XIX}) + \overline{CH_2{\cdot}SiMe_2{\cdot}CH_2{\cdot}SiMe_2} \longrightarrow (\text{XVII}) \qquad (10)$$

The electron-withdrawing phenyl groups in adduct (XVIII) render the silicon atom of the Ph_3Si group susceptible to further nucleophilic attack by silanol. This explains why the trimethylsilanol adducts (XV) and (XVI) do not react further with trimethylsilanol; the $+I$ effect of the methyl groups in the $Me_3Si{\cdot}O$ groupings of these adducts render the silicon atoms far less susceptible to nucleophilic attack.

Disilacyclobutane (II) did not react with triphenylsilanol even after prolonged reflux in acetonitrile, and this is attributed to increased steric effects on replacement of $SiMe_2$ groups in disilacyclobutane (I) by SiMePh groups.

EXPERIMENTAL

Products were separated by fractional distillation (20 cm columns) at atmospheric or reduced pressure, were purified where necessary by column chromatography [Laporte Industries Chromatographic Alumina type H with light petroleum (b.p. 30—40 °C) as the eluant] or g.l.c. [4 m columns packed with Silicone MS 550 oil (20%) on Celite], and were identified by elemental analysis, molecular-weight determination (Mechrolab model 301A vapour-pressure osmometer), i.r. spectroscopy (Perkin-Elmer 457 spectrophotometer with sodium chloride optics), ^1H n.m.r. spectroscopy (Perkin-Elmer R10 instrument operating at 60·0 MHz or a Varian Associates HA 100 spectrometer operating at 100·0 MHz, with internal cyclohexane as the reference), and mass spectrometry (A.E.I. MS 2H instrument). Refractive indices were determined with an Abbé refractometer illuminated with a sodium-vapour lamp.

1,1,3,3-Tetramethyl-1,3-disilacyclobutane, (I), and 1,3-dimethyl-1,3-diphenyl-1,3-disilacyclobutane, (II), were prepared in 44 and 64% yield, respectively, by the addition of magnesium to the appropriate chloro(chloromethyl)silane in tetrahydrofuran,[13] while 1,1,3,3-tetraphenyl-1,3-disilacyclobutane, (III) (30%), was prepared by the reaction of chloro(chloromethyl)diphenylsilane with magnesium in diethyl ether.[14] Trimethylsilanol (94%) was prepared from hexamethyldisiloxane [15] and other reactants were commercial samples which were purified before use.

Reactions of 1,1,3,3-*Tetramethyl*-1,3-*disilacyclobutane*.—(a) *With tin*(IV) *chloride*. The disilacyclobutane (5·0 g, 35·0 mmol) was added slowly to tin(IV) chloride (10·0 g, 38·0 mmol) in nitromethane (25 cm^3) at room temperature and the reaction mixture was stirred at room temperature (2 h). Fractional distillation of the resulting material at reduced pressure through a vacuum-jacketed column (20 cm) gave 2,6,6,6-*tetrachloro*-2,4,4-*trimethyl*-2,4-*disila*-6-*stannahexane* (11·2 g, 27·8 mmol, 79%) (Found: C, 17·6; H, 4·1%; *M*, 830. Calc. for $C_6H_{16}Cl_4Si_2Sn$: C, 17·8; H, 3·9%; *M*, 405), b.p. 109—112 °C at 12 mmHg, n_D^{20} 1·5252, and a polymeric residue (2·1 g).

Attempted reactions of the disilacyclobutane with germanium and silicon tetrachlorides (equimolar amounts) carried out under reflux in solvent nitromethane gave only unchanged reactants.

(b) *With trichlorosilane in the presence of hexachloroplatinic*(IV) *acid*. The disilacyclobutane (4·8 g, 33·0 mmol), trichlorosilane (4·5 g, 33·0 mmol), and hexachloroplatinic(IV) acid (45 mg), sealed *in vacuo* in a Pyrex ampoule (*ca.* 250 cm^3) and heated at 88 °C (24 h), gave (*i*) unchanged trichlorosilane (*ca.* 0·1 g), (*ii*) 1,1,5-*trichloro*-3,3,5-*trimethyl*-1,3,5-*trisilahexane* (7·4 g, 26·5 mmol, 80%) (Found: C, 25·7; H, 6·2%; *M*, 281. Calc. for $C_6H_{17}Cl_3Si_3$: C, 25·8; H, 6·2%; *M*, 280), b.p. 104—106 °C at 10 mmHg, n_D^{20} 1·4637, and (*iii*) a higher-boiling residue (1·6 g).

