Organosilicon Chemistry. Part XX.[1] Further Reactions of 1,1,3,3-Tetramethyl-, 1,3-Dimethyl-1,3-diphenyl-, and 1,1,3,3-Tetraphenyl-1,3-disilacyclobutane

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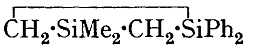
1,1,3,3-Tetramethyl-1,3-disilacyclobutane, (I), reacts with iodine monochloride or sodium benzenethiolate in benzenethiol to give reasonable yields of ring-opened 1 : 1 adducts, while reaction with bromobis(trifluoromethyl)-amine affords a mixture of perfluoro-2-azapropene and 1-bromo-4-fluoro-2,2,4-trimethyl-2,4-disilapentane *via* decomposition of the initially formed 1 : 1 adduct. 1,3-Dimethyl-1,3-diphenyl-1,3-disilacyclobutane, (II), reacts similarly with sodium benzenethiolate in benzenethiol and the bromoamine, but reaction with iodine monochloride affords mainly polymeric material. The reaction of sulphur trioxide with compound (II) results in insertion into a ring Si–CH$_2$ bond and a Si–Ph bond in the ratio 9 : 90, while reaction with 1,1,3,3-tetraphenyl-1,3-disilacyclobutane, (III), gives the Si–Ph insertion product exclusively. Both the phenyl-substituted disilacyclobutanes react with mercury(II) acetate in ethanol to give ring-opened products of the type $AcO{\cdot}Hg{\cdot}CH_2{\cdot}\overset{|}{\underset{|}{Si}}{\cdot}CH_2{\cdot}\overset{|}{\underset{|}{Si}}{\cdot}OEt$ in high yield.

It has been reported that 1,1,3,3-tetramethyl-1,3-disilacyclobutane (I),[2,3] 1,3-dimethyl-1,3-diphenyl-1,3-disilacyclobutane (II),[4] 1,1,3,3-tetraphenyl-1,3-disilacyclobutane (III),[4] and 1,1-dimethyl-3,3-diphenyl-1,3-disilacyclobutane (IV) [4] react with chlorine or bromine to give ring-opened products; with disilacyclobutanes (II)—(IV) some Si–Ph bond cleavage also occurred. The reactions of disilacyclobutanes (I)—(III) with iodine monochloride were investigated in the present work to determine if comparable ring-opening reactions took place.

$CH_2{\cdot}SiRR'{\cdot}CH_2{\cdot}SiRR'$

(I) R = R′ = Me, (II) R = Me, R′ = Ph, (III) R = R′ = Ph



$CH_2{\cdot}SiMe_2{\cdot}CH_2{\cdot}SiPh_2$

(IV)

$Me_2SiCl{\cdot}CH_2{\cdot}SiMe_2{\cdot}CH_2I$

(V)

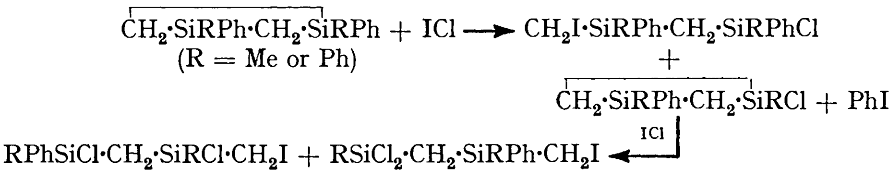
$$\text{(I)} + Br_2 \longrightarrow Me_2SiBr{\cdot}CH_2{\cdot}SiMe_2{\cdot}CH_2Br \quad (1)$$

$$\text{(IV)} + Cl_2 \longrightarrow CH_2Cl{\cdot}SiMe_2{\cdot}CH_2{\cdot}SiPh_2Cl + CH_2Cl{\cdot}SiPhCl{\cdot}CH_2{\cdot}SiMe_2Cl \quad (2)$$

RESULTS AND DISCUSSION

Disilacyclobutane (I) on reaction with iodine monochloride in refluxing dichloromethane (5 h) gave 4-chloro-1-iodo-2,2,4-trimethyl-2,4-disilapentane, (V) (53%), and ring-opened polymeric material. The observed slow reaction is in contrast to the corresponding reactions of chlorine or bromine which take place rapidly at −25 and −20 °C, respectively.[3] The adduct (V) was identified by i.r. ($\nu_{max.}$ at 1 050s cm^{-1}, linear Si·CH$_2$·Si) and n.m.r. spectroscopy (two SiMe$_2$ groups, a CH$_2$ group, and a CH$_2$I group with the expected chemical shifts and relative intensities), and mass spectrometry [strong peak at *m/e* 293 and 291 (M − Me)$^+$ and base peak at *m/e* 167 and 165 (M − CH$_2$I)$^+$]. The reactions of the disilacyclobutanes (II) and (III) with iodine monochloride in carbon tetrachloride were also slow (8 h reflux) and attempts to separate the products from reactant disilacyclobutane were unsuccessful. Examination of the recovered solvent from both reactions showed the presence of iodobenzene formed from Si–Ph bond cleavage. The i.r. spectra of the crude product from both reactions showed bands at *ca.* 950 (reactant disilacyclobutane), *ca.* 930 (a second disilacyclobutane), and *ca.* 1 050 cm^{-1} (ring-opened material).

