Organosilicon Chemistry. Part XVIII.[1] Some Reactions of 1,3-Dimethyl-1,3-diphenyl-, 1,1,3,3-Tetraphenyl-, and 1,1-Dimethyl-3,3-diphenyl-1,3-disilacyclobutane

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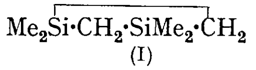
Ring-opening of 1,3-dimethyl-1,3-diphenyl- and 1,1,3,3-tetraphenyl-1,3-disilacyclobutane takes place on treatment with halogens, hydrogen halides, lithium aluminium hydride, sodium hydroxide, or sulphuric acid, but the reactions with halogens and hydrogen halides are complicated by silicon–phenyl bond scission. 1,1-Dimethyl-3,3-diphenyl-1,3-disilacyclobutane is conveniently prepared by reaction of an equimolar mixture of the silanes $Me_2SiCl{\cdot}CH_2Cl$ and $Ph_2SiCl{\cdot}CH_2Cl$ in tetrahydrofuran with magnesium. It reacts with hydroxide, methoxide, ethoxide, hydride ion, hydrogen chloride, or hydrogen bromide to give major products arising *via* $SiMe_2–CH_2$ bond scission, but in contrast it reacts with chlorine or bromine to give major products arising *via* $SiPh_2–CH_2$ bond scission.

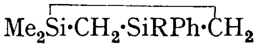
THE synthesis and chemistry of 1,3-disilacyclobutanes has been reviewed recently.[2] Such compounds have been observed to undergo ready ring-opening reactions with strong electrophiles and nucleophiles and ring-insertion reactions with certain reagents, *e.g.* sulphur trioxide and dichlorocarbene. Most interest has been centred around methyl- and chlorine-substituted derivatives, especially 1,1,3,3-tetramethyl-1,3-disilacyclobutane (I), and although the phenyl-substituted compounds (II)—(IV) have been synthesised [3-5] their chemistry has been little investigated, apart from certain polymerisation reactions.[4]

In the present work 1,1-dimethyl-3,3-diphenyl-1,3-disilacyclobutane, (V), has been synthesised and some reactions of this compound and the disilacyclobutanes (III) and (IV) with electrophiles and nucleophiles have been carried out.



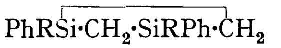
$Me_2Si{\cdot}CH_2{\cdot}SiMe_2{\cdot}CH_2$

(I)



$Me_2Si{\cdot}CH_2{\cdot}SiRPh{\cdot}CH_2$

(II) R = Me
(V) R = Ph



$PhRSi{\cdot}CH_2{\cdot}SiRPh{\cdot}CH_2$

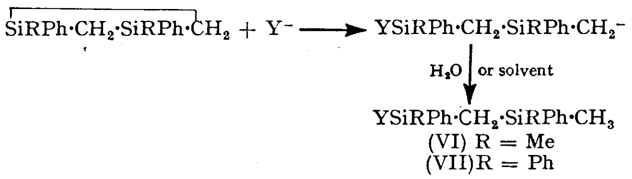
(III) R = Me
(IV) R = Ph

Preparation of Disilacyclobutane (*V*).—The first straight-forward preparation of the disilacyclobutane (I) in 10—20% yield involved reaction of chloro(chloromethyl)dimethylsilane with magnesium in tetrahydrofuran,[6] but it was later reported that the inverse addition procedure, *i.e.* addition of magnesium to the chlorosilane in tetrahydrofuran, gave a much improved yield (50%).[3]

Addition of magnesium to an equimolar mixture of chloro(chloromethyl)dimethylsilane and chloro(chloromethyl)diphenylsilane in tetrahydrofuran gave a mixture of the disilacyclobutanes (I) (10%), (IV) (10%), and (V) (38%), together with 1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane (26%) and unidentified higher-boiling material. On statistical grounds, providing both the reactant chlorosilanes are of equal reactivity, the ratio of the disilacyclobutane products (I), (IV), and (V) should be 1 : 1 : 2; the reason for the observed ratio (1 : 1 : 4), *i.e.* the enhanced yield of compound (V), is not apparent.

Reactions of Disilacyclobutanes (*III*) *and* (*IV*).—The ^1H n.m.r. spectrum † of disilacyclobutane (III) showed that it was a *ca.* 50 : 50 mixture of the *cis*- and *trans*-isomers and it was used as such in the following reactions.

The reactions of disilacyclobutanes (III) and (IV) with the nucleophilic reagents sodium hydroxide and lithium aluminium hydride gave the compounds (VI; R = Me, Y = OH) 99 and (VI; R = Me, Y = H) 93%, and (VII; R = Ph, Y = OH) 96 and (VII; R = Ph, Y = H) 94%, respectively.



$$SiRPh{\cdot}CH_2{\cdot}SiRPh{\cdot}CH_2 + Y^- \longrightarrow YSiRPh{\cdot}CH_2{\cdot}SiRPh{\cdot}CH_2^- \xrightarrow{H_2O \text{ or solvent}} YSiRPh{\cdot}CH_2{\cdot}SiRPh{\cdot}CH_3$$

(VI) R = Me
(VII) R = Ph

The structure of compound (VII; Y = H) was confirmed by the following unambiguous synthesis:

$$ClCH_2{\cdot}SiPh_2Cl \xrightarrow{\text{i}} \underset{(55\%)}{ClCH_2{\cdot}SiPh_2H} + \underset{(56\%)}{MePh_2SiH}$$

$$ClCH_2{\cdot}SiPh_2H \xrightarrow{\text{ii, iii}} Ph_2SiH{\cdot}CH_2{\cdot}SiMePh_2$$

Reagents: i, $LiAlH_4–Et_2O$ at 35 °C; ii, Mg; iii, $MePh_2SiCl$.

In the first stage the formation of the silane $MePh_2SiH$ was unexpected since a Si–Cl bond is normally much more reactive than a C–Cl bond towards lithium aluminium hydride and selective reduction of the former bond

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† Detailed ^1H n.m.r. and i.r. spectral data for the new compounds described in this paper are deposited as a Supplementary publication (SUP No. 21374; 6 pp.). See Notices to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[1] Part XVII, A. M. Devine, P. A. Griffin, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, *J.C.S. Dalton*, 1975, 1434.

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

[3] W. A. Kriner, *J. Org. Chem.*, 1964, **29**, 1601.

[4] N. S. Nametkin, V. M. Vdovin, and A. V. Zalenaya, *Doklady Akad. Nauk S.S.S.R.*, 1966, **170**, 972.

[5] N. S. Nametkin, V. M. Vdovin, V. I. Zav'yalov, and P. L. Grinberg, *Izvest Akad. Nauk S.S.S.R. Ser. Khim.*, 1965, 902.

[6] H. Gilman and W. H. Atwell, *J. Organometallic Chem.*, 1964, **2**, 277.

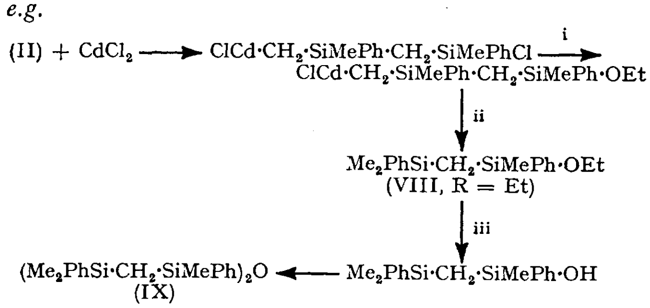
can be achieved.[7] Further examples of concomitant reduction of C–Cl and Si–Cl bonds observed in the present work include the compounds $MePhSiCl{\cdot}CH_2Cl$ and $ClCH_2{\cdot}SiMePh{\cdot}CH_2{\cdot}SiMePhCl$.

The isolation of the silanols (VI and VII; Y = OH), rather than the corresponding disiloxanes, from the hydroxide reactions indicates that condensation of the silanols is not favoured, probably because of steric hindrance, *cf.* $Bu^tSiMe_2{\cdot}OH$[8] and $Ph_3Si{\cdot}SiPh_2{\cdot}OH$.[9] This is supported by the observation that the thin-film i.r. spectra of the silanols * show decreased hydrogen bonding in the order $Me_3Si{\cdot}CH_2{\cdot}SiMe_2{\cdot}OH$ > (VI; Y = OH) > (VII; Y = OH), *i.e.* as methyl is replaced by bulkier phenyl, the strengths of the hydrogen bonds, as measured by the frequency differences between the free and hydrogen-bonded OH groups,[10] also decrease in the same order. These changes may be interpreted as indicating increasing steric hindrance to hydrogen bonding, particularly since the spectra of dilute solutions of the silanols in carbon tetrachloride show that the hydrogen bonding is intermolecular.

Reaction did not take place between ethanol and disilacyclobutane (III) at *ca.* 80 °C, *cf.* disilacyclobutane (I),[1] but alcoholysis did occur with ethanol in the presence of zinc or cadmium chlorides or with methanol in the presence of thallium(I) formate.

$$\text{(III)} + ROH \xrightarrow{\text{catalyst}} \underset{\text{(VIII)}}{RO{\cdot}SiMePh{\cdot}CH_2{\cdot}SiMe_2Ph} + \underset{\text{(IX)}}{(Me_2PhSi{\cdot}CH_2{\cdot}SiMePh)_2O}$$

It is probable that organometallic adducts are initially formed which subsequently react with alcohol, *e.g.*



$$\text{(II)} + CdCl_2 \longrightarrow ClCd{\cdot}CH_2{\cdot}SiMePh{\cdot}CH_2{\cdot}SiMePhCl \xrightarrow{\text{i}} ClCd{\cdot}CH_2{\cdot}SiMePh{\cdot}CH_2{\cdot}SiMePh{\cdot}OEt \xrightarrow{\text{ii}} \underset{\text{(VIII, R = Et)}}{Me_2PhSi{\cdot}CH_2{\cdot}SiMePh{\cdot}OEt} \xrightarrow{\text{iii}} Me_2PhSi{\cdot}CH_2{\cdot}SiMePh{\cdot}OH \longrightarrow \underset{\text{(IX)}}{(Me_2PhSi{\cdot}CH_2{\cdot}SiMePh)_2O}$$

Reagents: i, EtOH (−HCl); ii, H^+ or H_2O; iii, H^+ ($-H_2O$); iv, H^+($-H_2O$).

and in support of this the recovered inorganic material showed, in all cases, the presence of OH groups (i.r.).

