

Organosilicon Chemistry. Part XVII.¹ Some Reactions of 1,1,3,3-Tetramethyl-1,3-disilacyclobutane²

By Anthony M. Devine, Peter A. Griffin, Robert N. Haszeldine,* Michael J. Newlands, and Anthony E. Tipping, Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 Q1D

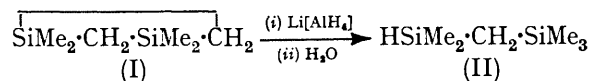
1,1,3,3-Tetramethyl-1,3-disilacyclobutane, (I), reacts with halogens, hydrogen halides, sulphuric acid, lithium tetrahydroaluminate, phenyl-lithium, phenylmagnesium bromide, ethanolic silver(I) nitrate, ethanolic mercury(II) chloride, and ethanolic mercury(II) acetate to give ring-opened products in high yields; (I) is unaffected by trifluoroiodomethane, *N*-bromosuccinimide, benzenethiol, heptan-1-ol, basic alumina, sulphur, phenylmercury chloride, or mercury(II) acetate in benzene. Photochemical reaction of *t*-butyl hypochlorite with (I) gives comparable amounts of 1-chloromethyl-1,3,3-trimethyl-, 2-chloro-1,1,3,3-tetramethyl-, and 2,2-dichloro-1,1,3,3-tetramethyl-1,3-disilacyclobutane, together with lesser amounts of the ring-opened hydrogen chloride and chlorine 1:1 adducts.

THE preparation and chemistry of 1,3-disilacyclobutanes has been reviewed recently in a wider survey of cyclobutanes containing heterocyclic silicon and germanium.³ 1,3-Disilacyclobutanes undergo facile ring-opening reactions with strong electrophiles or nucleophiles, a property which has been made use of in the preparation of Si·CH₂· polymers, and also ring expansion takes place with sulphur dioxide,⁴ sulphur trioxide,⁵ or dichlorocarbene.⁶

The ring-opening reactions of 1,1,3,3-tetramethyl-1,3-disilacyclobutane, (I), which have been reported previously include those with bromine,^{7,8} hydrogen bromide,⁸ silver ion,^{7,9} and mercury(II) chloride,¹⁰ all of which possibly involve initial electrophilic attack on carbon; few reactions with strong nucleophiles have been investigated. In the present work further ring-opening reactions of (I) have been studied and free-radical chlorination using *t*-butyl hypochlorite has also been carried out.

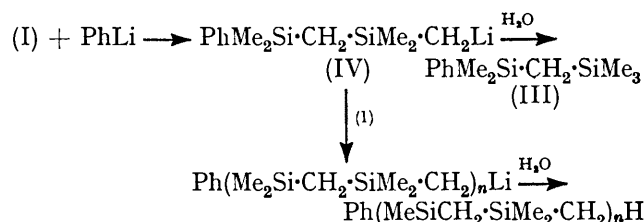
RESULTS AND DISCUSSION

(a) *Nucleophilic Ring-opening Reactions*.—Reaction of compound (I) with Li[AlH₄] heated under reflux in tetrahydrofuran (thf) gave 2,2,4-trimethyl-2,4-disilapentane, (II) (80%), after hydrolysis; attempted reaction at room temperature or in refluxing diethyl ether gave near quantitative recoveries of the reactant (I). Thus compound (I) is less susceptible to attack by hydride ion than is 1,1,2-triphenylsilacyclobutane which is reported¹¹ to react at room temperature in ether



solution. With excess of phenyl-lithium in ether solution compound (I) gave 2,2,4-trimethyl-4-phenyl-2,4-disilapentane, (III) (54%), and polymeric material after hydrolysis. The polymeric material probably arises *via* nucleophilic attack of the intermediate

lithium compound (IV) on reactant (I) at silicon. The product (III) could not be readily separated from

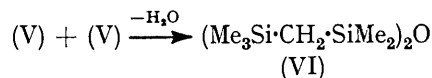
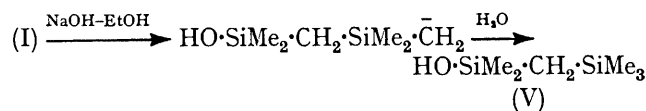


biphenyl, also formed in the reaction, but it was identified by comparison with an authentic sample prepared in 35% yield by the following route:



Phenylmagnesium bromide reacted only slowly with compound (I) heated under reflux in thf to give, after hydrolysis, unchanged (I) (85%), (III) (1–2%), biphenyl, and a Si·CH₂· polymer.

Reaction between aqueous ethanolic sodium hydroxide and (I) at room temperature was exothermic and gave a mixture of the silanol (V) (72%) and the corresponding disiloxane (VI) (11%). Condensation of the silanol (V) may be hindered by the bulky (trimethylsilyl)methyl group, the silicon analogue of the neopentyl group.



Compound (I) was recovered unchanged (i) after passage through a basic alumina column, (ii) after attempted reaction with benzenethiol under reflux alone or in carbon tetrachloride solution, and (iii) after attempted reaction with ethanol or *n*-heptanol under reflux. In

⁶ D. Seyferth, R. Damrauer, and S. S. Washburne, *J. Amer. Chem. Soc.*, 1967, **89**, 1538.

⁷ W. H. Knoth and R. V. Lindsey, *J. Org. Chem.*, 1958, **23**, 1392.

⁸ R. Mueller, R. Koehne, and H. Beyer, *Chem. Ber.*, 1962, **95**, 3030.