These observations are best interpreted as in equation (3). It is also probable that ring-opened polymeric material is present in the products.



$$CH_2{\cdot}SiRPh{\cdot}CH_2{\cdot}SiRPh + ICl \longrightarrow CH_2I{\cdot}SiRPh{\cdot}CH_2{\cdot}SiRPhCl + CH_2{\cdot}SiRPh{\cdot}CH_2{\cdot}SiRCl + PhI \quad (R = Me \text{ or } Ph)$$

$$CH_2{\cdot}SiRPh{\cdot}CH_2{\cdot}SiRCl \xrightarrow{ICl} RPhSiCl{\cdot}CH_2{\cdot}SiRCl{\cdot}CH_2I + RSiCl_2{\cdot}CH_2{\cdot}SiRPh{\cdot}CH_2I \quad (3)$$

Disilacyclobutane (I) was first prepared [5] by the reaction of 1-chloro-4-fluoro-2,2,4-trimethyl-2,4-disilapentane, (VI), with magnesium in diethyl ether [equation (4)]

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

[2] R. Muller, R. Koehne, and H. Beyer, *Chem. Ber.*, 1962, **95**, 3030.

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

[4] A. M. Devine, P. A. Griffin, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, *J.C.S. Dalton*, 1975, 1822.

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

and later by the reaction of chloro(chloromethyl)dimethylsilane with magnesium in tetrahydrofuran (thf) [equation (5)] either by the normal procedure [6] or better by the inverse addition procedure.[7] This latter method is considered to involve the intermediacy of the dichloride (VII). The adduct (V) when treated with

$$\begin{array}{l} \qquad\qquad\qquad\quad \underset{\text{(VI)}}{\mathrm{Me_2SiF{\cdot}CH_2{\cdot}SiMe_2{\cdot}CH_2Cl}} \xrightarrow[(i)]{(4)} \text{(I)} \\ \mathrm{Me_2SiCl{\cdot}CH_2Cl} \xrightarrow[\text{thf}]{\text{(ii)}} \underset{\text{(VII)}}{\mathrm{Me_2SiCl{\cdot}CH_2{\cdot}SiMe_2{\cdot}CH_2Cl}} \xrightarrow[(ii)]{(5)} \text{(I)} \end{array}$$

(*i*), Mg and Et_2O; (*ii*), Mg and thf

magnesium in diethyl ether gave only polymeric material and the disilacyclobutane (I) was not detected. It has been found [8] previously that reaction of the silanes $Me_2SiCl{\cdot}CH_2X$ (X = Br or Cl) in thf with magnesium affords the disilacyclobutane (I) (21%, X = Br; 50%, X = Cl) presumably *via* the intermediate $Me_2SiCl{\cdot}CH_2{\cdot}SiMe_2{\cdot}CH_2X$ (X = Br or Cl). Thus the yield of the disilacyclobutane (I) decreases as the size of the halogen in the CH_2X group increases; the present result is consistent with this.

Bromobis(trifluoromethyl)amine reacts with electron-rich olefins in the liquid phase at low temperature in the dark by an electrophilic mechanism to give 1 : 1 adducts in high yield,[9-11] while reaction with olefins in the vapour phase in light affords the expected free-radical 1 : 1 adducts,[9,12] *e.g.* equations (6) and (7). The reaction of

$$\mathrm{CH_2{:}CH{\cdot}N(CF_3)_2} + \mathrm{(CF_3)_2NBr} \left\{ \begin{array}{l} \xrightarrow[(i)]{(6)} \mathrm{CH_2Br{\cdot}CH[N(CF_3)_2]_2} \\ \xrightarrow[(ii)]{(7)} \mathrm{(CF_3)_2N{\cdot}CH_2{\cdot}CHBr{\cdot}N(CF_3)_2} \end{array} \right.$$

(*i*), −78 °C in the dark; (*ii*), gas phase in the light

the bromoamine with disilacyclobutane (I) at −78 °C in the dark gave perfluoro-2-azapropene (97%) and 1-bromo-4-fluoro-2,2,4-trimethyl-2,4-disilapentane, (VIII) (96%), which was identified by i.r. and n.m.r. spectroscopy and mass spectrometry (see Experimental section). It has been reported [13] that the chloroamine $(CF_3)_2NCl$ on reaction with bis(trimethylsilyl)mercury afforded bistrifluoromethylaminotrimethylsilane which decomposed rapidly at room temperature to give perfluoro-2-azapropene and fluorotrimethylsilane [equation (8)].

$$\mathrm{(Me_3Si)_2Hg + (CF_3)_2NCl \longrightarrow HgCl_2 + (CF_3)_2N{\cdot}SiMe_3 \longrightarrow FSiMe_3 + CF_3{\cdot}N{:}CF_2} \quad (8)$$

In order to determine whether the product (VIII) in the present reaction was formed similarly, *i.e. via* the 1 : 1 adduct (IX), the reaction was repeated in an n.m.r. tube and the ^{19}F n.m.r. spectrum recorded immediately after reaction was complete. The spectrum ($CF_3{\cdot}CO_2H$ reference) exhibited weak absorptions due to the azapropene, a weak absorption at +73·5 p.p.m. (nonet, 1F, *J* 7·4 Hz) assigned to the fluorine in the $Me_2SiF{\cdot}CH_2$ group of compound (VIII), and a strong absorption at −30·4 p.p.m. (s, 15F) assigned to the $(CF_3)_2N$ group in the 1 : 1 adduct (IX) [*cf.* $(CF_3)_2N{\cdot}SiMe_3$,[13] *ca.* −30 p.p.m.]. The relative intensities of the ^{19}F bands indicated that compounds (VIII) and (IX) were present in the ratio *ca.* 30 : 70. When the ^{19}F spectrum was recorded after an interval of 12 h the bands assigned to the azapropene and the SiF group of compound (VIII) had greatly increased in intensity relative to the absorption at −30·4 p.p.m. The reaction is therefore considered to take place as in equation (9).