(c) *With dichloro*(*methyl*)*silane in the presence of hexachloroplatinic*(IV) *acid*. The disilacyclobutane (5·0 g, 35·0 mmol), dichloro(methyl)silane (4·1 g, 37·0 mmol), and hexachloroplatinic(IV) acid (45 mg), sealed *in vacuo* in a Pyrex ampoule (*ca.* 250 cm^3) and heated at 88 °C (24 h), gave unchanged dichloro(methyl)silane (0·4 g, 3·5 mmol, 9% recovered) and higher-boiling material (8·7 g) which on fractionation at reduced pressure yielded a colourless liquid (6·2 g, 23·1 mmol, 66%), b.p. 145—150 °C at 120 mmHg, and a polymeric residue (2·5 g). The two components in the liquid product, present in the ratio 93 : 7, were separated by g.l.c. (4 m column at 110 °C) and identified as 1,5-*dichloro*-3,3,5-*trimethyl*-1,3,5-*trisilahexane* (5·75 g, 21·3 mmol, 61%) (Found: C, 32·4; H, 7·5%; *M*, 261. Calc. for $C_7H_{20}Cl_2Si_3$: C, 32·4; H, 7·7%; *M*, 259), b.p. 147 °C at 120 mmHg, and 5,5-*dichloro*-1,3,3-*trimethyl*-1,3,5-*trisilahexane* (0·45 g, 0·17 mmol, 5%) (Found: C, 32·5; H, 7·5%; *M*, 260), b.p. 139—140 °C at 130 mmHg.

(d) *With silicon tetrachloride in the presence of hexachloroplatinic*(IV) *acid*. A mixture of the disilacyclobutane (4·7 g, 26·0 mmol), silicon tetrachloride (4·4 g, 26·0 mmol), and hexachloroplatinic(IV) acid (45 mg), sealed *in vacuo* in a Pyrex ampoule (*ca.* 250 cm^3) and heated at 88 °C (24 h), gave unchanged silicon tetrachloride (0·68 g, 4·0 mmol, 15%) and a higher-boiling residue (7·9 g), which was shown (i.r.) to

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contain polymeric material with linear $SiCH_2$ chains (strong bands at 1 000—1 060 cm^{-1}), and which reacted vigorously with water with the evolution of hydrogen chloride.

(e) *With trimethylsilanol.* The silanol (3·1 g, 35·0 mmol) was added to the disilacyclobutane (5·0 g, 35·0 mmol) in acetonitrile (30 cm^3) and the mixture was heated under reflux (3 h). The solvent was removed *in vacuo* and the resulting material was fractionated to afford 2,2,4,4,6,6-hexamethyl-3-oxa-2,4,6-trisilaheptane (7·6 g, 32·0 mmol, 91%) (Found: C, 46·5; H, 10·8%; *M*, 237. Calc. for $C_9H_{26}OSi_3$: C, 46·2; H, 11·1%; *M*, 234), b.p. 190—192 °C, n_D^{20} 1·4164 (lit.,[10] b.p. 96—97 °C at 57 mmHg, n_D^{20} 1·4137), $\nu_{max.}$ at 1 055s cm^{-1} (Si–O–Si str. and linear Si–CH_2–Si).

(f) *With triphenylsilanol.* A mixture of the silanol (4·6 g, 16·5 mmol) and the disilacyclobutane (2·4 g, 16·5 mmol) in solvent acetonitrile (25 cm^3) was heated under reflux (2 h) and the solvent removed *in vacuo*. The resulting material was treated with light petroleum (b.p. 30—40 °C, 10 cm^3) and filtered to give a solid (4·0 g, *ca.* 7·5 mmol, *ca.* 90%), which was identified as hexaphenyldisiloxane contaminated with a small amount of unchanged triphenylsilanol (i.r.). The filtrate was fractionated under reduced pressure to afford 1,1,3,3-tetramethyl-1,3-bis(trimethylsilylmethyl)disiloxane (2·2 g, 7·2 mmol, 87%) (Found: C, 47·0; H, 11·4%; *M*, 303. Calc. for $C_{12}H_{34}OSi_4$: C, 47·1; H, 11·2%; *M*, 304), b.p. 92—95 °C at 1 mmHg, n_D^{20} 1·4342 (lit.,[16] b.p. 93—94 °C at 3·5 mmHg, n_D^{20} 1·4340).