⁹ R. Mueller, C. Dathe, and R. Koehne, *Z. Chem.*, 1963, **3**, 427.

¹⁰ R. Mueller and R. Koehne, *Z. Chem.*, 1969, **9**, 429.

¹¹ H. Gilman and W. H. Atwell, *J. Amer. Chem. Soc.*, 1964, **86**, 2687.

¹ Part XVI, N. J. Archer, R. N. Haszeldine, and R. V. Parish, *J. Organometallic Chem.*, 1974, **81**, 335.

² Presented in part at the 2nd Internat. Symp. on 'The Chemistry of Organosilicon Compounds,' Bordeaux, 1968.

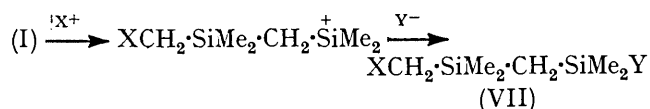
³ R. Damrauer, *Organometallic Chem. Rev.*, 1972, **A8**, 67.

⁴ J. Dubac, P. Mazerolles, M. Joly, W. Kitching, C. W. Fong, and W. H. Atwell, *J. Organometallic Chem.*, 1970, **25**, C20.

⁵ H. Schmidbauer, L. Sechser, and M. Schmidt, *Chem. Ber.*, 1969, **102**, 376.

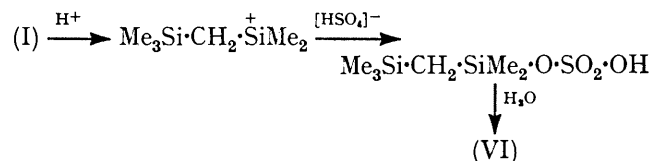
contrast 1,1,2-triphenylsilacyclobutane is ring opened by basic alumina¹¹ and 1,1-dimethylsilacyclobutane reacts with n-heptanol to give the ether $\text{Pr}^n\text{SiMe}_2 \cdot \text{O} \cdot \text{C}_7\text{H}_{15-n}$ (58%),¹² although reaction with benzenethiol has not been reported. It is thus apparent that the 1,3-disilacyclobutane ring is less susceptible to nucleophilic cleavage than is the silacyclobutane ring; this is possibly due to lower ring strain in the former.

(b) *Electrophilic Ring-opening Reactions.*—Ring-opening of (I) by electrophilic attack on carbon takes place as shown in the following scheme:

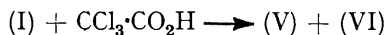


In the present work reaction of (I) with chlorine, bromine, hydrogen chloride, hydrogen bromide, and hydrogen iodide gave [VII; X = Y = Cl (76%), X = Y = Br (86%), X = H, Y = Cl (84%), X = H, Y = Br (79%), and X = H, Y = I (90%)]. The only difficulties encountered were that further chlorination of compound (VII; X = Y = Cl) occurred if the reaction temperature rose above 0 °C and (VII; X = H, Y = I) readily liberated iodine even in subdued light.

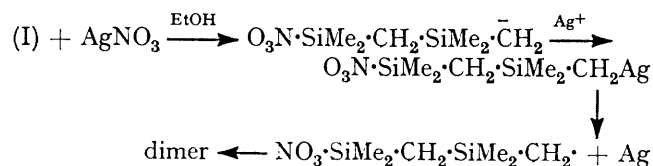
The heterogeneous reaction between compound (I) and concentrated sulphuric acid at -10 °C was exothermic and gave 1,1,3,3-tetramethyl-1,3-bis(trimethylsilylmethyl)disiloxane, (VI) (91%), after hydrolysis.



Unless hydrolysis was carried out immediately after addition of (I) to the acid complex polymeric products were obtained. It has been reported previously that monosilacyclobutanes are cleaved readily by concentrated H_2SO_4 ¹³ and that (I) reacts with trichloroacetic acid.¹⁴



(c) *Other Ionic Reactions.*—It has been reported that (I) does not react with aqueous silver(I) nitrate, but in the presence of a small amount of ethanol reduction to silver takes place.^{7,9} Although the silicon-containing products were not characterised, the following mechanism⁹ was postulated:

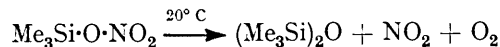


¹² N. S. Nametkin, V. M. Vdovin, and P. L. Grinberg, *Doklady Akad. Nauk S.S.S.R.*, 1964, **155**, 849.

¹³ L. H. Sommer and G. A. Baum, *J. Amer. Chem. Soc.*, 1954, **76**, 5002.

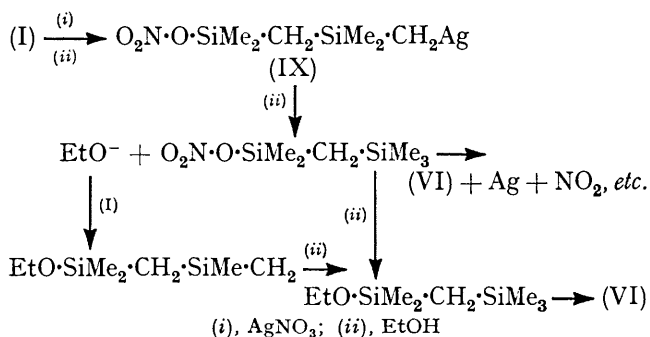
¹⁴ W. R. Bamford, J. C. Lovic, and J. A. C. Watt, *J. Chem. Soc. (C)*, 1966, 1137.