$$\begin{array}{c} \mathrm{(CF_3)_2\overset{\delta-}{N}{-}\overset{\delta+}{Br}} + \text{(I)} \longrightarrow \underset{\text{(IX)}}{\mathrm{(CF_3)_2N{\cdot}SiMe_2{\cdot}CH_2{\cdot}SiMe_2{\cdot}CH_2Br}} \\ \downarrow \\ \underset{\text{(VIII)}}{\mathrm{Me_2SiF{\cdot}CH_2{\cdot}SiMe_2{\cdot}CH_2Br}} + \mathrm{CF_3{\cdot}N{:}CF_2} \quad (9) \end{array}$$

The reaction of the bromoamine with disilacyclobutane (II) (−78 to +20 °C, dark, 16 h) gave a mixture (60%) of perfluoro-2-azapropene and bistrifluoromethylamine together with a higher-boiling liquid. A ^{19}F n.m.r. spectrum of the liquid recorded *ca.* 12 h after reaction showed absorption bands due to the azapropene together with bands at −30·9 (s, *ca.* 6 F), −21·5 to −21·9 (complex, *ca.* 1 F), and +75·6 p.p.m. (sextet, *ca.* 1·75 F, *J* 7·6 Hz), assigned to the $(CF_3)_2N$ group in the 1 : 1 adduct (X), a $(CF_3)_2N{-}C{\leqslant}$ group (reported chemical shifts −17 to −24 p.p.m.), and the $MePhSiF{\cdot}CH_2$ group in the decomposition product (XI). A complex ^1H n.m.r. absorption band at −1·5 to −1·1 p.p.m. (cyclohexane reference) was assigned to either or both CH_2Br and CHBr protons; absorption bands were also present at −6·03 (SiPh) and 1·0—1·3 p.p.m. (SiMe and CH_2). The i.r. spectrum of the liquid exhibited bands at 948 (reactant disilacyclobutane), 930 (a second disilacyclobutane), and 1 050 cm^{-1} (ring-opened material).

From these spectral observations and the presence of bistrifluoromethylamine in the products, it is suggested that both an ionic and a free-radical reaction (possibly on work-up in light) are involved. The ionic reaction affords the 1 : 1 adduct (X) which decomposes to give perfluoro-2-azapropene and 1-bromo-4-fluoro-2-methyl-

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

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

[8] P. A. Griffin, R. N. Haszeldine, and M. J. Newlands, unpublished work.

[9] E. S. Alexander, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, *J. Chem. Soc.* (*C*), 1968, 796.

[10] M. G. Barlow, G. L. Fleming, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc.* (*C*), 1971, 2744.

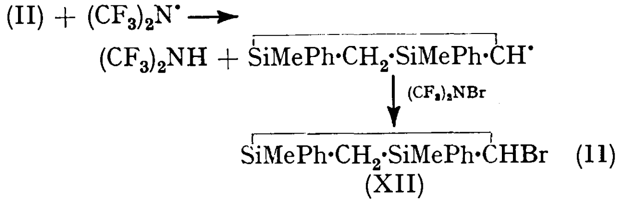
[11] D. H. Coy, G. L. Fleming, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, *J.C.S. Perkin I*, 1972, 1880.

[12] R. N. Haszeldine and A. E. Tipping, *J. Chem. Soc.*, 1965, 6141.

[13] H. J. Ang, *J. Chem. Soc.* (*A*), 1968, 2734.

2,4-diphenyl-2,4-disilapentane, (XI), *i.e.* as in equation (10). A free-radical reaction would involve initial attack on disilacyclobutane (II) by the bistrifluoromethylamino-radical at a methyl or more likely a methylene hydrogen, *i.e.* as in equation (11). The free-radical reaction of t-butyl hypochlorite with disilacyclobutane (I) affords products derived mainly from initial radical attack at a methylene hydrogen.[3] Therefore the disilacyclobutane formed in the reaction of the bromoamine with (II) probably has structure (XII), but it is not possible at the present time to assign a structure to the $(CF_3)_2N\cdot C\leqslant$ compound (*ca.* 5%) inferred as present in the products (^{19}F n.m.r. spectrum).

$$\mathrm{(II)} + \mathrm{(CF_3)_2NBr} \longrightarrow \underset{\mathrm{(X)}}{\mathrm{(CF_3)_2N\cdot SiMePh\cdot CH_2\cdot SiMePh\cdot CH_2Br}} \longrightarrow \mathrm{CF_3\cdot N{:}CF_2} + \underset{\mathrm{(XI)}}{\mathrm{MeSiPhF\cdot CH_2\cdot SiMePh\cdot CH_2Br}} \qquad (10)$$



$$\mathrm{(II)} + \mathrm{(CF_3)_2N^{\cdot}} \longrightarrow \mathrm{(CF_3)_2NH} + \mathrm{SiMePh\cdot CH_2\cdot SiMePh\cdot CH^{\cdot}} \xrightarrow{\mathrm{(CF_3)_2NBr}} \underset{\mathrm{(XII)}}{\mathrm{SiMePh\cdot CH_2\cdot SiMePh\cdot CHBr}} \qquad (11)$$

It has been reported that the disilacyclobutane (I) reacts with mercury(II) acetate in ethanol to give a compound, possibly of structure (XIII), which when hydrolysed with aqueous sodium hydrogencarbonate afforded the cyclic compound (XIV) [equation (12)]. In the present work the comparable reactions (13) of the disilacyclobutanes (II) and (III) with mercury(II) acetate in ethanol gave acetic acid, mercury(I) acetate (small amounts), and the compounds (XV) (72%) or (XVI) (91%), respectively. The products (XV) and (XVI) were identified by i.r. [bands at 1 050 (linear $Si\cdot CH_2\cdot Si$), 948 and 1 080 (EtOSi), and 1 580 cm^{-1} (C=O str. in metal acetates)] and n.m.r. spectroscopy; the mass spectra were also consistent with the assigned structures.