In the chloride-catalysed reactions the ratio of products (VIII) : (IX) was *ca.* 3 : 1, while in the thallium(I) formate reaction the ratio was *ca.* 9 : 1, which suggests that the extent of silanol condensation depends on the strength of the acid liberated (HCl > HCO_2H).

Neither of the disilacyclobutanes (III) or (IV) was affected by basic alumina, *cf.* disilacyclobutane (I),[1] a reagent which causes ring-opening of 1,1,2-triphenylsilacyclobutane.[11] This is further evidence in favour of lower ring strain in the disilacyclobutanes than in monosilacyclobutanes.[1]

Sulphuric acid, hydrogen chloride, hydrogen bromide, chlorine, or bromine also effected ring-opening of the two disilacyclobutanes. These reagents are normally regarded as electrophilic and the ring-opening reactions probably involve initial electrophilic attack at a ring carbon atom although nucleophilic attack at silicon cannot be ruled out on the present evidence.

The reactions with concentrated sulphuric acid were vigorously exothermic and the solid products were apparently polymeric [i.r. band at 1 050 cm^{-1} (Si–O–Si)]. The spectra also showed an absence of characteristic phenyl bands, indicating that Si–phenyl bond cleavage had occurred, as observed in the reactions of sulphuric acid with other compounds containing aryl–silicon bonds.[12]

Of the halogen and hydrogen halide reactions only that of hydrogen chloride with disilacyclobutane (III) was straightforward. This gave the expected ring-opened 1 : 1 adduct, $Me_2PhSi{\cdot}CH_2{\cdot}SiMePhCl$ (96%), which showed three Si–methyl absorptions in its ^1H n.m.r. spectrum indicating that the methyls in the *gem*-dimethyl group are non-equivalent.

In contrast the reaction of an excess of hydrogen bromide with disilacyclobutane (III) gave a linear dibromide (97%) which contained only one phenyl group.

$$\text{(III)} + 2HBr \longrightarrow PhMe_3Si_2(CH_2)Br_2 + C_6H_6$$

The ^1H n.m.r. spectrum of the product showed three bands in the Si–methyl region, indicating the presence of a *gem*-dimethyl group in which the methyls are non-equivalent. This suggests that the product is 2,4-dibromo-2-methyl-4-phenyl-2,4-disilapentane, (X), the asymmetric silicon atom of which renders the methyls in the Me_2SiBr group non-equivalent, and not the alternative 2,2-dibromo-4-methyl-4-phenyl-2,4-disilapentane (XI) which contains no asymmetric silicon atom. The

$$\underset{\text{(X)}}{Me_2SiBr{\cdot}CH_2{\cdot}SiMePhBr} \qquad \underset{\text{(XI)}}{Me_2PhSi{\cdot}CH_2{\cdot}SiMeBr_2}$$

structure (X) for the product was confirmed by reduction or fluorination of the bromine atoms to give 2-methyl-4-phenyl-2,4-disilapentane (XII) (98%) and 2,4-difluoro-2-methyl-4-phenyl-2,4-disilapentane (XIII) (82%), respectively. The ^1H n.m.r. spectrum of the reduced product showed two Si–H absorptions at τ 5.85 (nonet) and 5.41 (sextet) as expected for structure (XII); the spectrum of the reduced compound $Me_2PhSi{\cdot}CH_2{\cdot}SiMeH_2$ would have been expected to shown one Si–H absorption

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* See Supplementary publication; details in footnote on p. 1822.

[7] H. D. Kaesz and F. G. A. Stone, *J. Chem. Soc.*, 1957, 1433.

[8] L. H. Sommer and L. J. Tyler, *J. Amer. Chem. Soc.*, 1954, **76**, 1030.

[9] H. Gilman and J. J. Goodman, *J. Amer. Chem. Soc.*, 1953, **75**, 1250.

[10] M. Tichy, *Adv. Org. Chem. Methods and Results*, 1965, **5**, 115.

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

[12] C. Eaborn, 'Organosilicon Compounds,' Butterworths, London, 1960.

appearing as a sextet. Similarly the ^{19}F n.m.r. spectrum of the fluorinated product showed two absorptions of equal intensity at τ 7.37 (nonet) and 8.01 (sextet) p.p.m. to high field of external trifluoroacetic acid in accord

$$\begin{tikzcd}[column sep=small] & \mathrm{Me_2SiH{\cdot}CH_2{\cdot}SiMePhH}\ \mathrm{(XII)} \\ \mathrm{Me_2SiBr{\cdot}CH_2{\cdot}SiMePhBr} \arrow[ur, "\mathrm{i}"] \arrow[dr, "\mathrm{ii}"'] & \\ & \mathrm{Me_2SiF{\cdot}CH_2{\cdot}SiMePhF}\ \mathrm{(XIII)} \end{tikzcd}$$

Reagents: i, $LiAlH_4$; ii, SbF_3.

with structure (XIII); the compound $Me_2PhSi{\cdot}CH_2{\cdot}SiMeF_2$ would be expected to show a single sextet absorption in its spectrum.

The reduced product (XII) was also unambiguously synthesised by the following route:

$$\mathrm{PhMe_2SiCl} \xrightarrow{\mathrm{i}} \mathrm{PhMeSiCl{\cdot}CH_2Cl} \xrightarrow{\mathrm{ii}}$$

$$\underset{(23\%)}{\mathrm{PhMeSiH{\cdot}CH_2Cl}} + \underset{(48\%)}{\mathrm{PhMe_2SiH}} + \mathrm{(ClCH_2{\cdot}SiMePh)_2O}$$

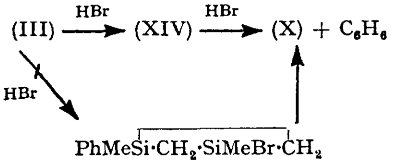
$$\mathrm{PhMeSiH{\cdot}CH_2Cl} \xrightarrow{\mathrm{iii,\ iv}} \underset{(50\%)}{\mathrm{Me_2SiH{\cdot}CH_2{\cdot}SiMePhH}}$$

Reagents: i, Cl_2; ii, $LiAlH_4$; iii, Mg; iv, Me_2SiHCl.

Treatment of disilacyclobutane (III) with a deficiency of hydrogen bromide, followed by reduction with lithium aluminium hydride under conditions where ring-opening does not take place (Et_2O, 35 °C), gave a mixture of unchanged (III) and 2,4-diphenyl-2-methyl-2,4-disilapentane (VI; R = Me, Y = H), *i.e.*

$$\mathrm{(III)} \xrightarrow{\mathrm{HBr}} \underset{\mathrm{(XIV)}}{\mathrm{Me_2PhSi{\cdot}CH_2{\cdot}SiMePhBr}} \xrightarrow{\mathrm{LiAlH_4}} \mathrm{Me_2PhSi{\cdot}CH_2{\cdot}SiMePhH}$$

This shows that in the reaction of disilacyclobutane (III) with an excess of hydrogen bromide ring-opening first occurs to give the adduct (XIV) followed by Si–Ph cleavage and not *vice versa, i.e.*



$$\begin{tikzcd} \mathrm{(III)} \arrow[r, "\mathrm{HBr}"] \arrow[dr, "\mathrm{HBr}"'] & \mathrm{(XIV)} \arrow[r, "\mathrm{HBr}"] & \mathrm{(X)} + \mathrm{C_6H_6} \\ & \mathrm{PhMeSi{\cdot}CH_2{\cdot}SiMeBr{\cdot}CH_2} \arrow[ur] & \end{tikzcd}$$

The Me_2PhSi-group in adduct (XIV) is thus more susceptible to Si–Ph cleavage by hydrogen bromide than is the BrPhMeSi group.

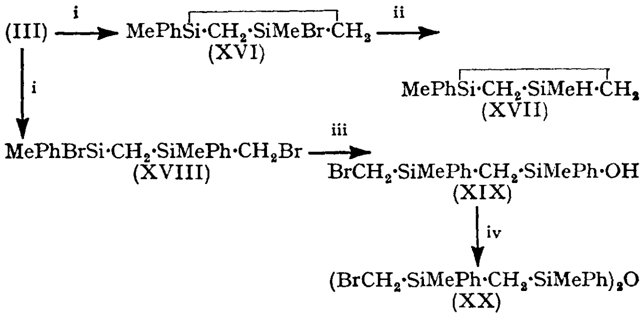
Treatment of disilacyclobutane (IV) with an excess of hydrogen bromide followed by immediate reduction of the product with lithium aluminium hydride gave 1,1,3-triphenyl-1,3-disilabutane (XV) (91%) the structure of which was proved by its n.m.r. spectrum [two Si–H absorptions of equal intensity at τ 5.02 (t) and 5.48 (sextet)].

$$\mathrm{(IV)} \xrightarrow{\mathrm{HBr}} \mathrm{MePh_2Si{\cdot}CH_2{\cdot}SiPh_2Br} \xrightarrow{\mathrm{HBr}} \mathrm{C_6H_6} +$$

$$\mathrm{MePhSiBr{\cdot}CH_2{\cdot}SiPh_2Br} \xrightarrow{\mathrm{LiAlH_4}} \mathrm{MePhSiH{\cdot}CH_2{\cdot}SiPh_2H}\quad \mathrm{(XV)}$$

The reactions of disilacyclobutanes (III) and (IV) with halogens were much slower than the corresponding reactions with disilacyclobutane (I) [1] and were complicated by Si–Ph cleavage. Treatment of disilacyclobutane (III) with bromine in carbon tetrachloride gave two products. The minor product, a hydrolytically unstable liquid, showed a strong absorption in its i.r. spectrum at 940 cm^{-1} (ring Si–CH_2–Si) and was suspected to be 1-bromo-1,3-dimethyl-3-phenyl-1,3-disilacyclobutane (XVI) (31%) The bromide was reduced with lithium aluminium hydride (Et_2O, 20 °C) to 1,3-dimethyl-1-phenyl-1,3-disilacyclobutane (XVII) (95%), the structure of which follows from a consideration of its i.r., n.m.r., and mass spectra. The n.m.r. spectrum † showed the expected resonances with the correct relative intensities and the Si–H absorption appeared as a regular octet. The i.r. spectrum showed, apart from phenyl and Si–Me bands, a strained ring band at 943 cm^{-1} and an absorption at 2 120 cm^{-1} (Si–H str.). The mass spectrum contained a strong parent peak (37.5%) at *m/e* 192, characteristic of 1,3-disilacyclobutanes, and a base peak at *m/e* 177 ($(M - Me)^+$), characteristic of many MeSi compounds.