Chemical evidence was not presented in support of the scheme and no account was taken of the observation that the silicon nitrate group is unstable and decomposes rapidly at low temperature with evolution of oxides of nitrogen,¹⁵ e.g.:



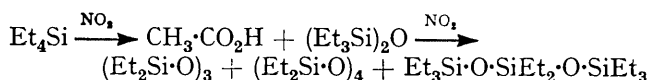
In the present work it was found that the major product of the reaction of (I) with ethanolic AgNO_3 (1 : 1 molar ratio) at room temperature was the disiloxane (VI) (78%) which contained a small amount of the cyclo-octane derivative $\text{O} \cdot (\text{SiMe}_2 \cdot \text{CH}_2 \cdot \text{SiMe}_2)_2 \cdot \text{O}$, (VIII) (ca. 1%); oxides of nitrogen were evolved during the reaction.

The reactions of silver salts with trialkylsilyl halides, pseudohalides, and sulphides have been postulated as involving nucleophilic attack on silicon.¹⁶ Compound (I) does not react with aqueous AgNO_3 or ethanol but it is possible that with ethanolic AgNO_3 the reaction proceeds as follows:



A 1 : 1 ratio of reactants gave a ca. 20% yield of silver, unchanged AgNO_3 (77%), and the disiloxane (VI) in relatively high yield (78%). The full mechanism of this reaction is not yet understood.

A violent exothermic reaction took place when excess of gaseous nitrogen dioxide was passed into neat liquid (I) or a solution of (I) in carbon tetrachloride at 0 °C. The major product from both reactions was a polysiloxane (M ca. 2000), but the cyclo-octane derivative (VIII) was also formed in low yield (1–2%) and was identified by comparison of its physical properties with those reported¹⁷ and by n.m.r. spectroscopy [δ 1.34 (12 H, 2 SiMe_2) and 1.59 p.p.m. (2 H, $\text{Si} \cdot \text{CH}_2 \cdot \text{Si}$) relative to internal cyclohexane, cf. $(\text{Me}_3\text{Si} \cdot \text{CH}_2 \cdot \text{SiMe}_2)_2\text{O}$ δ 1.36 (SiMe_2) and 1.62 p.p.m. ($\text{Si} \cdot \text{CH}_2 \cdot \text{Si}$)] and mass spectrometry $\{m/e$ 292 (1 M^+) and 277 (100% [$M - \text{Me}$] $^+$)}. Alkylsilanes have been observed previously to react with nitrogen dioxide to yield siloxanes,¹⁸ e.g.:



The reaction of (I) with mercury(II) chloride in

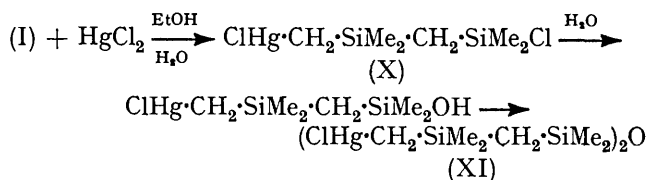
¹⁵ I. R. Beattie and G. Leigh, *J. Chem. Soc.*, 1961, 4249; M. Schmidt and H. Schmidbauer, *Angew. Chem.*, 1959, **71**, 220.

¹⁶ C. Eaborn, *J. Chem. Soc.*, 1950, 3077.

¹⁷ B. H. Bluestein, *J. Amer. Chem. Soc.*, 1948, **70**, 3068.

¹⁸ L. Spialter and J. D. Austin, *J. Amer. Chem. Soc.*, 1966, **88**, 1828.

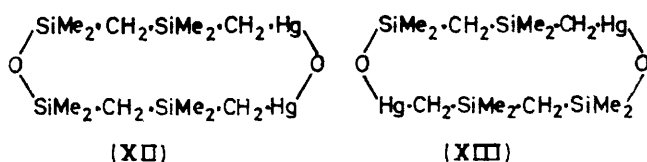
aqueous ethanol has been reported¹⁰ to give the adduct (X) which under the reaction conditions hydrolyses and then condenses to afford the disiloxane (XI). How-



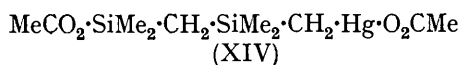
ever, good analytical data for the disiloxane (XI) were not obtained and it was suggested that the compound was contaminated with other products which arose by further reaction of adduct (X) with (I) followed by hydrolysis and condensation. In the present work slow addition of (I) to an excess of HgCl_2 in ethanol followed by hydrolysis of the initial product gave, after repeated recrystallisation from light petroleum, pure disiloxane (XI) (49%). The product possibly arises *via* initial ring-opening of the disilacyclobutane by electrophilic

$(I) + [\text{ClHg}]^+ \longrightarrow \text{ClHg}\cdot\text{CH}_2\cdot\text{SiMe}_2\cdot\text{CH}_2\cdot\overset{+}{\text{Si}}\text{Me}_2 \xrightarrow{\text{Cl}^-} (\text{X})$ attack on carbon, followed by hydrolysis and condensation. Attempted reaction of phenylmercury chloride in ethanol with (I) at *ca.* 80 °C was unsuccessful.