$$\mathrm{(I)} + \mathrm{Hg(O\cdot OCMe)_2} \longrightarrow \underset{\mathrm{(XIII)}}{\mathrm{MeCO\cdot O\cdot Hg\cdot CH_2\cdot SiMe_2\cdot CH_2\cdot SiMe_2\cdot O\cdot OCMe}} \xrightarrow{\mathrm{NaHCO_3-H_2O}} \underset{\mathrm{(XIV)}}{\left(\mathrm{O\cdot Hg\cdot CH_2\cdot SiMe_2\cdot CH_2\cdot SiMe_2}\right)_2} \qquad (12)$$

$$\mathrm{(II)\ or\ (III)} + \mathrm{Hg(O\cdot OCMe)_2} \longrightarrow \mathrm{MeCO\cdot O\cdot Hg\cdot CH_2\cdot SiPhR\cdot CH_2\cdot SiPhR\cdot O\cdot OCMe} \xrightarrow{\mathrm{EtOH}} \mathrm{MeCO_2H} + \mathrm{MeCO\cdot O\cdot Hg\cdot CH_2\cdot SiPhR\cdot CH_2\cdot SiPhR\cdot OEt} \qquad (13)$$

(XV) R = Me, (XVI) R = Ph

When both compounds as solutions in ethanol were treated with aqueous hydrogencarbonate the polymeric products showed strong bands in their i.r. spectra at 1 000—1 090 cm^{-1} (Si·O·Si str.); bands due to the ester carbonyl and ethoxy-groups were absent. Thus hydrolysis of the initial compounds (XV) and (XVI) takes place at both the ester and ethoxy-groups to afford the diol (XVII) [equation (14)] which reacts further by condensation to afford polymeric products containing $SiPhR\cdot O\cdot Hg\cdot CH_2$, $SiPhR\cdot CH_2\cdot Hg\cdot O\cdot Hg$, or $SiPhR\cdot O\cdot SiPhR$ linkages (where R = Me or Ph). It is thus likely that the intermediate isolated in the reaction of disilacyclobutane (I) with mercury(II) acetate[3] has the structure $MeCO\cdot O\cdot Hg\cdot CH_2\cdot SiMe_2\cdot CH_2\cdot SiMe_2\cdot OEt$ [corresponding to (XV) and (XVI)]. The reason why this compound cyclises on treatment with aqueous hydrogencarbonate while compounds (XV) and (XVI) do not is possibly due to steric hindrance to cyclisation by the bulky phenyl groups in the latter compounds.

$$\mathrm{(XV)\ or\ (XVI)} \xrightarrow{\mathrm{NaHCO_3}} \underset{\mathrm{(XVII)}}{\mathrm{HO\cdot Hg\cdot CH_2\cdot SiPhR\cdot CH_2\cdot SiPhR\cdot OH}} \qquad (14)$$

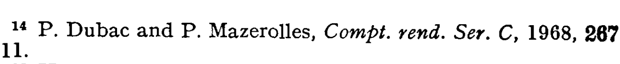
The insertion reactions of sulphur trioxide into a number of silicon-element bonds have been reported,[14] *e.g.* (15) and (16). Insertion of sulphur trioxide into trimethyl(phenyl)silane[15] occurs exclusively at the Si–Ph bond rather than an Si–Me bond [equation (17)].

$$\mathrm{Me_4Si} + \mathrm{SO_3} \xrightarrow{6-10\,^{\circ}\mathrm{C}} \mathrm{Me_3Si\cdot O\cdot SO_2Me} \qquad (15)$$

$$\mathrm{Me_3SiCl} + \mathrm{SO_3} \longrightarrow \mathrm{Me_3Si\cdot O\cdot SO_2Cl} \qquad (16)$$

$$\mathrm{Me_3SiPh} + \mathrm{SO_3} \longrightarrow \mathrm{Me_3Si\cdot O\cdot SO_2Ph}$$

Similarly the reaction of 1-methyl-1-phenyl-silacyclobutane with sulphur trioxide results in major insertion into the Si–Ph bond and only minor insertion into a Si–CH_2 ring bond.[14] More recently the reaction of disilacyclobutane (I) with sulphur trioxide [equation (18)] has been reported[16] to result in exclusive insertion into a ring Si–CH_2 bond to afford the cyclic compound (XVIII).



$$\mathrm{(I)} + \mathrm{SO_3} \xrightarrow[-78\,^{\circ}\mathrm{C}]{\mathrm{CH_2Cl_2}} \underset{\mathrm{(XVIII)}}{\mathrm{Me_2Si\cdot O\cdot SO_2\cdot CH_2\cdot SiMe_2\cdot CH_2}} \qquad (18)$$

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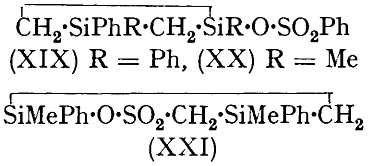
[14] P. Dubac and P. Mazerolles, *Compt. rend. Ser. C*, 1968, **267**, 411.

[15] H. Schmidbaur, L. Sechser, and M. Schmidt, *J. Organometallic Chem.*, 1968, **15**, 77.

[16] H. Schmidbaur, L. Sechser, and M. Schmidt, *Chem. Ber.*, 1969, **102**, 376.