The major product from the bromination reaction is less well characterised, but it is considered to be 1,4-dibromo-2-methyl-2,4-diphenyl-2,4-disilapentane (XVIII) (57%) on the basis of chemical reactions and i.r. spectra. Hydrolysis under mildly basic conditions gave the silanol (XIX) (80%) with i.r. bands at 3 636 and 3 367 cm^{-1} (Si–OH), which was converted into the corresponding disiloxane (XX) (73%) by passage through an alumina column; the i.r. spectrum of the disiloxane contained a band at 1 060 cm^{-1} (Si–O–Si), but the ebullioscopic molecular weight (790) was higher than expected (712).



$$\begin{tikzcd}[column sep=small] \mathrm{(III)} \arrow[r, "\mathrm{i}"] \arrow[d, "\mathrm{i}"] & \underset{\mathrm{(XVI)}}{\mathrm{MePhSi{\cdot}CH_2{\cdot}SiMeBr{\cdot}CH_2}} \arrow[r, "\mathrm{ii}"] & \underset{\mathrm{(XVII)}}{\mathrm{MePhSi{\cdot}CH_2{\cdot}SiMeH{\cdot}CH_2}} \\ \underset{\mathrm{(XVIII)}}{\mathrm{MePhBrSi{\cdot}CH_2{\cdot}SiMePh{\cdot}CH_2Br}} \arrow[rr, "\mathrm{iii}"] & & \underset{\mathrm{(XIX)}}{\mathrm{BrCH_2{\cdot}SiMePh{\cdot}CH_2{\cdot}SiMePh{\cdot}OH}} \arrow[d, "\mathrm{iv}"] \\ & & \underset{\mathrm{(XX)}}{\mathrm{(BrCH_2{\cdot}SiMePh{\cdot}CH_2{\cdot}SiMePh)_2O}} \end{tikzcd}$$

Reagents: i, Br_2–CCl_4; ii, $LiAlH_4$; iii, H_2O; iv, Al_2O_3.

The corresponding reaction with chlorine in carbon tetrachloride gave a disilacyclobutane mixture (*ca.* 10%) and 1,4-dichloro-2-methyl-2,4-diphenyl-2,4-disilapentane (XXI) (*ca.* 90%) which was reduced with lithium aluminium hydride to 2-methyl-2,4-diphenyl-2,4-disilapentane (VI; R = Me, Y = H) (87%).

$$\mathrm{(III)} \xrightarrow{\mathrm{i}} \underset{\mathrm{(XXI)}}{\mathrm{MePhSiCl{\cdot}CH_2{\cdot}SiMePh{\cdot}CH_2Cl}} \xrightarrow{\mathrm{ii}} \mathrm{MePhSiH{\cdot}CH_2{\cdot}SiMe_2Ph}$$

Reagents: i, Cl_2; ii, $LiAlH_4$.

The major reaction occurring is therefore ring-opening

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† See footnote on page 1822.

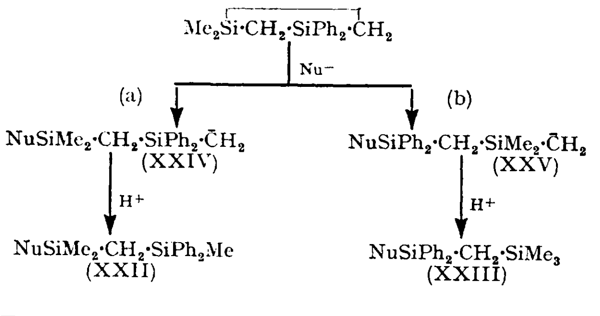
without Si–Ph cleavage. However, a qualitative incomplete chlorination reaction indicated that, although the major reaction involved ring-opening, some chlorination occurred to give a chlorodisilacyclobutane [shoulder on 936 cm^{-1} band].

A similar qualitative bromination of disilacyclobutane (IV) indicated that ring-opening, Si–Ph scission (detection of bromobenzene), and formation of a bromodisilacyclobutane had taken place.

Disilacyclobutane (I) reacts with t-butyl hypochlorite under free radical conditions,[1] but is unaffected by *N*-bromosuccinimide; [1] neither disilacyclobutane (III) nor (IV) reacted with the latter reagent in the presence of benzoyl peroxide, and disilacyclobutane (IV) was unaffected by t-butyl hypochlorite.

The disilacyclobutanes (III) and (IV) also were unaffected by a number of reagents which react with other strained heterocyclic ring compounds. Thus disilacyclobutane (III) was recovered unchanged after treatment with sulphur (250 °C or u.v. irradiation at 190 °C); it has been reported that sulphur inserts into Ge–C bonds in germacyclobutanes.[13] Cyclosilanes containing Si–Si bonds undergo Si–Si scission with phosphorus(v) chloride and with mercury(II) acetate,[14] but disilacyclobutane (IV) did not react with either reagent. Oxidising agents also failed to affect the ring system, *i.e.* disilacyclobutane (III) was recovered unchanged after being heated under reflux with a pyridine solution of potassium permanganate and disilacyclobutane (IV) did not react with nitrobenzene under reflux.

Reactions of Disilacyclobutane (*V*).—(a) *With hydroxide, alkoxide, and hydride ion.* Reaction of the disilacyclobutane (V) with sodium ethoxide in ethanol, sodium methoxide in methanol, sodium hydroxide in ethanol, or lithium aluminium hydride in tetrahydrofuran gave, in each case, a reasonable yield of a mixture of two products. These products were identified by n.m.r. spectroscopy as the compounds of type (XXII) and (XXIII) resulting from initial nucleophilic attack on the $SiMe_2$ [route (a)] and $SiPh_2$ [route (b)] groups, respectively, and the yields and ratios of the products formed are shown in Table 1.



The n.m.r. spectra of the adduct mixtures (Nu = HO, MeO, or EtO) showed absorptions at *ca.* τ 2.60 (10H), 9.25 (3H), 9.45 (2H), and 9.85 (6H), which were assigned to $SiPh_2$, SiMe, CH_2, and $SiMe_2$ groups, respectively, in adducts of type (XXII); absorptions at *ca.* τ 2.60 (10H), 9.55 (2H), and 9.90 (9H) were assigned to $SiPh_2$, CH_2, and $SiMe_3$ groups, respectively, in adducts of type (XXIII). The two products from the lithium aluminium hydride reaction were readily distinguished by their SiH n.m.r. absorptions; τ 5.82 (nonet, $HSiMe_2$, $J_{H-CH_2} \simeq J_{H-Me}$) for adduct (XXII; Nu = H) and τ 4.89 (t, $HSiPh_2$, J_{H-CH_2}) for adduct (XXIII; Nu = H).

TABLE 1

Reactions of nucleophiles with disilacyclobutane (V)

Nucleophile	Total yield of product (%)	Ratio (XXII) : (XXIII)
HO^-	86	58 : 42 *
MeO^-	71	70 : 30 †
EtO^-	65	68 : 32 †
H^-	88	73 : 27

* Average of three experiments. † Average of four experiments.

From Table 1 it can be seen that major nucleophilic attack on disilacyclobutane (V) occurs at the $SiMe_2$ group. This observation can be explained by (i) the $-I$ inductive effect of the phenyl groups on the adjacent silicon atom stabilising the intermediate carbanion (XXIV), the $+I$ inductive effect of the methyl groups on the adjacent silicon atom in carbanion (XXV) would have a destabilising effect, and(ii) steric hindrance, which would be less for attack at the $SiMe_2$ group than at the $SiPh_2$ group.

The mixture of silanols (XXII and XXIII; Nu = OH) showed no tendency to condense to form disiloxanes under the reaction conditions, *cf.* compounds (VI and VII; Y = OH).

(b) *With hydrogen halides.* The disilacyclobutane (V) on reaction with an excess of hydrogen chloride at 0 °C in solvent carbon tetrachloride gave a mixture of 2-chloro-4,4-diphenyl-2-methyl-2,4-disilapentane (XXVI) (76%) and 1-chloro-3,3-dimethyl-1,1-diphenyl-1,3-disilabutane (XXVII) (3%) in the ratio 95 : 5 as determined by n.m.r. spectroscopy.

$Me_2SiCl{\cdot}CH_2{\cdot}SiPh_2Me$ (XXVI) $Me_3Si{\cdot}CH_2{\cdot}SiPh_2Cl$ (XXVII)

The n.m.r. spectrum of the mixture showed bands at τ 2.56 (10H), 9.23 (2H), 9.29 (3H), and 9.71 (6H), assigned to $SiPh_2$, CH_2, SiMe, and $SiMe_2$ groups, respectively, in adduct (XXVI) and bands at τ 2.56 (10H), 9.11 (2H), and 9.92 (9H), assigned to $SiPh_2$, CH_2, and $SiMe_3$ groups, respectively, in adduct (XXVII).

Thus predominant cleavage of a $SiMe_2$–CH_2 bond in compound (V) rather than a $SiPh_2$–CH_2 bond has taken place. It has been reported [15] previously that reaction of hydrogen chloride with the disilacyclobutanes $Me_2Si{\cdot}CH_2{\cdot}SiMeCl{\cdot}CH_2$ and $Me_2Si{\cdot}CH_2{\cdot}SiHMe{\cdot}CH_2$ gave

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[13] P. Mazerolles, J. Dubac, and M. Lesbre, *J. Organometallic Chem.*, 1968, **12**, 143.

[14] H. Gilman and W. H. Atwell, *J. Org. Chem.*, 1963, **28**, 2905.

[15] E. D. Babich, V. N. Karel'skii, N. S. Nametkin, and V. M. Vdovin, *Doklady Akad. Nauk S.S.S.R.*, 1969, **189**, 334.

products resulting from $Me_2Si{-}CH_2$ and $XSiMe{-}CH_2$ cleavage in the ratios 95 : 5 (for X = Cl) and 87 : 13 (for X = H), *i.e.*, predominant $Me_2Si{-}CH_2$ fission was also observed.