Reaction between mercury(II) acetate and (I) did not occur in refluxing benzene, but in refluxing ethanol reaction was rapid and gave a small amount of mercury(I) acetate and an oily residue which was contaminated with acetic acid. Hydrolysis of the residue with aqueous sodium hydrogencarbonate gave a crystalline product (53%). The product did not contain acetate or hydroxyl groups (*i.r.*) and elemental analysis and a molecular-weight determination showed that it had the molecular formula $(\text{C}_6\text{H}_{16}\text{HgOSi}_2)_2$. The n.m.r. spectrum showed absorptions at 0.67 (2 H, $\text{Si}\cdot\text{CH}_2\cdot\text{Hg}$), 1.07 (6 H, SiMe_2), 1.09 (6 H, SiMe_2), and 1.38 (2 H, $\text{Si}\cdot\text{CH}_2\cdot\text{Si}$) p.p.m. to high field of internal cyclohexane. The two most probable structures which fit these observations are



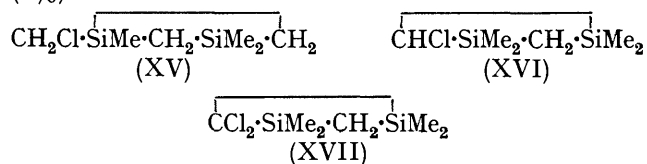
(XII) and (XIII) * which could both be formed by hydrolysis and condensation of the initial 1:1 adduct (XIV).



(d) *Free-radical and Insertion Reactions.*—Photochemical reaction of trifluoriodomethane with (I) (2:1 molar ratio) gave unchanged (I) (95%), hexafluoroethane (86%), iodine, and a small amount of an unidentified higher-boiling liquid. Thus under such conditions hydrogen abstraction from (I) by trifluoromethyl

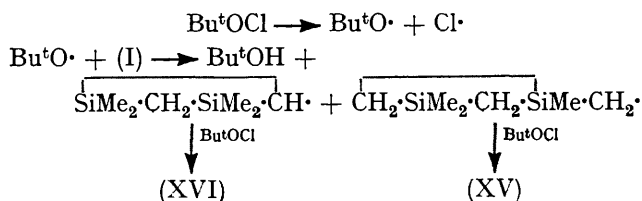
* An attempt to determine the structure by X-ray crystallography failed because the compound decomposed in the X-ray beam (R. F. Bryan, personal communication).

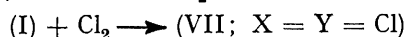
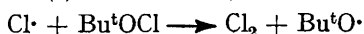
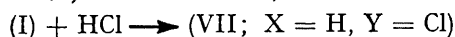
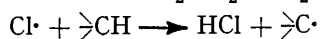
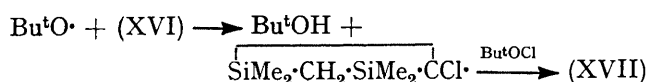
radicals is not favoured. Similarly (I) was unaffected on irradiation with *N*-bromosuccinimide in carbon tetrachloride or on heating with *N*-bromosuccinimide in the presence of benzoyl peroxide or azobisisobutyronitrile. However, photochemical reaction of a 1:1 molar mixture of (I) and *t*-butyl hypochlorite in solvent carbon tetrachloride gave *t*-butyl alcohol, unchanged (I) (53%), 2-chloro-2,4,4-trimethyl-2,4-disilapentane, (VII; X = H, Y = Cl) (7%), a mixture of 1-chloromethyl-1,3,3-trimethyl-1,3-disilacyclobutane, (XV) (18%), and 2-chloro-1,1,3,3-tetramethyl-1,3-disilacyclobutane, (XVI) (18%), 2,2-dichloro-1,1,3,3-tetramethyl-1,3-disilacyclobutane, (XVII) (19%), and 1,4-dichloro-2,2,4-trimethyl-2,4-disilapentane, (VII; X = Y = Cl) (9%).



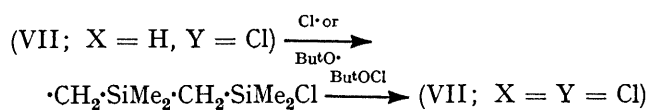
The ¹H n.m.r. spectra of products (VII; X = H, Y = Cl) and (VII; X = Y = Cl) were identical to those found for these compounds prepared by the reactions of (I) with hydrogen chloride and chlorine, respectively. The ¹H n.m.r. spectrum of a mixture of products (XV) and (XVI) showed absorptions at +0.9—1.2 (complex, 27 H), -1.28 (s, 1 H), and -1.40 p.p.m. (s, 2 H) relative to internal cyclohexane. The protons of a $\text{Si}\cdot\text{CH}_2\text{Cl}$ group would be expected to absorb in the region -1.35 to -1.50 p.p.m. and the absorption at -1.40 p.p.m. is assigned to this group in compound (XV). The tertiary proton in a CHCl group would be expected to absorb to lower field than the protons in a CH_2Cl group, but if the CHCl group is bonded to two silicon atoms, the proton would be more shielded than those in a $\text{Si}\cdot\text{CH}_2\text{Cl}$ group and so absorb to higher field; thus the absorption at -1.28 p.p.m. is assigned to the CHCl group in compound (XVI). The *i.r.* spectrum of the mixture showed strong absorption at 941 cm^{-1} (characteristic of disilacyclobutane rings) and the mass spectrum exhibited a strong parent peak at m/e 180 and 178 and strong peaks at m/e 129 [$M - \text{CH}_2\text{Cl}$]⁺, 165 and 163 [$M - \text{Me}$]⁺, and 150 and 152 [$M - \text{C}_2\text{H}_4$]⁺. The ¹H n.m.r. spectrum of product (XVII) showed absorptions at 0.95 (s, 2 H, CH_2) and 0.85 p.p.m. (s, 12 H, 2 SiMe_2), the *i.r.* spectrum contained a strong band at 945 cm^{-1} , and the mass spectrum exhibited a strong parent peak at m/e 217, 215, and 213, thus confirming the structure.