In the present work the reactions of the disilacyclobutanes (II) and (III) with sulphur trioxide have been investigated. The reaction of disilacyclobutane (III) with sulphur trioxide at −78 °C in solvent dichloromethane gave 1,3,3-triphenyl-1,3-disilacyclobutyl benzenesulphonate, (XIX) (*ca.* 98%), which could not be obtained absolutely pure due to decomposition on attempted distillation. The product was identified by



$$\mathrm{CH_2{\cdot}SiPhR{\cdot}CH_2{\cdot}SiR{\cdot}O{\cdot}SO_2Ph}$$

(XIX) R = Ph, (XX) R = Me

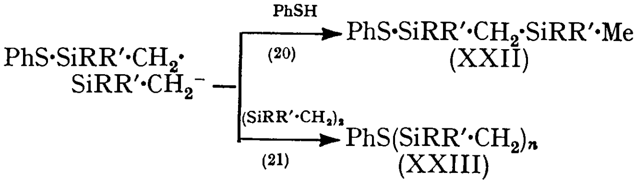
$$\mathrm{SiMePh{\cdot}O{\cdot}SO_2{\cdot}CH_2{\cdot}SiMePh{\cdot}CH_2}$$

(XXI)

i.r. [bands at 930 (disilacyclobutane) and 1 195 and 1 390 cm^{-1} (SO_2 group)] and n.m.r. spectroscopy [absorptions at −6·1 (20H, 4 Ph) and 0·28 p.p.m. (4 H, 2 CH_2) relative to cyclohexane reference]. The reaction of disilacyclobutane (II) with sulphur trioxide under comparable conditions gave the Si–Ph insertion product (XX) (90%) and the ring Si–CH_2 insertion product (XXI) (9%) which could not be separated by distillation or liquid chromatography. The n.m.r. spectrum of the product mixture showed absorptions at −5·93 (complex, 10 H, 2 Ph), −1·43 (s, 0·2 H, $CH_2{\cdot}SO_2$), and 0·7—1·2 p.p.m. (complex 9·8 H, CH_2 and SiMe); the absorption at −1·43 p.p.m. was assigned by comparison with the chemical shift reported (*ca.* −1·41 p.p.m.) for the $CH_2{\cdot}SO_2$ protons in the compound (XVIII).[16] The i.r. spectrum of the mixture was also consistent with the assigned structures and showed strong absorption at 920 (disilacyclobutane ring), 1 060 (Si–O str.), and 1 200 and 1 330 cm^{-1} (SO_2 str.). Thus the reactions of the disilacyclobutanes (I)—(III) with sulphur trioxide show a marked change from Si–CH_2 ring insertion with (I) to mainly Si–Ph insertion with (II) and exclusive Si–Ph insertion with (III) as methyl groups are successively replaced by phenyl groups.

The reactions of the disilacyclobutanes (I) and (II) with sulphur dioxide were carried out to determine whether analogous insertion reactions took place to those observed with sulphur trioxide, but only unchanged reactants were obtained. On reaction with a mixture of sodium benzenethiolate and benzenethiol in solvent dimethylformamide the disilacyclobutanes (I) and (II) afforded the expected adducts (XXII; $R = R^1 = Me$, 61%; $R = Me, R^1 = Ph$, 84%) together with polymeric material. The comparable reactions of the disilacyclobutanes (I)—(III) in the absence of benzenethiol gave polymeric material only of probable structure (XXIII) ($R = R^1 = Me$; $R = Me, R^1 = Ph$; or $R = R^1 = Ph$). Disilacyclobutane (III) underwent a slow reaction with a mixture of sodium benzenethiolate and benzenethiol in dimethylformamide to give the expected adduct (XXII; $R = R^1 = Ph$), but on attempted separation of the product from unchanged disilacyclobutane by chromatography on a neutral alumina column only unreacted disilacyclobutane (III) (49%) was obtained. It has been reported [3] previously that disilacyclobutane

$$\mathrm{RR'Si{\cdot}CH_2{\cdot}SiRR'{\cdot}CH_2 + PhS^- \longrightarrow PhS{\cdot}SiRR'{\cdot}CH_2{\cdot}SiRR'{\cdot}CH_2^-} \quad (19)$$



(I) does not react with benzenethiol in refluxing carbon tetrachloride.

EXPERIMENTAL

Products were separated by fractional distillation or chromatography (Laporte Industries alumina type H) and were examined by i.r. spectroscopy (Perkin-Elmer 457 spectrophotometer with sodium chloride optics), n.m.r. spectroscopy (Perkin-Elmer R10 instrument operating at 60·0 MHz for ^1H and 56·46 MHz for ^{19}F, or a Varian HA 100 instrument operating at 100·00 MHz for ^1H and 94·16 MHz for ^{19}F with internal cyclohexane and external trifluoroacetic acid as the respective references), mass spectrometry (A.E.I. MS/2H instrument), molecular-weight determination (Mechrolab 301A vapour-pressure osmometer), and gas–liquid chromatography (where necessary) [columns (2 m) packed with Silicone MS 550 oil on Celite].

The disilacyclobutanes were prepared by inverse addition[7] of magnesium to the appropriate chloro(chloromethyl)silane in tetrahydrofuran and bromobis(trifluoromethyl)amine was prepared by the reaction of bromine with mercury(II) bis(trifluoromethyl)amide *in vacuo*.[12]

Reactions of 1,1,3,3-*Tetramethyl*-1,3-*disilacyclobutane*.—(a) *With iodine monochloride.* Iodine monochloride (8·1 g, 50·0 mmol) in dichloromethane (25 cm^3) was added to a solution of the disilacyclobutane (10·0 g, 72·0 mmol) in dichloromethane (20 cm^3) and the reaction mixture heated under reflux (5 h). The resulting material was shaken with mercury (10 g) in the dark (2 h), filtered, and then fractionated to afford (*i*) unchanged disilacyclobutane (3·6 g, 27·0 mmol, 36% recovered), b.p. 61—62 °C at 100 mmHg, (*ii*) 4-*chloro*-1-*iodo*-2,2,4-*trimethyl*-2,4-*disilapentane* (7·3 g, 23·8 mmol, 53%) (Found: C, 23·4; H, 5·3; *M*, 298. Calc. for $C_6H_{16}ClISi_2$: C, 23·4; H, 5·2%; *M*, 307), b.p. 117—118 °C at 20 mmHg, n_D^{20} 1·5532, ^1H n.m.r. bands at −0·91 (s, 2 H, CH_2I), 0·92 (s, 6 H, $SiMe_2Cl$), 1·04 (s, 2 H, CH_2), and 1·13 p.p.m. (s, 6 H, $SiMe_2$), *m/e* 293 and 291 [38%, $(M - Me)^+$], 200 (22%, $C_3H_9SiI^+$), 167 and 165 [100%, $(M - CH_2I)^+$], and 95 and 93 (7%, Me_2SiCl^+), and (*iii*) a polymeric residue (4·3 g), b.p. >118 °C at 20 mmHg.