Reaction of an excess of hydrogen bromide with the disilacyclobutane (V) at room temperature in solvent carbon tetrachloride gave 2,4-dibromo-2-methyl-4-phenyl-2,4-disilapentane (X) (85%). This product was also formed by reaction of hydrogen bromide with disilacyclobutane (III) (see earlier), a reaction in which ring-opening was shown to occur before Si–Ph cleavage. The present reaction is considered to follow an identical course, *i.e.*

$$\text{(V)} \xrightarrow{\text{HBr}} Ph_2MeSi{\cdot}CH_2{\cdot}SiMe_2Br \xrightarrow[\text{Si–Ph cleavage}]{\text{HBr}} \underset{\text{(X)}}{PhMeSiBr{\cdot}CH_2{\cdot}SiMe_2Br}$$

As with the hydrogen chloride reaction major attack is observed at a $SiMe_2{-}CH_2$ bond rather than a $SiPh_2{-}CH_2$ bond.

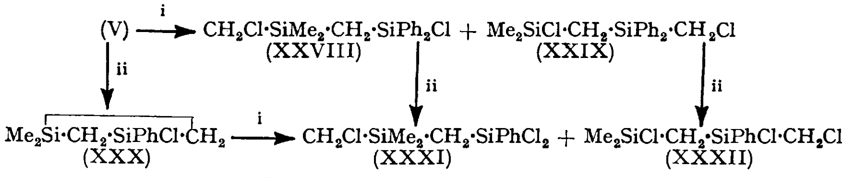
(*c*) *With chlorine and bromine.* In contrast to the ready ring-opening of the disilacyclobutane by the hydrogen halides the reaction with chlorine was slow. However, after passage of gaseous chlorine (6 h) through a solution of disilacyclobutane (V) in carbon tetrachloride at room temperature, the i.r. spectrum of the resultant material showed a strong band at 1 050 cm^{-1} (linear $Si{-}CH_2{-}Si$) and an absence of a band at 950 cm^{-1} (ring $Si{-}CH_2{-}Si$). Attempted separation of the high-boiling product (>90% if 1 : 1 adduct) by distillation at reduced pressure was unsuccessful.

The n.m.r. spectrum of the product showed absorption bands at τ 2.55 (8.4H), 7.13 (0.35H), 7.18 (1.5H), and 9.36 to 9.85 (*ca.* 8H), assigned to SiPh, CH_2Cl, CH_2Cl and $SiMe_2$, plus $SiCH_2$ groups, respectively. The SiPh : CH_2Cl : $SiMe_2$ + $SiCH_2$ ratio observed, *ca.* 8.4 : 2 : 8, rather than the ratio 10 : 2 : 8 expected for 1 : 1 adducts, suggests that some Si–Ph cleavage had taken place. From the ratio of the CH_2Cl absorptions it would appear that two compounds were formed in the ratio *ca.* 4.5 : 1.

In order to obtain further information as to the structure of the products the mixture was treated with lithium aluminium hydride. The n.m.r. spectrum of the resultant distilled product showed bands at τ 2.63 (8.2H, SiPh), 4.91 (t, 0.8H, SiH, *J* 4.0 Hz), 5.51 (sextet, 0.2H, SiH, *J* 4.0 Hz), 5.94 (complex, 0.2H, SiH), and 9.43 to 9.95 (11H, SiMe and $SiCH_2$).

Si-H Proton n.m.r. chemical shifts are very dependent on the other substituents on the silicon atom, *e.g.* $Me_3Si{\cdot}CH_2{\cdot}SiHMe_2$ (τ 5.99, nonet, *J* 4.0 Hz), $MePh_2Si{\cdot}CH_2{\cdot}SiHMe_2$ (τ 5.82, nonet, *J* 3.9 Hz), $Me_2PhSi{\cdot}CH_2{\cdot}SiHMePh$ (τ 5.52, sextet, *J* 3.8 Hz), $Me_2PhSi{\cdot}CH_2{\cdot}SiHPh_2$ (τ 5.00, t, *J* 4.2 Hz), and $Me_3Si{\cdot}CH_2{\cdot}SiHPh_2$ (τ 4.89, t, *J* 4.2 Hz). The Si–H absorptions observed in the n.m.r. spectrum of the reduced material at τ 5.94 5.51, and 4.91 are therefore assigned to $Me_2SiH{\cdot}CH_2$, $MePhSiH{\cdot}CH_2$, and $Ph_2SiH{\cdot}CH_2$ groups, respectively.

The possible products from the chlorination reaction are shown in the following scheme.



i, Cl_2 (Si–C fission); ii, Cl_2 (Ph cleavage).

Reduction of these possible products by lithium aluminium hydride would afford the compounds (XXXIII) to (XXXVI).

$$\text{(XXVIII)} \longrightarrow \underset{\text{(XXXIII)}}{Me_3Si{\cdot}CH_2{\cdot}SiHPh_2}$$

$$\text{(XXIX)} \longrightarrow \underset{\text{(XXXIV)}}{Me_2SiH{\cdot}CH_2{\cdot}SiPh_2Me}$$

$$\text{(XXXI)} \longrightarrow \underset{\text{(XXXV)}}{Me_3Si{\cdot}CH_2{\cdot}SiH_2Ph}$$

$$\text{(XXXII)} \longrightarrow \underset{\text{(XXXVI)}}{Me_2SiH{\cdot}CH_2{\cdot}SiHMePh}$$

From the n.m.r. spectrum of the reduced material the possible products are thus (XXXIII), (XXXIV), and (XXXVI), but if both the compounds (XXXIV) and (XXXVI) were present the n.m.r. absorption at τ 5.94 (Me_2SiH) should be of greater intensity than that at τ 5.51 (MePhSiH). Since these absorptions are of equal intensity they are assigned to the two SiH protons in the compound (XXXVI). The products are therefore the compounds (XXXIII) and (XXXVI), present in the ratio *ca.* 4 : 1, and the original chlorination products are the compounds (XXVIII) and (XXXII) also present in this ratio (*ca.* 4.5 : 1 from n.m.r. spectrum of original chlorinated mixture).

The major chlorination product (XXVIII) results from cleavage of disilacyclobutane (V) at a $SiPh_2{-}CH_2$ bond, while the minor product (XXXII) could result either from initial cleavage at a $SiMe_2{-}CH_2$ bond to give compound (XXIX) followed by Si–Ph fission, or from initial Si–Ph cleavage to give the disilacyclobutane (XXX), followed by ring fission at a $Me_2Si{-}CH_2$ bond. It has been observed [16] that the stability of Si–Ph bonds towards cleavage by halogens is greatly increased by the presence of electron-withdrawing groups at the silicon atom. The present results are consistent with this observation if initial reaction of disilacyclobutane (V) with chlorine involves ring fission to give the adducts (XXVIII) and (XXIX); the latter adduct being more susceptible to Si–Ph cleavage then reacts further to afford compound (XXXII).

The reaction of the disilacyclobutane (V) with bromine

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[16] R. C. Moore, Ph.D. Thesis, University of Leicester, 1961.

was also slow and reflux (5 h) of a solution of (V) and bromine in carbon tetrachloride was found to be necessary for complete reaction. The i.r. spectrum of the high-boiling product showed no absorption at *ca.* 950 cm^{-1} (strained disilacyclobutane ring) and the n.m.r. spectrum showed absorptions at τ 2.58 (10H), 7.56 (0.2H), 7.62 (1.8H), and 8.60 to 9.86 (8H), which were assigned to SiPh, CH_2Br, CH_2Br, and $SiMe_2$ plus $SiCH_2$ groups, respectively. These absorptions are in the expected ratio for a mixture of two 1 : 1 adducts in the ratio *ca.* 9 : 1.

Reduction of this product with lithium aluminium hydride followed by distillation of the resultant material gave a mixture which was indicated by n.m.r. spectroscopy to consist of 2,2-dimethyl-4,4-diphenyl-2,4-disilabutane (XXXIII) (SiH, τ 4.96, intensity 7.9), 2-methyl-4-phenyl-2,4-disilapentane (XXXVI) ($SiHMe_2$, τ 5.96, intensity 0.1; SiHMePh, τ 5.52, intensity 0.1), and 2-methyl-4,4-diphenyl-2,4-disilapentane (XXXIV) ($SiHMe_2$, τ 5.96, intensity 0.8) present in the ratio 90 : 1 : 9.

The original products from the bromination reaction are, therefore, 1,4-dibromo-2,2-dimethyl-4,4-diphenyl-2,4-disilabutane (XXXVII), 1,2,4-tribromo-4-methyl-2-phenyl-2,4-disilapentane (XXXVIII), and 1,4-dibromo-2,2-diphenyl-4-methyl-2,4-disilapentane (XXXIX) in the approximate ratio 90 : 1 : 9.

$CH_2Br{\cdot}SiMe_2{\cdot}CH_2{\cdot}SiBrPh_2$
(XXXVII)

$CH_2Br{\cdot}SiPhBr{\cdot}CH_2{\cdot}SiBrMe_2$
(XXXVIII)

$CH_2Br{\cdot}SiPh_2{\cdot}CH_2{\cdot}SiBrMe_2$
(XXXIX)

Disilacyclobutane (III) reacts with bromine in refluxing carbon tetrachloride to afford a mixture of the disilacyclobutane $MePh\overline{Si{\cdot}CH_2{\cdot}SiBrMe{\cdot}C}H_2$ (XVI) and ring-opened material. An analogous reaction with disilacyclobutane (V) would give the compound $Me_2\overline{Si{\cdot}CH_2{\cdot}SiBrPh{\cdot}C}H_2$ which was not detected although it may have been present in the products in low yield.

Thus, as in the chlorination reaction, major cleavage of the disilacyclobutane ring occurs at a $SiPh_2$–CH_2 bond to give the 1 : 1 adduct (XXXVII), but in contrast to the chlorination reaction the minor 1 : 1 adduct (XXXIX) only undergoes Si–Ph cleavage to a minor extent to give the tribromide (XXXVIII).