Reactions of 1,3-*Dimethyl*-1,3-*diphenyl*-1,3-*disilacyclobutane*.—(a) *With tin*(IV) *chloride.* A mixture of the disilacyclobutane (5·0 g, 18·5 mmol) and tin(IV) chloride (4·8 g, 18·5 mmol) in solvent nitromethane (20 cm^3) was stirred at room temperature (3 h) to give, after removal of nitromethane, a high-boiling residue identified as 2,6,6,6-*tetrachloro*-4-*methyl*-2,4-*diphenyl*-2,4-*disila*-6-*stannahexane* (9·4 g, 17·8 mmol, 96%) (Found: C, 36·6; H, 3·5%; *M*, 981. Calc. for $C_{16}H_{20}Cl_4Si_2Sn$: C, 36·2; H, 3·8%; *M*, 528).

(b) *With trichlorosilane in the presence of hexachloroplatinic*(IV) *acid.* A mixture of the disilacyclobutane (5·0 g, 18·6 mmol), trichlorosilane (2·5 g, 18·6 mmol), and hexachloroplatinic(IV) acid (45 mg), sealed *in vacuo* in a Pyrex ampoule (*ca.* 250 cm^3) and heated at 88 °C (24 h), gave unchanged trichlorosilane (0·3 g, 2·2 mmol, 12% recovered) and higher-boiling material (7·0 g). The latter product on distillation at reduced pressure afforded a colourless oil (1·2 g), b.p. 165 °C at 2 mmHg, and a residue (5·8 g) which was shown (i.r.) to contain linear $SiCH_2$ linkages. A coupled g.l.c. (4 m column at 210 °C)–mass-spectrometric analysis of the mixture showed it to consist of four components in the ratio 10 : 47 : 5 : 38 of which the major three components were identified as biphenyl (*ca.* 0·06 g, *ca.* 0·4 mmol), dimethyldiphenylsilane (*ca.* 0·43 g, *ca.* 2·0 mmol, *ca.* 12%), and 1,1,5-trichloro-3-methyl-3,5-diphenyl-1,3,5-trisilahexane (*ca.* 0·65 g, *ca.* 1·6 mmol, *ca.* 10%).

(c) *With trimethylsilanol.* The silanol (3·6 g, 40·0 mmol) was added to the disilacyclobutane (10·0 g, 37·4 mmol) in acetonitrile (50 cm^3) and the mixture was heated under reflux (6 h). The solvent was removed *in vacuo* and the resulting material was fractionated and then purified by chromatography using light petroleum (b.p. 30—40 °C) to give 2,2,4,6-*tetramethyl*-4,6-*diphenyl*-3-*oxa*-2,4,6-*trisilaheptane* (11·1 g, 31·0 mmol, 83%) (Found: C, 63·8; H, 7·9%; *M*, 351. Calc. for $C_{19}H_{30}OSi_3$: C, 63·8; H, 8·3%; *M*, 358), b.p. 130—131 °C at 0·1 mmHg; n_D^{20} 1·5091; $\nu_{max.}$ at 1 020s and 1 050s cm^{-1} (Si–O–Si str. and linear Si–CH_2–Si).

(d) *With triphenylsilanol.* A mixture of the silanol (3·7 g, 13·5 mmol) and the disilacyclobutane (3·5 g, 13·0 mmol) in solvent acetonitrile (20 cm^3), heated under reflux (30 g) and the solvent removed *in vacuo*, gave only a mixture of unchanged reactants.

Attempted Reaction of 1,1,3,3-*Tetraphenyl*-1,3-*disilacyclobutane with Trimethylsilanol.*—A mixture of the silanol (1·25 g, 13·8 mmol) and the disilacyclobutane (5·4 g, 13·8 mmol) in solvent acetonitrile (30 cm^3) when heated under reflux (30 h) gave only unchanged reactants after removal of the solvent.

Other Attempted Reactions.—The following attempted reactions gave only unchanged reactants: (*a*) a mixture of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (15·0 g, 105 mmol) and t-butyl alcohol (8·5 g, 115 mmol) in acetonitrile (30 cm^3) after reflux (12 h); (*b*) a mixture of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (6·0 g, 41·6 mmol) and phenol (3·9 g, 41·5 mmol) in acetonitrile (30 cm^3) after reflux (12 h); and (*c*) a mixture of 1,3-dimethyl-1,3-diphenyl-1,3-disilacyclobutane (6·0 g, 22·4 mmol) and phenol (2·2 g, 23·2 mmol) in acetonitrile (20 cm^3) after reflux (12 h).

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