(b) *With bromobis(trifluoromethyl)amine.* A mixture of the disilacyclobutane (1·0 g, 7·0 mmol) and the bromoamine (1·0 g, 4·3 mmol), maintained in a Pyrex ampoule (*ca.* 60 cm^3) at −78 °C in the dark (3 h) and then allowed to warm to room temperature in the dark (24 h), gave (*i*) perfluoro-2-azapropene (0·54 g, 4·2 mmol, 98%) (Found: *M*, 136. Calc. for C_2F_5N: *M*, 133), (*ii*) unchanged disilacyclobutane (0·37 g, 2·6 mmol, 38% recovered), and (*iii*) 1-*bromo*-4-*fluoro*-2,2,4-*trimethyl*-2,4-*disilapentane* (1·02 g, 4·1 mmol, 97%) (Found: C, 29·1; H, 6·4%; *M*, 251. Calc. for $C_6H_{16}BrFSi_2$: C, 29·4; H, 6·5%; *M*, 243), b.p. (Siwoloboff) 198 °C, ^{19}F n.m.r. band at 73·5 p.p.m. (nonet, *J* 7·2 Hz), ^1H n.m.r. bands at $-1·21$ (s, 2 H, CH_2Br), 0·95 (d, 6 H, $SiMe_2F$), 0·98 (d, 2 H, CH_2), and 1·01 p.p.m. (s, 6 H, $SiMe_2$), $\nu_{max.}$ at 1 050 s (linear $Si{\cdot}CH_2{\cdot}Si$) and 953 and 942 s (Si–F str.) cm^{-1}, *m/e* 244 and 242 (7%, M^+), 230 and 228 [7%, $(M - Me)^+$], 149 [100%, $(M - CH_2Br)^+$], and 77 (33%, Me_2SiF^+).

(c) *With sodium benzenethiolate in benzenethiol.* A mixture of the disilacyclobutane (4·3 g, 30·0 mmol), sodium benzenethiolate (4·0 g, 30·6 mmol), and benzenethiol (7·3 g, 80·0 mmol) in dimethylformamide (50 ml) was heated under reflux (3 h) and the solvent and excess of benzenethiol were removed *in vacuo*. The resulting material was treated with light petroleum (30 cm^3, b.p. 30—40 °C), the solid material filtered and identified as unchanged sodium benzenethiolate (2·9 g, 22·1 mmol, 72% recovered), and the solvent removed from the filtrate *in vacuo*. The remaining liquid was fractionated at reduced pressure through a vacuum-jacketed column (30 cm) to afford 2,4,4-*trimethyl*-2-*phenylthio*-2,4-*disilapentane* (4·65 g, 18·3 mmol, 61%) (Found: C, 56·4; H, 8·5%; *M*, 270. Calc. for $C_{12}H_{22}SSi_2$: C, 56·6; H, 8·7%; *M*, 254), b.p. 123—126 °C at 15 mmHg, n_D^{20} 1·4891, ^1H n.m.r. bands at $-5·9$ (complex, 5 H, Ph), 1·08 (s, 6 H, $SiMe_2$), 1·45 (s, 2 H, CH_2), and 1·46 p.p.m. (s, 9 H, $SiMe_3$), *m/e* 253 [5%, $(M - H)^+$], 239 [100%, $(M - Me)^+$], 223 [20%, $(M - C_2H_7)^+$], 165 (29%, $C_8H_{11}SiS^+$), and 73 (14%, Me_3Si^+), and a polymeric residue (2·3 g).

(d) *With sodium benzenethiolate.* A mixture of the disilacyclobutane (4·3 g, 30·0 mmol) and sodium benzenethiolate (4·0 g, 30·6 mmol) in dimethylformamide (50 cm^3) was heated under reflux (2 h) and the products worked-up as in the previous experiment to give unchanged sodium benzenethiolate (3·1 g, 23·7 mmol, 77%) and a yellow oil (4·0 g; *M*, 1 620) which was shown by i.r. spectroscopy to contain linear $SiCH_2$ chains.

Reactions of 1,3-*Dimethyl*-1,3-*diphenyl*-1,3-*disilacyclobutane*.—(a) *With iodine monochloride.* A mixture of iodine monochloride (4·8 g, 30·0 mmol) and the disilacyclobutane (9·5 g, 35·5 mmol) in carbon tetrachloride (30 cm^3) was heated under reflux (6 h), and the resulting material was shaken with mercury (10 g) in the dark (2 h) to remove iodine. The solvent was removed *in vacuo* to afford an oil (13·8 g) which was shown (i.r.) to contain (*i*) unchanged disilacyclobutane, (*ii*) a second disilacyclobutane ($\nu_{max.}$ at 930 cm^{-1}), and (*iii*) ring-opened material ($\nu_{max.}$ at 1 050 cm^{-1}). Attempted fractional distillation of the mixture in the dark resulted in decomposition with the formation of iodine. The recovered solvent was shown [i.r. and g.l.c. (2 m column at 125 °C)] to contain iodobenzene.