The reactions of the disilacyclobutane (V) with chlorine and bromine are thus in marked contrast to those with the hydrogen halides, and alkoxide, hydroxide, or hydride ion which result mainly in cleavage of a $SiMe_2$–CH_2 bond. This possibly indicates that the mechanism of ring-opening with the halogens is somewhat different to those with hydrogen halides or nucleophiles.

Spectroscopic Studies.—The diagnostic i.r. bands and the n.m.r. absorption bands of the new compounds have been treated as a supplementary publication; see footnote on p. 1822.

EXPERIMENTAL

Techniques used were as described previously[1] except that n.m.r. spectra were run on a Perkin-Elmer R10 instrument operating at 60.0 MHz for ^1H and 56.46 MHz for ^{19}F or a Varian Associates HA 100 spectrometer operating at 100.0 MHz for ^1H with internal cyclohexane (^1H) and external trifluoroacetic acid (^{19}F) as the references.

1,3-Dimethyl-1,3-diphenyl-1,3-disilacyclobutane (III) was prepared in 64% yield by the addition of magnesium to chloro(chloromethyl)phenylmethylsilane in tetrahydrofuran,[3] while 1,1,3,3-tetraphenyl-1,3-disilacyclobutane (IV) was prepared in 30% yield by the reaction of chloro-(chloromethyl)diphenylsilane with magnesium in diethyl ether.[5] Other reactants were either commercial samples or were prepared by literature methods and, where necessary, were purified before use.

Preparation of 1,1-*Dimethyl*-3,3-*diphenyl*-1,3-*disilacyclobutane* (*V*).—To a small amount of magnesium turnings covered by tetrahydrofuran (20 ml) was added four drops of methyl iodide followed by a small portion of a 1 : 1 mixture of chloro(chloromethyl)dimethylsilane and chloro-(chloromethyl)diphenylsilane to initiate the reaction. The remainder of the 1 : 1 mixture of chloro(chloromethyl)dimethylsilane (32.0 g, 0.22 mol) and chloro(chloromethyl)diphenylsilane (59.0 g, 0.22 mol) in tetrahydrofuran (350 ml) was then rapidly added. Further portions of magnesium turnings (total 14.6 g, 0.6 g-atom) were added (2.5 h) to the stirred solution at a rate sufficient to maintain the reaction temperature at 50—60 °C. The reaction mixture was further refluxed (1 h), cooled, and then poured onto crushed ice (250 g). The organic layer was separated, washed with ice-water (5 × 50 ml), dried ($MgSO_4$, 48 h), and fractionated through a Bucchi spinning-band column (100 cm) to afford (i) 1,1,3,3-tetramethyl-1,3-disilacyclobutane (1.6 g, 11.0 mmol, 10%), b.p. 118—120 °C, n_D^{20} 1.4390 (lit.,[17] b.p. 60—61 °C at 100 mmHg, n_D^{20} 1.4380), (ii) 1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane (4.1 g, 19.0 mmol, 26%), b.p. 112—114 °C at 52 mmHg, n_D^{20} 1.4600 (lit.,[18] b.p. 112—114 °C at 50 mmHg, n_D^{20} 1.4606), (iii) 1,1-*dimethyl*-3,3-*diphenyl*-1,3-*disilacyclobutane* (22.2 g, 83.0 mmol, 38%) (Found: C, 71.6; H, 7.5%; *M*, 275. $C_{16}H_{20}Si_2$ requires C, 71.6; H, 7.5%; *M*, 268), b.p. 158—161 °C at 0.5 mmHg, n_D^{20} 1.5621, *m/e* 268 (54%, M^+), 253 [100%, $(M - Me)^+$], and 191 [72%, $(M - Ph)^+$]; (iv) 1,1,3,3-tetraphenyl-1,3-disilacyclobutane (4.3 g, 11.0 mmol, 10%), m.p. 132 °C (from light petroleum, b.p. 40—60 °C) [lit.,[5] m.p. 120 °C (benzene)], and (v) a residue (12.0 g) which was not investigated.

Reactions of 1,3-*Dimethyl*-1,3-*diphenyl*-1,3-*disilacyclobutane* (*III*).—(a) *With lithium aluminium hydride.* A mixture of the disilacyclobutane (9.83 g, 36.8 mmol) and lithium aluminium hydride (9.05 g, 0.239 mol) in tetrahydrofuran (THF) (50 ml) was heated under reflux (1.5 h) and the resultant material was cooled and hydrolysed carefully (50% aqueous THF, 300 ml). The organic layer was separated, dried ($MgSO_4$), and fractionated to give 2-*methyl*-2,4-*diphenyl*-2,4-*disilapentane* (9.21 g, 34.1 mmol, 93%) (Found: C, 70.9; H, 8.5%; *M*, 262. $C_{16}H_{22}Si_2$ requires C, 71.1; H, 8.2%; *M*, 270), b.p. 109—111 °C at 0.02 mmHg, n_D^{23} 1.5487; *m/e* 255 [25%; $(M - Me)^+$], and 177 (100%, $C_9H_{13}Si_2^+$).

(b) *With sodium hydroxide.* An exothermic reaction occurred when the disilacyclobutane (10.05 g, 37.5 mmol) was slowly added to an excess of ethanolic sodium hydroxide (0.1M; 100 ml). When the reaction had abated the solution

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[17] W. H. Knoth and R. V. Lindsay, *J. Org. Chem.*, 1958, **23**, 1392.

[18] N. S. Nametkin, A. V. Topchiev, and V. I. Zerkin, *Doklady Akad. Nauk S.S.S.R.*, 1953, **93**, 1045.

was refluxed (2 h), cooled, diluted with water (200 ml), and extracted with ether (2 × 30 ml). The ether extracts were combined, washed with water (2 × 10 ml), dried ($MgSO_4$), and fractionated to give 4-*hydroxy*-2-*methyl*-2,4-*diphenyl*-2,4-*disilapentane* (10.0 g, 37.0 mmol, 99%) (Found: C, 67.4; H, 7.8%; *M*, 304. $C_{16}H_{22}OSi_2$ requires C, 67.2; H, 7.7%; *M*, 286), b.p. 121—122 °C at 0.02 mmHg, n_D^{20} 1.5447, m/e 271 [24%, $(M - Me)^+$] and 193 [100%, $(M - PhH)^+$].

(c) *With ethanol and cadmium chloride*. Cadmium chloride (3.87 g, 21.2 mmol) was slowly added to a solution of the disilacyclobutane (9.13 g, 32.8 mmol) in refluxing ethanol (100 ml) and the reflux continued (9 h). The ethanol was removed by distillation and the resultant material was filtered to give a white solid (3.34 g), the i.r. spectrum of which showed only the presence of OH groups, and a filtrate which was fractionated to afford 4-*ethoxy*-2-*methyl*-2,4-*diphenyl*-2,4-*disilapentane* (6.48 g, 20.6 mmol, 63%) (Found: C, 69.1; H, 8.2%; *M*, 344. $C_{18}H_{26}OSi_2$ requires C, 68.8; H, 8.3%; *M*, 314), b.p. 132—133 °C at 0.01 mmHg, n_D^{20} 1.5353, m/e 299 [100%, $(M - Me)^+$], and a residue, which on purification by passage through a neutral alumina column in light petroleum (b.p. 40—60 °C), yielded 1,3-*bis*(*dimethylphenylsilylmethyl*)-1,3-*dimethyl*-1,3-*diphenyldisiloxane* (2.72 g, 4.9 mmol, 30%) (Found: C, 69.0; H, 7.3%; *M*, 574. $C_{32}H_{42}OSi_4$ requires C, 69.3; H, 7.6%; *M*, 554), n_D^{20} 1.5588.

An experiment carried out under the same conditions (1.2 h) with zinc chloride (2.40 g, 17.6 mmol) and the disilacyclobutane (4.73 g, 17.6 mmol) in refluxing ethanol (100 ml), gave a white solid (2.46 g), 4-ethoxy-2-methyl-2,4-diphenyl-2,4-disilapentane (3.32 g, 10.6 mmol, 60%), and 1,3-bis(dimethylphenylsilylmethyl)-1,3-dimethyl-1,3-diphenyldisiloxane (1.46, 2.6 mmol, 30%).

The attempted reaction between the disilacyclobutane (4.72 g, 17.6 mmol) and ethanol (100 ml) under reflux (8 h) gave unchanged disilacyclobutane (99%).

(d) *With methanol and thallium*(I) *formate*. A mixture of the disilacyclobutane (4.12 g, 15.3 mmol) and thallium(I) formate (3.83 g, 15.3 mmol) in methanol (200 ml) was heated under reflux (4.45 h). The methanol was removed by distillation and the resultant mixture of solid and liquid was filtered to give a white crystalline solid (3.50 g, *ca*. 91% recovered) identified (i.r.) as unchanged thallium(I) formate contaminated with water. The filtrate was fractionated to afford 4-*methoxy*-2-*methyl*-2,4-*diphenyl*-2,4-*disilapentane* (3.87 g, 12.9 mmol, 84%) (Found: C, 67.8; H, 7.8%; *M*, 293. $C_{17}H_{24}OSi_2$ requires C, 68.0; H, 8.0%; *M*, 300), b.p. 122—124 °C at 0.01 mmHg, n_D^{20} 1.5414; m/e 285 [100%, $(M - Me)^+$], and a residue of 1,3-bis(dimethylphenylsilylmethyl)-1,3-dimethyl-1,3-diphenyldisiloxane (0.39 g, 0.7 mmol, 9%).

(e) *With sulphuric acid*. The disilacyclobutane (8.09 g, 30.2 mmol) was added dropwise (30 min) to concentrated sulphuric acid (3.70 g, 40.0 mmol) and an immediate violent exothermic reaction occurred. Addition of water (100 ml) precipitated a white solid which was filtered, washed with water (100 ml) and then with acetone (20 ml), and dried *in vacuo* at room temperature. The solid product (3.6 g) was shown by i.r. spectroscopy not to contain phenyl groups.