The products are considered to be formed as shown in the following reaction scheme:





The possibility that the dichloride (VII; X = Y = Cl) is formed *via* radical attack on the hydrogen chloride adduct (VII; X = H, Y = Cl) is considered to be less



probable because radical attack on adduct (VII; X = H, Y = Cl) would also be expected to occur to a major extent at the methylene group to afford eventually the dichloride $\text{Me}_3\text{Si-CHCl-SiMe}_2\text{Cl}$ which was not detected in the products. The cyclic products formed indicate that the ratio of t-butoxy radical attack on the methyl and methylene groups in (I) is *ca.* 1 : 2 and the statistical yield (allowing for the different numbers of primary and secondary hydrogens) is *ca.* 1 : 6. This statistical ratio is of the same order as reported¹⁹ for t-butoxy radical attack on methyl and methylene groups in hydrocarbons (*ca.* 1 : 8). The formation of compound (XVII) as the only dichlorinated cyclobutane derivative indicates that the tertiary hydrogen in compound (XVI) is far more easily abstracted than a secondary or primary hydrogen atom. This tertiary hydrogen is also far more readily abstracted than a hydrogen atom in a methyl, methylene, or chloromethyl group in the monochloro-compound (XV).

It has been observed²⁰ that elemental sulphur will insert into germacyclobutanes to give a five-membered ring containing the Ge-S-C unit. However, the attempted reaction between (I) and sulphur in refluxing decalin gave unchanged (I) (93%).

EXPERIMENTAL

Reactants and products were manipulated where possible in a conventional vacuum system to avoid contamination with air or moisture. Products were examined by elemental analysis, molecular-weight determination (Mechrolab model 301A vapour-pressure osmometer), i.r. spectroscopy (Perkin-Elmer 457 spectrophotometer), n.m.r. spectroscopy (Perkin-Elmer R10 instrument operating at 60.0 MHz for ¹H 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. Starting materials were either industrially available or were prepared by literature methods and were thoroughly purified before use. 1,1,3,3-Tetramethyl-1,3-disilacyclobutane, (I) (44%),

¹⁹ C. Walling and B. B. Jacknow, *J. Amer. Chem. Soc.*, 1960, **82**, 6108.

²⁰ P. Mazerolles, J. Dubac, and M. Lesbre, *J. Organometallic Chem.*, 1966, **5**, 35.

²¹ W. A. Kriner, *J. Org. Chem.*, 1964, **29**, 1601.

was prepared by inverse addition of magnesium to a solution of chloro(chloromethyl)dimethylsilane in tetrahydrofuran (thf).²¹

Reactions of (I).—(a) *With hydrogen chloride.* A vigorous exothermic reaction occurred when an excess of dry hydrogen chloride was passed through a solution of (I) (4.60 g, 32.0 mmol) in dry carbon tetrachloride (20 cm³) at 0 °C. Distillation of the product at reduced pressure gave 2-chloro-2,4,4-trimethyl-2,4-disilapentane (4.93 g, 27.0 mmol, 84%) (Found: C, 40.1; H, 9.5; Cl, 19.4. Calc. for C₆H₁₇ClSi₂: C, 39.9; H, 9.5; Cl, 19.6%), b.p. 88–89 °C at 95 mmHg, *n*_D²⁰ 1.4315 (lit.,²² b.p. 153 °C, *n*_D²⁰ 1.4310).

(b) *With hydrogen bromide.* Reaction of (I) (5.49 g, 38.0 mmol) with an excess of hydrogen bromide in dry carbon tetrachloride (20 cm³) carried out as in experiment (a) at 0 °C gave 2-bromo-2,4,4-trimethyl-2,4-disilapentane (6.69 g, 30.0 mmol, 79%) (Found: C, 32.3; H, 7.7; Br, 35.3. Calc. for C₆H₁₇BrSi₂: C, 32.1; H, 7.6; Br, 35.5%), b.p. 104–105 °C at 86 mmHg, *n*_D²⁰ 1.4540 (lit.,²³ b.p. 170 °C, *n*_D²⁰ 1.4547).

(c) *With hydrogen iodide.* Reaction of (I) (5.31 g, 36.8 mmol) with excess of hydrogen iodide in dry carbon tetrachloride, carried out as in experiment (a) at 0 °C, gave 2-iodo-2,4,4-trimethyl-2,4-disilapentane (9.0 g, 33.2 mmol, 90%) (Found: C, 26.6. C₆H₁₇ISI₂ requires C, 26.4%), b.p. 59–60 °C at 5 mmHg, *n*_D²⁰ 1.4865. The compound readily liberated iodine in subdued daylight.

(d) *With chlorine.* Reaction of (I) (4.93 g, 34.0 mmol) with chlorine in dry carbon tetrachloride (20 cm³) at 0 °C, carried out as in experiment (a), gave 1,4-dichloro-2,2,4-trimethyl-2,4-disilapentane (5.58 g, 26.0 mmol, 76%) (Found: C, 33.3; H, 7.5; hydrolysable Cl, 16.3. Calc. for C₆H₁₆Cl₂Si₂: C, 33.4; H, 7.5; hydrolysable Cl, 16.5%), b.p. 88–90 °C at 12 mmHg, *n*_D²⁰ 1.4635 (lit.,²⁴ b.p. 88–90 °C at 12 mmHg, *n*_D²⁰ 1.4642).