(b) *With bromobis(trifluoromethyl)amine.* A mixture of the disilacyclobutane (2·0 g, 7·5 mmol) and the bromoamine (1·9 g, 8·2 mmol), sealed in a Pyrex ampoule (*ca.* 60 cm^3) and allowed to warm slowly from -78 °C to room temperature in the dark (16 h), gave a mixture (0·68 g, 5·0 mmol, 60%) (Found: *M*, 143) of perfluoro-2-azapropene and bistrifluoromethylamine and a higher-boiling oil (3·1 g) which was shown by i.r. and n.m.r. spectroscopy to consist of unchanged disilacyclobutane, a second disilacyclobutane ($\nu_{max.}$ at 930 cm^{-1}), and ring-opened material ($\nu_{max.}$ at 1 050 cm^{-1}). An attempt to separate the high-boiling mixture by fractional distillation (Nester–Faust spinning-band column, 30 cm) at reduced pressure was unsuccessful.

(c) *With sodium benzenethiolate in benzenethiol.* A mixture of the disilacyclobutane (5·2 g, 19·5 mmol), sodium benzenethiolate (3·0 g, 22·8 mmol), and benzenethiol (7·3 g, 80·0 mmol) in dimethylformamide (70 ml) was heated under reflux (3 h) and the solvent and excess of benzenethiol were removed *in vacuo*. The resultant material was treated with light petroleum (25 cm^3, b.p. 30—40 °C) and filtered to afford a residue of unchanged sodium benzenethiolate (2·1 g, 16·5 mmol, 72% recovered) and a filtrate from which the solvent petroleum was removed *in vacuo*. The remaining liquid (7·2 g) was chromatographed on a neutral alumina column (30 cm) using light petroleum (b.p. 30—40 °C) as the eluant to afford 2-*methyl*-2,4-*diphenyl*-4-*phenylthio*-2,4-*disilapentane* (6·3 g, 16·5 mmol, 84%) (Found: C, 70·1; H, 6·6%; *M*, 394. Calc. for $C_{22}H_{26}SSi_2$: C, 69·8; H, 6·9%; *M*, 378), b.p. 172—174 °C at 0·1 mmHg, ^1H n.m.r. bands at $-6·01$ (complex, 15 H, 2 SiPh and SPh), 1·03 (s, 2 H, CH_2), 1·10 (s, 3 H, SiMe), and 1·18 p.p.m. (2s, 6 H, 2 non-equivalent Me in Me_2Si); *m/e* 363 [5%, $(M - Me)^+$], 289 [10%, $(M - Me\ and\ Ph)^+$], and 153 [100%, $C_7H_9SiS^+$].

(d) *With sodium benzenethiolate.* A mixture of the disilacyclobutane (8·0 g, 30·0 mmol) and sodium benzenethiolate (4·0 g, 30·6 mmol) in dimethylformamide, heated under reflux (3 h) and the products worked-up as in the previous experiment, gave unchanged sodium benzenethiolate (3·0 g, 22·9 mmol, 75% recovered) and a viscous polymeric yellow oil (7·5 g; *M*, 2 140).

(c) *With sulphur trioxide.* The disilacyclobutane (7·0 g, 26·0 mmol) in dichloromethane (10 ml) was slowly added to a solution of sulphur trioxide (2·2 g, 27·4 mmol) in dichloromethane (25 cm^3) at -78 °C and the reaction mixture allowed to warm to room temperature and stirred (2 h). Removal of the solvent *in vacuo* gave a viscous yellow oil (9·1 g, 25·75 mmol, 99%) (Found: *M*, 379. Calc. for $C_{16}H_{20}O_3SSi_2$: *M*, 348) which was shown by g.l.c. (2 m column at 240 °C) and i.r. and n.m.r. spectroscopy to contain 1,3-dimethyl-3-phenyl-1,3-disilacyclobutyl benzenesulphonate (8·2 g, 23·5 mmol, 90%) and 4,6-dimethyl-2,2-dioxo-4,6-diphenyl-1-oxa-2-thia-4,6-disilacyclohexane (0·9 g, 2·25 mmol, 9%).

(f) *With mercury*(II) *acetate.* The disilacyclobutane (3·5 g, 14·2 mmol) was slowly added (20 min) to a solution of mercury(II) acetate (6·35 g, 20·0 mmol) in refluxing ethanol (200 cm^3) and the resulting mixture heated under reflux (1 h). The product was filtered to give a residue of mercury(I) acetate (0·45 g, 1·2 mmol) and the solvent was removed from the filtrate *in vacuo* to give a colourless oil (9·7 g). The oil was treated with light petroleum (15 cm^3, b.p. 30—40 °C) and the precipitate (1·2 g) of mercury(I) and mercury(II) acetates was filtered off. The light petroleum was removed from the filtrate *in vacuo*, the resulting material (6·4 g) was heated at 60 °C *in vacuo* (16 h) to remove acetic acid, and the residue was identified as *acetato*(2,4-*dimethyl*-2,4-*diphenyl*-5-*oxa*-2,4-*disilaheptyl*)*mercury* (5·7 g, 10·1 mmol, 72%) (Found: C, 42·1; H, 4·8%; *M*, 530. Calc. for $C_{20}H_{28}HgO_3Si_2$: C, 41·9; H, 4·9%; *M*, 572), n_D^{20} 1·5451, ^1H n.m.r. bands at $-6·1$ (complex, 10 H, 2 SiPh), $-2·16$ [q, 2 H, OCH_2, $J(CH_2,Me)$ 6·1 Hz], $-0·68$ (s, 3 H, MeCO), 0·09 (t, 3 H, Me, *J* 6·1 Hz), 0·43 and 0·32 (2 centre bands of AB, 2 H, and $HgCH_2$), and 0·82—0·97 p.p.m. (complex, 8 H, 2 SiMe, and CH_2), *m/e* 513 [2%, $(M - CH_3CO_2)^+$], 393 [3%, $(M - CH_2{\cdot}SiMePh{\cdot}OEt)^+$], 313 [7%, $(M - CH_3CO_2Hg)^+$], 200 (100%, Hg^+), 100 (13%, Hg^{2+}), 78 (100%, $C_6H_6^+$), and 77 (50%, $C_6H_5^+$ and $C_2H_5OSi^+$).