(f) *With hydrogen chloride*. An excess of dry hydrogen chloride was passed into a solution of the disilacyclobutane (9.88 g, 36.9 mmol) in carbon tetrachloride (30 ml) at — 5 to — 10 °C (80 min). Fractionation of the solution gave 4-*chloro*-2-*methyl*-2,4-*diphenyl*-2,4-*disilapentane* (10.7 g, 35.5 mmol, 96%) (Found: C, 63.4; H, 6.9%; *M*, 346. $C_{16}H_{21}ClSi_2$ requires C, 63.1; H, 6.9%; *M*, 304), b.p. 124—125 °C at 0.03 mmHg, n_D^{20} 1.5534; m/e 289 [100%, $(M - Me)^+$].

(g) *With an excess of hydrogen bromide*. Under similar experimental conditions to those described in the previous experiment an excess of hydrogen bromide was slowly passed into a solution of the disilacyclobutane (8.46 g, 31.6 mmol) in carbon tetrachloride (30 ml) at −5 to −10 °C to give impure 2,4-dibromo-2-methyl-4-phenyl-2,4-disilapentane (9.94 g, 30.6 mmol, 97%) (Found: C, 36.5; H, 5.1. Calc. for $C_{10}H_{16}Br_2Si_2$: C, 34.4; H, 4.6%), b.p. 105—107 °C at 0.01 mmHg, n_D^{20} 1.5494. Proof of structure of the product was obtained by reduction with lithium aluminium hydride and fluorination with antimony(III) fluoride.

(i) Reduction with lithium aluminium hydride. A mixture of the dibromide (2.83 g, 8.8 mmol) and lithium aluminium hydride (5.0 g, 0.132 mol) in THF (50 ml) was heated under reflux (1 h). The resultant material was carefully hydrolysed with aqueous THF (30%, 100 ml), and the organic layer was separated, dried ($MgSO_4$), and fractionated to give 2-*methyl*-4-*phenyl*-2,4-*disilapentane* (1.42 g, 8.6 mmol, 98%) (Found: C, 61.7; H, 9.1. $C_{10}H_{18}Si_2$ requires C, 61.8; H, 9.3%), b.p. 94—95 °C at 10 mmHg, n_D^{20} 1.4974; m/e 193 [8%, $(M - H)^+$], 179 [34%, $(M - Me)^+$], and 116 [100%, $(M - PhH)^+$].

(ii) Reaction with antimony(III) fluoride. The fluoride (10.9 g, 61.0 mmol) was added slowly (40 min) to a solution of the dibromide (24.8 g, 92.8 mmol) in carbon tetrachloride (50 ml) and the mixture was heated under reflux (15 min), cooled, filtered, and the filtrate fractionated to give 2,4-*difluoro*-2-*methyl*-4-*phenyl*-2,4-*disilapentane* (17.4 g, 76.0 mmol, 82%) (Found: C, 52.1; H, 7.1. $C_{10}H_{16}F_2Si_2$ requires C, 52.1; H, 7.0%), b.p. 103—104 °C at 10 mmHg, n_D^{20} 1.4667; m/e 215 [100%, $(M - Me)^+$].

(h) *With a deficiency of hydrogen bromide*. A slow stream of hydrogen bromide was passed into a solution of the disilacyclobutane in carbon tetrachloride until the disilacyclobutane (*ca*. 50%) had reacted as judged by the intensity of the i.r. band at 1 050 cm^{-1} (linear $Si-CH_2-Si$). The solvent was removed and the oil was slowly added to an excess of lithium aluminium hydride in diethyl ether. The resultant slurry was heated under reflux (15 min), cooled, the excess of hydride hydrolysed carefully with water, and the ether layer separated, dried ($MgSO_4$), and fractionated. The i.r. and n.m.r. spectra of the residual oil indicated only the presence of unchanged disilacyclobutane and 2-methyl-2,4-diphenyl-2,4-disilapentane.

(i) *With bromine*. A solution of bromine (5.65 g, 35.4 mmol) in carbon tetrachloride (10 ml) was slowly added (3 h) to a solution of the disilacyclobutane (9.48 g, 35.4 mmol) in carbon tetrachloride (50 ml) heated under reflux (reaction did not take place at room temperature). Fractionation of the resultant material gave (i) a distillate which was shown by i.r. and n.m.r. spectroscopy to be impure 1-bromo-1,3-dimethyl-3-phenyl-1,3-disilacyclobutane (3.0 g, *ca*. 11.2 mmol, *ca*. 31%), b.p. 120—130 °C at 0.05 mmHg, and (ii) a residue of impure 1,4-dibromo-2-methyl-2,4-diphenyl-2,4-disilapentane (8.58 g, *ca*. 20.2 mmol, *ca*. 57%).

The distillate (3.0 g, 11.2 mmol) was slowly added to a slurry of lithium aluminium hydride (3.0 g, 78.0 mmol) in diethyl ether (25 ml) and the mixture was stirred at room temperature (3 h). Water (20 ml) was then added, and the ether layer was separated, dried ($MgSO_4$), and fractionated to give 1,3-*dimethyl*-3-*phenyl*-1,3-*disilacyclobutane* (2.05 g, 10.7 mmol, 95%) (Found: C, 62.8; H, 8.7%; M^+, 192. $C_{10}H_{16}Si_2$ requires C, 62.5; H, 8.3%; *M*, 192), n_D^{20} 1.5269; m/e 192 (30%, M^+) and 177 [100%, $(M - Me)^+$].

The residue (8.58 g, 20.1 mmol) was dissolved in diethy ether (20 ml) and aqueous sodium carbonate (20%, 50 ml) was slowly added to the stirred solution. The ether layer was separated, dried ($MgSO_4$), and the ether removed *in vacuo* to give a yellow oil (5.80 g, 80%) tentatively identified as crude 1-bromo-4-hydroxy-2-methyl-2,4-diphenyl-2,4-disilapentane. A solution of this material in light petroleum (b.p. 40—60 °C) on passage through a neutral alumina column gave 1,3-bis(bromomethylmethylphenylsilylmethyl)-1,3-dimethyl-1,3-diphenyldisiloxane (4.16 g, 5.9 mmol, 73%).

(j) *With chlorine.* An excess of chlorine was slowly passed (5.5 h) through a solution of the disilacyclobutane (8.06 g, 30.1 mmol) in carbon tetrachloride (40 ml) maintained at −20 °C. Fractionation of the resultant material gave a distillate (0.9 g), b.p. 140—145 °C at 0.09 mmHg, $\nu_{max.}$ 940 cm^{-1}, and a residue (9.2 g). The residue was added to a stirred slurry of lithium aluminium hydride (3.0 g, 78.0 mmol) in diethyl ether (50 ml) and the mixture heated under reflux (3 h). Water (50 ml) was then added, and the ether layer was separated, dried ($MgSO_4$), and fractionated to give 2-methyl-2,4-diphenyl-2,4-disilapentane (7.10 g, 26.3 mmol, 87%), b.p. 109—110 °C at 0.02 mmHg, n_D^{20} 1.5475.

(k) *With* N-*bromosuccinimide.* Treatment of a mixture of the disilacyclobutane (3.20 g, 12.0 mmol) and *N*-bromosuccinimide (2.21 g, 12.4 mmol) in carbon tetrachloride (80 ml) under reflux first with a catalytic amount (0.5 g, 1 h) and then with an excess (1.67 g, 6.9 mmol, 6 h) of benzoyl peroxide gave a residue of succinimide (0.92 g, 9.3 mmol, 75%) and a complex intractable mixture containing unchanged disilacyclobutane, biphenyl, and a small amount of ring-opened material.

(l) *With other reagents.* Near quantitative recoveries of unchanged disilacyclobutane were obtained from the following attempted reactions: (i) with an equimolar quantity of sulphur at 200 °C (2.5 h), or at 250 °C (3 h), or on u.v. irradiation in silica at 190 °C (5.5 h); (ii) with an equimolar quantity of potassium permanganate in pyridine under reflux (2 h); (iii) passage, as a solution in light petroleum (b.p. 40—60 °C), through a basic alumina column (Aluminium Oxide Woelm, grade I).

Synthesis of 2-*Methyl*-4-*phenyl*-2,4-*disilapentane*.—(a) *Reduction of* (*chloromethyl*)*methylphenylchlorosilane*. The chlorosilane (100.0 g, 0.487 mol) was slowly added (30 min) to a slurry of lithium aluminium hydride (25.0 g, 0.659 mol) in diethyl ether (800 ml) and when the exothermic reaction had subsided the mixture was heated under reflux (30 min). Water (40 ml) was added slowly and the ether layer was separated, dried ($MgSO_4$), and fractionated to give (i) dimethylphenylsilane (31.5 g, 0.232 mol, 48%) (Found: C, 70.7; H, 8.6. Calc. for $C_8H_{12}Si$: C, 70.5; H, 8.8%), b.p. 95—96 °C at 100 mmHg, n_D^{20} 1.4972 (lit.,[19] b.p. 157 °C at 744 mmHg, n_D^{20} 1.4995), (ii) (chloromethyl)methylphenylsilane (18.7 g, 0.11 mol, 23%) (Found: C, 56.7; H, 6.3. Calc. for $C_8H_{11}ClSi$: C, 56.5; H, 6.5%), b.p. 116—117 °C at 25 mmHg, n_D^{20} 1.5281 (lit.,[20] b.p. 99—100 °C at 14 mmHg, n_D^{20} 1.5326), and (iii) a residue of 1,3-bis(chloromethyl)-1,3-dimethyl-1,3-diphenyldisiloxane (16.2 g, 64.0 mmol, 26%).

(b) *Reaction of methylphenylsilylmethylmagnesium chloride with dimethylchlorosilane*. (Chloromethyl)methylphenylsilane (6.34 g, 37.2 mmol) was added slowly to iodine-activated magnesium turnings (1.0 g, 41.0 mmol) in diethyl ether (50 ml). The mixture was refluxed (10 min), cooled, and chlorodimethylsilane (3.5 g, 37.0 mmol) was slowly added. After heating under reflux (2.5 h) the solvent was removed and the residue was heated at 50 °C (30 min). Fresh ether (50 ml) was then added followed by water (40 ml), the organic layer was then separated, dried ($MgSO_4$), and fractionated to give 2-methyl-4-phenyl-2,4-disilapentane (3.62 g, 18.7 mmol, 50%) (Found: C, 61.8; H, 9.0. Calc. for $C_{10}H_{18}Si_2$: C, 61.8; H, 9.3%), b.p. 98—99 °C at 12 mmHg, n_D^{20} 1.4987.