(e) *With bromine.* Addition of bromine to a solution of (I) (5.45 g, 35.0 mmol) in dry carbon tetrachloride (20 cm³) at 0 °C gave, after distillation, 1,4-dibromo-2,2,4-trimethyl-2,4-disilapentane (9.26 g, 30.0 mmol, 86%) (Found: C, 23.9; H, 5.0; hydrolysable Br, 26.0. Calc. for C₆H₁₆Br₂Si₂: C, 23.7; H, 5.3; hydrolysable Br, 26.3%), b.p. 105–106 °C at 10 mmHg, *n*_D²⁰ 1.4987 (lit.,⁸ b.p. 235–250 °C).

(f) *With trifluoroiodomethane.* A mixture of the iodide (8.23 g, 42.0 mmol) and (I) (3.31 g, 23.0 mmol), sealed *in vacuo* in a silica tube (*ca.* 300 cm³) and the tube shaken and irradiated at a distance of *ca.* 15 cm from a Hanovia 500 W mercury-resonance lamp (48 h), gave (i) hexafluoroethane (2.48 g, 18.0 mmol, 86%), (ii) unchanged (I) (3.14 g, 21.8 mmol, 95%), and (iii) a mixture of higher-boiling material (trace) and iodine. An attempted reaction in a sealed tube *in vacuo* at room temperature in the dark (48 h) gave only unchanged reactants.

(g) *With lithium tetrahydridoaluminate.* Compound (I) (7.03 g, 48.9 mmol) was added slowly (10 min) to a stirred slurry of Li[AlH₄] (10.0 g, 0.264 mol) in thf (100 cm³) under reflux. The solution was further refluxed (1 h), cooled, and the excess of hydride destroyed by hydrolysis. The organic layer was dried and distilled to afford 2,2,4-trimethyl-2,4-disilapentane (5.71 g, 39.2 mmol, 80%) which was purified further by g.l.c. (3 m Silicone SE 30 column at

²² M. Kumada, J. Nakajima, M. Ishikawa, and Y. Yamamoto, *J. Org. Chem.*, 1958, **23**, 292.

²³ H. S. Nametkin, A. V. Topchiev, and L. S. Povarov, *Doklady Akad. Nauk S.S.S.R.*, 1956, **109**, 787.

²⁴ G. Fritz and H. Burdt, *Z. anorg. Chem.*, 1962, **314**, 35.

100 °C) to afford material (Found: C, 49.5; H, 12.4. Calc. for $C_6H_{18}Si_2$: C, 49.4; H, 12.4%), b.p. 119–119.5 °C, n_D^{20} 1.4129 (lit.,²³ b.p. 120 °C, n_D^{20} 1.4122). An analogous reaction at room temperature gave unchanged (I) (96%) and comparable experiments in refluxing diethyl ether also gave near quantitative recoveries of (I).

(h) *With phenyl-lithium.* Compound (I) (4.11 g, 28.5 mmol) was added slowly to phenyl-lithium (0.20 mol) in diethyl ether (200 cm³) under an atmosphere of argon. The resulting solution was heated under reflux (2.8 h), then cooled and hydrolysed and the organic layer separated, dried, and fractionated to give impure 2,2,4-trimethyl-4-phenyl-2,4-disilapentane (4.98 g), b.p. 115–125 °C at 20 mmHg, and a higher-boiling residue (2.0 g). Examination of the impure disilapentane fraction by g.l.c. (3 m Silicone SE 30 column at 180 °C) showed that it consisted of 2,2,4-trimethyl-4-phenyl-2,4-disilapentane (3.38 g, 15.3 mmol, 54%) and biphenyl present in the ratio 68 : 23 as confirmed by a comparison of the i.r. spectrum and g.l.c. retention times with those of authentic samples.

A sample of the disilapentane was prepared *via* the dropwise addition of chlorodimethylphenylsilane (19.5 g, 0.116 mol) to the Grignard reagent made from (chloromethyl)trimethylsilane (16.0 g, 0.130 mol) and magnesium (3.1 g, 0.130 mol) in diethyl ether (100 cm³). The mixture was hydrolysed with aqueous sulphuric acid (2N, 100 cm³), and the organic layer was separated, dried, and fractionated to yield 2,2,4-trimethyl-4-phenyl-2,4-disilapentane (8.96 g, 40.0 mmol, 35%) (Found: C, 65.1; H, 10.0. Calc. for $C_{12}H_{22}Si_2$: C, 64.9; H, 9.95%), b.p. 120 °C at 20 mmHg, n_D^{20} 1.4895 (lit.,²⁵ b.p. 120 °C at 20 mmHg, n_D^{20} 1.4790) and a residue of 1,1,3,3-tetramethyl-1,3-diphenyldisiloxane (9.87 g, 35.0 mmol, 61%).

(i) *With phenylmagnesium bromide.* Compound (I) (4.40 g, 30.5 mmol) was added slowly to phenylmagnesium bromide (0.10 mol) in thf (150 cm³) and the reaction mixture was heated under reflux (45 min) then cooled and hydrolysed. Fractionation of the dried organic layer gave unchanged (I) (3.7 g, 26.0 mmol, 85%) and a higher-boiling residue (1.97 g) which was shown by i.r. spectroscopy and g.l.c. (3 m SE 30 oil at 180 °C) to contain 2,2,4-trimethyl-4-phenyl-2,4-disilapentane (1–2%), biphenyl, and polymeric material.