Reactions of 1,1,3,3-*Tetraphenyl*-1,3-*disilacyclobutane* (*IV*).—(a) *With lithium aluminium hydride*. A mixture of the disilacyclobutane (2.6 g, 6.6 mmol) and lithium aluminium hydride (2.0 g, 52.8 mmol) in THF (100 ml) was heated under reflux (2 h). The resultant material was cooled, carefully hydrolysed with hydrochloric acid (2M; 50 ml), and the organic layer was separated, dried ($MgSO_4$), and the solvent removed *in vacuo* to give a yellow oil (2.6 g). The oil was purified by passage through a neutral alumina column in light petroleum (b.p. 40—60 °C) to give colourless 1,1,3,3-*tetraphenyl*-1,3-*disilabutane* (2.45 g, 6.3 mmol, 94%) (Found: C, 79.0; H, 6.5%; *M*, 397. $C_{26}H_{26}Si_2$ requires C, 79.1; H, 6.6%; *M*, 394), n_D^{20} 1.6080.

Reaction did not take place when the disilacyclobutane was treated with lithium aluminium hydride in diethyl ether at room or reflux temperature.

(b) *With sodium hydroxide*. The disilacyclobutane (2.0 g, 5.1 mmol) was added to an excess of ethanolic sodium hydroxide (0.1M; 100 ml), and the solution was heated under reflux (2 h). Water (200 ml) was then added and the resultant mixture was extracted with ether (2 × 30 ml). The combined ether extracts were washed with water (2 × 10 ml), dried ($MgSO_4$), and fractionated to give 1-*hydroxy*-1,1,3,3-*tetraphenyl*-1,3-*disilabutane* (2.05 g, 4.9 mmol, 96%) (Found: C, 76.1; H, 6.4%; *M*, 410. $C_{26}H_{26}OSi_2$ requires C, 76.1; H, 6.4%; *M*, 410), b.p. 212—214 °C at 0.07 mmHg, n_D^{20} 1.6125, *m*/*e* 197 (100%, Ph_2SiMe^+).

(c) *With sulphuric acid*. The slow addition of the disilacyclobutane (1.98 g, 5.1 mmol) to concentrated sulphuric acid (2.0 g, 20.4 mmol) at −10 °C resulted in a vigorous exothermic reaction and gave a yellowish brown solution from which a white solid was precipitated by water (100 ml). The solid was filtered off, washed with water (100 ml) and then with methanol (50 ml), and dried *in vacuo* (24 h) to give a white powder (0.72 g) which was insoluble in chloroform, diethyl ether, benzene, and light petroleum (b.p. 40—60 °C) and showed an absence of phenyl absorptions in its i.r. spectrum.

Reaction did not occur when concentrated sulphuric acid was slowly added to a solution of the disilacyclobutane in diethyl ether at room temperature (30 min) and the disilacyclobutane (96%) was recovered unchanged.

(d) *With hydrogen bromide*. An excess of hydrogen bromide was passed (2 h) through a solution of the disilacyclobutane (2.54 g, 6.5 mmol) in carbon tetrachloride (50 ml). The solvent was removed *in vacuo* and the residual oil (3.1 g) was slowly added to a stirred slurry of lithium aluminium hydride (5.0 g, 0.132 mol) in diethyl ether (50 ml) and the mixture heated under reflux (15 min). Water (10 ml) was then slowly added and the ether layer separated, dried ($MgSO_4$), and fractionated to give a high-boiling residue which was purified by passage through a neutral alumina column in light petroleum (b.p. 40—60 °C) and identified as 1,1,3-*triphenyl*-1,3-*disilabutane* (1.87 g, 5.9 mmol, 91%) (Found: C, 75.4; H, 6.8. $C_{20}H_{22}Si_2$ requires C, 75.4; H, 6.95%), n_D^{20} 1.5920.

(e) *With bromine*. A solution of bromine (0.84 g, 5.3

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[19] R. A. Benkeser and D. J. Foster, *J. Amer. Chem. Soc.*, 1952, **74**, 5314.

[20] Z. V. Belyakova and S. A. Golubtsov, *Zhur. obshchei Khim.*, 1961, **31**, 3178.

mmol) in carbon tetrachloride (15 ml) was added to a solution of the disilacyclobutane (2.07 g, 5.3 mmol) in carbon tetrachloride (75 ml) and the mixture was stirred and heated at 35 °C (15 h). Removal of the solvent gave white crystals (2.0 g) the i.r. spectrum of which showed the presence of unchanged disilacyclobutane (band at 934 cm^{-1}), a second disilacyclobutane (shoulder on band at 934 cm^{-1}), and ring-opened material (band at 1 050 cm^{-1}). Attempted fractional crystallisation of the mixture from light petroleum (b.p. 40—60 °C) did not result in any separation of the components. A g.l.c. analysis of the original solvent fraction showed the presence of carbon tetrachloride and bromobenzene.

(f) *With other reagents*. The following attempted reactions gave near quantitative recoveries of unchanged disilacyclobutane. (i) An equimolar mixture of the disilacyclobutane and *N*-bromosuccinimide, heated under reflux (2 h) in carbon tetrachloride in the presence of a catalytic amount of benzoyl peroxide. (ii) U.v. irradiation (1 h) of a mixture of t-butyl hypochlorite and the disilacyclobutane (*ca.* 4 : 1 molar ratio) in carbon tetrachloride. (iii) A mixture of the disilacyclobutane and mercury(II) acetate (1:5 molar ratio) heated under reflux (11 h) in benzene. (iv) An equimolar mixture of the disilacyclobutane and phosphorus pentachloride heated under reflux (2 h) in benzene. (v) A mixture of the disilacyclobutane and nitrobenzene (1 : 5 molar ratio) heated under reflux (6 h). (vi) A solution of the disilacyclobutane in light petroleum (b.p. 40—60 °C) passed down a column packed with basic alumina.

Preparation of 2,2,4,4-*Tetraphenyl*-2,4-*disilapentane*.—(a) *Reduction of* (*chloromethyl*)*diphenylchlorosilane with lithium aluminium hydride*. The chlorosilane (57.0 g, 0.214 mol) was added dropwise to a stirred slurry of lithium aluminium hydride (10.0 g, 0.264 mol) in diethyl ether (100 ml) and the mixture was heated under reflux (1 h), cooled, and the excess hydride destroyed with hydrochloric acid (2M; 50 ml). The ether layer was separated, dried ($MgSO_4$), and fractionated to give diphenylmethylsilane (15.0 g, 76.2 mmol, 36%) (Found: C, 79.0; H, 6.9. Calc. for $C_{13}H_{14}Si$: C, 78.9; H, 7.1%), b.p. 79—80 °C at 0.1 mmHg, n_D^{20} 1.5721 (lit.,[21] b.p. 79 °C at 0.1 mmHg, n_D^{20} 1.5694), and (chloromethyl)diphenylsilane (27.2 g, 0.118 mol, 55%) (Found: C, 67.2; H, 5.4. Calc. for $C_{13}H_{13}ClSi$: C, 67.1; H, 5.6%), b.p. 112—113 °C at 0.1 mmHg, n_D^{20} 1.5901 (lit.,[20] b.p. 175—180 °C at 15 mmHg, n_D^{20} 1.5842).

(b) *Reaction of diphenylsilylmethylmagnesium chloride with methyldiphenylchlorosilane*. (Chloromethyl)diphenylsilane (11.7 g, 50.0 mmol) was slowly added to iodine-activated magnesium turnings (1.30 g, 50.0 mmol) in diethyl ether (100 ml) and the mixture was heated under reflux (1 h). Methyldiphenylchlorosilane (11.6 g, 50.0 mmol) was added to the cold Grignard solution and the mixture was heated under reflux (2 h); the solvent was then removed and the residue heated at 80 °C (3 h). The resultant material was treated with water (50 ml), the organic layer extracted with ether (2 × 20 ml), and the ether extract dried ($MgSO_4$). The ether was removed and the oily residue (10.3 g) eluted through an alumina column with light petroleum (b.p. 40—60 °C) to give a colourless oil, which was fractionated to yield diphenylmethylsilane (3.34 g, 10.0 mmol, 20%), b.p. 80—82 °C at 0.1 mmHg, and a residue of 2,2,4,4-tetraphenyl-2,4-disilapentane (6.71 g, 17.0 mmol, 34%) (Found: C, 79.2; H, 7.1. Calc. for $C_{26}H_{26}Si_2$: C, 79.1; H, 6.6%), n_D^{20} 1.6095.

Reactions of 1,1-*Dimethyl*-1,1-*diphenyl*-1,3-*disilacyclobutane* (*V*).—(a) *With hydrogen chloride*. An excess of hydrogen chloride was passed (1 h) through a solution of the disilacyclobutane (2.55 g, 10.0 mmol) in carbon tetrachloride (30 ml) and the product mixture distilled through a vacuum-jacketted column fitted with a partial take-off head to give: (i) carbon tetrachloride (*ca.* 30 ml); (ii) a colourless liquid (2.43 g, 7.9 mmol, 79%) (Found: C, 62.6; H, 6.8; Cl, 11.3%; *M*, 309. Calc. for $C_{16}H_{21}ClSi_2$; C, 62.9; H, 6.9; Cl, 11.6%; *M*, 304), b.p. 126—127 °C at 0.01 mmHg, n_D^{20} 1.5548; $\nu_{max.}$ 1 053s (linear $Si{\cdot}CH_2{\cdot}Si$) cm^{-1}; *m*/*e* 289 [100%, $(M - Me)^+$], 197 (58%, $C_8H_{10}Si_2Cl^+$), 93 (7%, Me_2SiCl^+), and 73 (3%, Me_3Si^+), which was shown by n.m.r. spectroscopy to consist of 2-chloro-2-methyl-4,4-diphenyl-2,4-disilapentane (2.3 g, 7.6 mmol, 76%) and 1-chloro-3,3-dimethyl-1,1-diphenyl-1,3-disilabutane (0.13 g, 0.3 mmol, 3%) present in the ratio 95 : 5; (iii) a residue (0.7 g), b.p. >127 °C at 0.01 mmHg, was not investigated.