(j) *With ethanolic sodium hydroxide solution.* Compound (I) (4.10 g, 28.0 mmol) was added to an excess of cold ethanolic sodium hydroxide solution (0.1M, 100 cm³). After the initial exothermic reaction had subsided the resultant solution was heated under reflux (30 min), cooled, diluted with water (100 cm³), and extracted with diethyl ether (2 × 50 cm³). The ether extract was washed with water (2 × 10 cm³), dried, and fractionated to give 2,4,4-trimethyl-2,4-disilapentane-2-ol (3.30 g, 20.5 mmol, 72%) (Found: C, 44.7; H, 10.95. Calc. for $C_6H_{18}OSi_2$: C, 44.4; H, 11.15%), b.p. 65–66 °C at 15 mmHg, n_D^{20} 1.4324 (lit.,²⁶ b.p. 50–52 °C at 5 mmHg, n_D^{20} 1.4318) and 1,1,3,3-tetramethyl-1,3-bis(trimethylsilylmethyl)disiloxane (0.64 g, 2.1 mmol, 11%) (Found: C, 47.0; H, 11.4. Calc. for $C_{12}H_{34}OSi_4$: C, 47.1; H, 11.2%), b.p. 119–120 °C at 15 mmHg, n_D^{20} 1.4335 (lit.,²⁶ b.p. 93–94 °C at 3.5 mmHg, n_D^{20} 1.4340).

(k) *With sulphuric acid.* Compound (I) (3.90 g, 27.0 mmol) was added dropwise (30 min) to concentrated

sulphuric acid (3.90 g, 40.0 mmol) at –10 °C. Water (100 cm³) was added immediately, the solution was extracted with diethyl ether (2 × 25 cm³), and the ether extract was washed with water (2 × 10 cm³), dried, and fractionated to give 1,1,3,3-tetramethyl-1,3-bis(trimethylsilylmethyl)disiloxane (3.71 g, 12.2 mmol, 91%).

(l) *With ethanolic silver(I) nitrate.* Compound (I) (8.00 g, 55.6 mmol) was slowly added (30 min) to a solution of $AgNO_3$ (9.45 g, 56.0 mmol) in ethanol (260 cm³) at room temperature; there was an immediate precipitation of metallic silver. The mixture was stirred (1 h) and the silver (1.08 g, 10.0 mmol, 18%) was filtered off. Evaporation of the filtrate gave unchanged $AgNO_3$ (6.18 g, 43.0 mmol, 77%) and 1,1,3,3-tetramethyl-1,3-bis(trimethylsilylmethyl)disiloxane (6.63 g, 21.7 mmol, 78%) which g.l.c. (as before) showed contained a small amount of higher-boiling material.

(m) *With nitrogen dioxide.* An excess of dry nitrogen dioxide was passed (1 h) into a stirred solution of compound (I) (4.03 g, 27.9 mmol) in dry carbon tetrachloride (25 cm³) maintained at 0 °C. The resulting material was fractionated to give a liquid (*ca.* 0.3 g), b.p. 60–61 °C at 0.3 mmHg, m.p. 28–30 °C, and a colourless residue (4.25 g) (Found: *M*, 2035) presumed to be a polysiloxane. The liquid was identical to the trace contaminant in the product from the previous experiment and was identified as 2,2,4,4,6,6,8,8-octamethyl-1,5-dioxo-2,4,6,8-tetrasilacyclo-octane [Found: C, 42.5; H, 9.4%; *M* (mass spec.), 292. Calc. for $C_{10}H_{28}O_2Si_4$: C, 41.1; H, 9.6%; *M*, 292] (lit.,¹⁷ b.p. 103–104 °C at 20 mmHg, m.p. 28–29 °C).

(n) *With mercury(II) chloride.* Compound (I) (4.32 g, 29.9 mmol) was added slowly to a solution of $HgCl_2$ (16.3 g, 60.0 mmol) in ethanol (200 cm³). After the initial exothermic reaction had subsided the reaction mixture was heated under reflux (30 min), then water (100 cm³) was added and the resulting mixture was stirred (15 min). The solution was extracted with diethyl ether (50 cm³), the ether layer was dried (Na_2SO_4), and the solvent removed to give a white solid (19.3 g). The solid was treated with carbon tetrachloride (30 cm³) and the excess of $HgCl_2$ was filtered off. Removal of the solvent from the filtrate gave solid material which was repeatedly recrystallised from light petroleum (b.p. 40–60 °C) to afford 1,3-bis[(chloromercuriomethyl)dimethylsilylmethyl]-1,1,3,3-tetramethyldisiloxane (5.67 g, 7.3 mmol, 49%) (Found: C, 18.3; H, 4.5%; *M*, 740. Calc. for $C_{12}H_{32}Cl_2Hg_2OSi_4$: C, 18.6; H, 4.2%; *M*, 774), m.p. 68–69 °C (lit.,⁹ *ca.* 75 °C).