(b) *With hydrogen bromide*. An excess of hydrogen bromide was passed (1.5 h) through a solution of the disilacyclobutane (3.3 g, 12.0 mmol) in carbon tetrachloride (30 ml) and the solvent was removed *in vacuo* to afford 2,4-dibromo-2-methyl-4-phenyl-2,4-disilapentane (3.6 g, 10.5 mmol, 85%) (Found: *M*, 361. Calc. for $C_{10}H_{16}Br_2Si_2$: *M*, 352).

A sample of the dibromide (2.46 g, 7.0 mmol) in carbon tetrachloride (30 ml), refluxed (30 min) over antimony trifluoride (1.65 g), gave 2,4-difluoro-2-methyl-4-phenyl-2,4-disilapentane (1.4 g, 6.1 mmol, 87%), b.p. 95—96 °C at 6 mmHg.

(c) *With chlorine*. An excess of chlorine was passed slowly (6 h) through a solution of the disilacyclobutane (7.6 g, 28.4 mmol) in carbon tetrachloride (35 ml). The solvent was removed *in vacuo* to afford a high-boiling mixture (9.4 g) which could not be separated into its components by distillation at reduced pressure and which was shown by i.r. and n.m.r. spectroscopy to consist of ring-opened material (i.r. band at 1 050s cm^{-1}).

The high-boiling mixture (9.0 g) was added slowly to lithium aluminium hydride (3.0 g, 78.0 mmol) in diethyl ether (60 ml) and the resultant mixture was heated under reflux (3 h). Water (50 ml) was then added slowly, the ether layer was separated, dried ($MgSO_4$, 24 h), filtered, and distilled through a vacuum-jacketted column (20 cm) to afford (i) diethyl ether, (ii) a colourless liquid (6.9 g), b.p. 95—106 °C at 0.05 mmHg, and (iii) a residue (0.2 g) which was not examined further.

The i.r. spectrum of the liquid product showed a strong band at 2 119 cm^{-1} (Si–H str.) and n.m.r. spectroscopy showed that it consisted of 2,2-dimethyl-4,4-diphenyl-2,4-disilabutane (*ca.* 5.85 g, 21.7 mmol, 76%) and 2-methyl-4-phenyl-2,4-disilapentane (*ca.* 1.05 g, 5.4 mmol, 19%) present in the ratio *ca.* 80 : 20.

(d) *With bromine*. Bromine (4.8 g, 30.0 mmol) in carbon tetrachloride (10 ml) was added (2 h) to a solution of the disilacyclobutane (8.0 g, 30.0 mmol) in carbon tetrachloride (50 ml) under reflux and the reaction mixture was further refluxed (3 h). The solvent was removed *in vacuo* to afford ring-opened product (11.5 g), $\nu_{max.}$ 1 050 cm^{-1} (linear $Si{\cdot}CH_2{\cdot}Si$), which was indicated by n.m.r. spectroscopy to consist of two 1 : 1 adducts present in the ratio *ca.* 90 : 10.

The product (11.0 g) was slowly added to lithium aluminium hydride (3.0 g, 78.0 mmol) in diethyl ether (60 ml) and the mixture was refluxed (3 h) and then worked up as in the previous experiment to afford a liquid product (7.1 g), b.p.

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[21] H. Gilman, G. D. Lichtenwalter, and D. Wittenberg, *J. Amer. Chem. Soc.*, 1959, **81**, 5320.

98—112 °C at 0.05 mmHg, and a higher-boiling residue (0.6 g).

The i.r. spectrum of the liquid product contained a strong band at 2 119 cm^{-1} (Si–H str.) and the product was shown by n.m.r. spectroscopy to consist of 2,2-dimethyl-4,4-diphenyl-2,4-disilabutane (*ca.* 6.4 g, 23.6 mmol, 79%), 2-methyl-4,4-diphenyl-2,4-disilapentane (*ca.* 0.6 g, 2.4 mmol, 8%), and 2-methyl-4-phenyl-2,4-disilapentane (*ca.* 0.1 g, 0.05 mmol, 1%) present in the ratio *ca.* 90 : 9 : 1.

(e) *With lithium aluminium hydride.* The disilacyclobutane (2.0 g, 7.5 mmol) was slowly added to a slurry of lithium aluminium hydride (2.0 g, 55.0 mmol) in tetrahydrofuran (30 ml) and the resultant mixture was heated under reflux (2 h). The product mixture was treated with water (30 ml), the organic layer separated, and the aqueous layer extracted with ether (3 × 6 ml). The organic layer and the ethereal extract were combined, dried ($MgSO_4$, 24 h), and then distilled through a vacuum-jacketted column (20 cm) to afford a colourless liquid (1.86 g, 6.8 mmol, 92%) (Found: C, 71.4; H, 8.2%; *M*, 281. Calc. for $C_{16}H_{22}Si_2$: C, 71.2; H, 8.1%; *M*, 270), b.p. 110—112 °C at 0.1 mmHg, n_D^{20} 1.5482; $\nu_{max.}$ 2 106s (Si–H str.) and 1 045s (linear Si·CH$_2$·Si) cm^{-1}; *m/e* 255 [50%, $(M - Me)^+$], 211 [50%, $(M - HSiMe_2)^+$], 192 [50%, $(M - C_6H_6)^+$], and 177 (100%, $C_9H_{13}Si_2^+$) which was shown by n.m.r. spectroscopy to consist of 4-methyl-2,2-diphenyl-2,4-disilapentane (1.37 g, 5.0 mmol, 68%) and 2,2-dimethyl-4,4-diphenyl-2,4-disilabutane (0.49 g, 1.8 mmol, 24%) present in the ratio 73 : 27.

(f) *With sodium ethoxide.* The disilacyclobutane (2.5 g, 9.2 mmol) in ethanol (10 ml) was added slowly to a solution of sodium ethoxide (2.0M) in ethanol (50 ml). The reaction mixture was refluxed (2 h), cooled, filtered, and the filtrate distilled through a vacuum-jacketted column (20 cm) to give a mixture of 1 : 1 adducts (1.90 g, 6.05 mmol, 66%) (Found: C, 68.5; H, 8.4%; *M*, 321. Calc. for $C_{18}H_{26}OSi_2$: C, 68.8; H, 8.3%; *M*, 314), b.p. 129—130 °C at 0.1 mmHg, n_D^{20} 1.5362; $\nu_{max.}$ 1 084s (EtOSi), 1 048s (linear Si·CH$_2$·Si), and 943m (EtOSi) cm^{-1}; *m/e* 299 [100%, $(M - Me)^+$] and 209 (100%, $C_{10}H_{17}OSi_2^+$), which was shown by n.m.r. spectroscopy to consist of 4,4-dimethyl-6,6-diphenyl-3-oxa-4,6-disilaheptane (1.2 g, 3.8 mmol, 41%) and 6,6-dimethyl-4,4-diphenyl-3-oxa-4,6-disilaheptane (0.7 g, 2.25 mmol, 24%) present in the ratio 63 : 37.

A higher-boiling residue (0.5 g) was also obtained from the reaction.

The reaction was repeated three times under similar conditions and gave comparable yields of the two 1 : 1 adducts in the ratios 68 : 32, 70 : 30, and 72 : 28.

(g) *With sodium methoxide.* A solution of the disilacyclobutane (2.5 g, 9.5 mmol) in methanol (10 ml) was added slowly to a solution of sodium methoxide (2.0M) in methanol (50 ml). The reaction mixture was heated under reflux (2 h) and the products were worked up as in the previous experiment to give a mixture of 1 : 1 adducts (2.04 g, 6.8 mmol, 74%) (Found: *M*, 295. Calc. for $C_{17}H_{24}OSi_2$: *M*, 300), b.p. 124—126 °C at 0.1 mmHg, n_D^{20} 1.5431; $\nu_{max.}$ 1 085s (MeOSi), and 1 046s (linear Si·CH$_2$·Si) cm^{-1}; *m/e* 285 [100%, $(M - Me)^+$] and 223 [100%, $(M - Ph)^+$], and a higher-boiling residue (0.4 g), b.p. > 126 °C at 0.1 mmHg. The 1 : 1 adduct mixture was shown by n.m.r. spectroscopy to consist of 3,3-dimethyl-5,5-diphenyl-2-oxa-3,5-disilahexane (1.37 g, 4.55 mmol, 48%) and 5,5-dimethyl-3,3-diphenyl-2-oxa-3,5-disilahexane (0.67 g, 2.24 mmol, 23%) present in the ratio 67 : 33.

The reaction was repeated three times under comparable conditions and gave similar yields of mixtures of the 1 : 1 adducts in the ratios 70 : 30, 71 : 29, and 74 : 26.

(h) *With sodium hydroxide.* A solution of the disilacyclobutane (4.5 g, 17.0 mmol) in ethanol (8 ml) was added slowly to a solution of sodium hydroxide (1.0M) in ethanol (50 ml). The reaction mixture was refluxed (1 h), water (100 ml) was then added, and the mixture extracted with diethyl ether (3 × 8 ml). The ethereal extract was dried ($MgSO_4$, 48 h) and fractionated through a vacuum-jacketted column (20 cm) to afford a colourless mixture of 1 : 1 adducts (4.2 g, 14.7 mmol, 87%) (Found: *M*, 288. Calc. for $C_{16}H_{22}OSi_2$: *M*, 286), b.p. 127—129 °C at 1 mmHg, n_D^{20} 1.5442; $\nu_{max.}$ 3 366m (O–H str.) and 1 039s (linear Si·CH$_2$·Si) cm^{-1}; *m/e* 271 [25%, $(M - Me)^+$], 193 (100%, $C_9H_{13}OSi_2^+$), and 154 (100%, $C_8H_{14}OSi^+$), and a higher-boiling residue (0.5 g), b.p. >129 °C at 1 mmHg.

The 1 : 1 adduct mixture was shown by n.m.r. spectroscopy to consist of 2-hydroxy-2-methyl-4,4-diphenyl-2,4-disilapentane (2.65 g, 9.25 mmol, 54%) and 1-hydroxy-3,3-dimethyl-1,1-diphenyl-1,3-disilabutane (1.55 g, 5.45 mmol, 32%) present in the ratio 63 : 37.

The reaction was repeated twice under comparable conditions and gave similar yields of a mixture of the 1 : 1 adducts in the ratio 55 : 45 and 57 : 43.

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