(o) *With mercury(II) acetate.* Compound (I) (4.32 g, 29.9 mmol) was added to a solution of $Hg(O_2CMe)_2$ (12.9 g, 29.9 mmol) in ethanol (200 cm³) under reflux and the mixture was further refluxed (30 min). Solid mercury(I) acetate (0.44 g, 1.2 mmol) was filtered off and removal of the solvent from the filtrate gave an oily liquid (odour of acetic acid) which was dissolved in ethanol (100 cm³) and treated with aqueous sodium hydrogencarbonate (5%, 50 cm³). The resulting material was extracted with diethyl ether (3 × 20 cm³), the extract was dried (Na_2SO_4), and the solvent removed *in vacuo* to give a dimeric product (6.26 g, 7.8 mmol, 53%) [Found: C, 20.3; H, 4.7%; *M* (osmometric), 805; *M* – 15 (mass spec.), 709. $C_{12}H_{32}Hg_2O_2Si_4$ requires C, 20.0; H, 4.5%; *M*, 722], m.p. 121–122 °C. A comparable reaction in which a mixture of (I) and $Hg(O_2CMe)_2$ (1 : 2 molar ratio) was heated under

²⁵ G. Fritz and J. Grobe, *Z. anorg. Chem.*, 1961, **311**, 325; G. Fritz, W. Kemmerling, G. Sonntag, H. J. Becher, E. A. V. Ebsworth, and J. Grobe, *ibid.*, 1963, **321**, 10.

²⁶ A. V. Topchiev, N. S. Nametkin, and L. S. Povarov, *Doklady Akad. Nauk S.S.S.R.*, 1964, **97**, 99.

reflux in benzene (20 h) gave a near quantitative recovery of (I).

(p) *Unsuccessful reactions.* The following reactions of (I) were investigated, but in all cases near quantitative amounts of unchanged (I) were recovered. (i) A mixture of (I) (4.32 g, 29.9 mmol), phenylmercury chloride (9.32 g, 29.9 mmol), ethanol (300 cm³), and benzene (200 cm³) was heated under reflux (1 h). (ii) A mixture of (I) (4.32 g, 29.9 mmol), sulphur (0.96 g, 30.0 mmol), and decalin (20 cm³) was heated under reflux (10.5 h). (iii) Compound (I) (2.50 g, 17.3 mmol) was eluted with light petroleum (b.p. 40–60 °C) from a basic alumina column (Al₂O₃, Woelm, activity grade 1). (iv) A mixture of (I) (7.02 g, 49.0 mmol) and benzenethiol (5.50 g, 50.0 mmol) was heated under reflux (2 h). (v) A mixture of (I) (5.0 g, 35.0 mmol) and heptan-1-ol (4.0 g, 34.2 mmol) was heated under reflux (12 h). (vi) A mixture of (I) (1.84 g, 13.0 mmol), *N*-bromosuccinimide (2.28 g, 13.0 mmol), benzoyl peroxide (0.13 mmol), and carbon tetrachloride (40 cm³) was heated under reflux (1 h). Further reactions using azobisisobutyronitrile as initiator and photochemical conditions were also unsuccessful.

(q) *With t-butyl hypochlorite.* The hypochlorite (12.0 g, 0.11 mol) was added slowly (1 h) to a solution of (I) (24.0 g, 0.167 mol) in carbon tetrachloride (70 cm³) while the solution was irradiated at a distance of 15 cm with a Hanovia S 500 medium-pressure lamp. The irradiation was continued (0.5 h), and the solvent, some unchanged (I), and *t*-butyl alcohol formed during the reaction were removed by fractionation at atmospheric pressure. Further fraction-

ation of the resulting material afforded unchanged (I) (12.7 g, 88.0 mmol, 53%), b.p. 118–120 °C, and a higher-boiling residue (12.4 g) which was shown by g.l.c. (2 m Silicone MS 550 oil at 100 °C) to contain two major and two minor components. These components were separated by g.l.c. (4 m Silicone at 115 °C) and identified as (i) 2-chloro-2,4,4-trimethyl-2,4-disilapentane (1.04 g, 5.5 mmol, 7%) by i.r. and n.m.r. spectroscopy, (ii) a mixture (5.35 g, 30.1 mmol, 37%) (Found: C, 40.4; H, 8.3%; *M*, 182. Calc. for C₆H₁₅ClSi₂: C, 40.3; H, 8.4%; *M*, 178), b.p. 174–176 °C, *n*_D²⁰ 1.4650, of 2-chloro-1,1,3,3-tetramethyl-1,3-disilacyclobutane (2.68 g, 15.1 mmol, 18%), ¹H n.m.r. band at –1.28 p.p.m. (Si·CHCl·Si) relative to internal cyclohexane, and 1-chloromethyl-1,3,3-trimethyl-1,3-disilacyclobutane (2.67 g, 15.0 mmol, 18%), ¹H n.m.r. band at –1.40 p.p.m. (Si·CH₂Cl), (iii) 2,2-dichloro-1,1,3,3-tetramethyl-1,3-disilacyclobutane (3.15 g, 14.7 mmol, 19%) (Found: C, 33.6; H, 6.8%; *M*, 214. C₆H₁₄Cl₂Si₂ requires C, 33.8; H, 6.6%; *M*, 213), *v*_{max} at 945s cm⁻¹ (ring Si·CH₂·Si), ¹H n.m.r. bands at 0.85 (s, 12 H, 2 SiMe₂) and 0.95 (s, 2 H, CH₂) p.p.m., *m/e* 217, 215, and 213 (50, *M*⁺), 85 (25, [C₂H₅Si₂]⁺), 84 (50, [C₂H₄Si₂]⁺), and 73 (100%, [Me₂SiHCH₂]⁺), and (iv) 1,4-dichloro-2,2,4-trimethyl-2,4-disilapentane (1.5 g, 7.0 mmol, 9%), by n.m.r. spectroscopy.

We thank Imperial Chemical Industries Limited (Nobel Division) for gifts of silicon starting materials and the S.R.C. for the award of a maintenance grant (to P. A. G.).

[4/1794 Received, 29th August, 1974]