Reactions of 1,1,3,3-*Tetraphenyl*-1,3-*disilacyclobutane*.—(a) *With iodine monochloride.* A mixture of the disilacyclobutane (1·5 g, 3·8 mmol) and iodine monochloride (0·64 g, 3·9 mmol) in carbon tetrachloride (23 cm^3) was heated under reflux (5 h) and the resulting solution was then filtered and the solvent removed *in vacuo* to give a mixture (2·1 g) of yellow solid and an oil which was shown by i.r. spectroscopy to consist of (*i*) unchanged disilacyclobutane, (*ii*) a second disilacyclobutane ($\nu_{max.}$ at 930 cm^{-1}), and (*iii*) ring-opened material ($\nu_{max.}$ at 1 050 cm^{-1}). An attempt to separate the components of the mixture by chromatography on a neutral alumina column (30 cm) was unsuccessful. The recovered carbon tetrachloride solvent was shown by i.r. spectroscopy and g.l.c. (as before) to contain iodobenzene.

(b) *With sodium benzenethiolate in benzenethiol.* A mixture of the disilacyclobutane (4·0 g, 10·4 mmol), sodium benzenethiolate, (1·6 g, 12·5 mmol), and benzenethiol (5·5 g, 50·0 mmol) in dimethylformamide (70 ml) was heated under reflux (3 h). The solvent and unchanged benzenethiol were removed *in vacuo* to afford a brown gum (*ca.* 5·5 g) which was chromatographed on a neutral alumina column with chloroform as the eluant to give only unchanged disilacyclobutane (2·0 g, 5·1 mmol, 49% recovered).

(c) *With sodium benzenethiolate.* A mixture of the disilacyclobutane (4·0 g, 10·4 mmol) and sodium benzenethiolate (1·6 g, 12·5 mmol) in dimethylformamide (25 cm^3) was heated under reflux (3 h). The solvent was then removed *in vacuo* to give a dark gum (4·9 g) which was shown (i.r.) to contain unchanged sodium benzenethiolate and polymeric material with linear $SiCH_2$ chains.

(d) *With sulphur trioxide.* A solution of the disilacyclobutane (3·3 g, 8·1 mmol) in dichloromethane (20 cm^3) was added slowly to a solution of sulphur trioxide (0·5 g, 6·0 mmol) in dichloromethane (10 cm^3) at −78 °C and the reaction mixture was stirred (1 h) while it warmed to room temperature. The solvent was removed *in vacuo* to afford a brown gum which could not be crystallised from dichloromethane or toluene and which was identified as 1,3,3-triphenyl-1,3-disilacyclobutyl benzenesulphonate (3·8 g, 8·0 mmol, 98%), ^{1}H n.m.r. bands at −6·1 (complex, 20 H, 3 SiPh and SO_3Ph) and 0·28 p.p.m. (s, 4 H, 2 CH_2). The product (2·5 g) was dissolved in ethanol (30 cm^3) and water (50 cm^3) was added slowly to give a white precipitate. The solid was filtered, dried *in vacuo* (3 d), and identified as polysiloxane (1·9 g), $\nu_{max.}$ at 1 030—1 080s cm^{-1} (Si–O str.).

(e) *With mercury*(II) *acetate.* A solution of the disilacyclobutane (2·5 g, 6·4 mmol) in ethanol (75 cm^3) was added slowly to a solution of mercury(II) acetate (2·5 g, 7·8 mmol) in refluxing ethanol (90 cm^3) and the reflux continued (1 h). The resulting material was filtered to give a residue of mercury(I) acetate (0·4 g), and the solvent was removed from the filtrate *in vacuo.* The product was washed with light petroleum (3 × 10 cm^3, b.p. 30—40 °C) and then sublimed at 70 °C *in vacuo* to afford *acetato*(2,2,4,4-*tetraphenyl*-5-*oxa*-2,4-*disilaheptyl*)*mercury* (4·1 g, 5·8 mmol, 91%) (Found: C, 53·1; H, 4·7%; *M*, 652. Calc. for $C_{30}H_{32}HgO_3Si_2$: C, 52·9; H, 4·6%; *M*, 696), m.p. 98 °C (sealed tube), ^{1}H n.m.r. bands at −6·2 (complex, 20 H, 2 $SiPh_2$), −2·45 [q, 2 H, OCH_2, $J(CH_2,Me)$ 6·1 Hz], −0·85 (s, 3 H, $CH_3{\cdot}CO_2$), 0·06 (s, 2 H, $HgCH_2$), 0·10 (t, 3 H, $CH_2{\cdot}CH_3$, J 6·1 Hz), and 0·95 p.p.m. (s, 2 H, CH_2), *m/e* 437 [trace, $(M - CH_3CO_2Hg)^+$], 315 (13%, $CH_2{\cdot}SiPh_2{\cdot}CH_2{\cdot}SiPh^+$), 200 (13%, Hg^+), 100 (100%, Hg^{2+}), and 77 (13%, Ph^+).

Reaction of 4-*Chloro*-1-*iodo*-2,2,4-*trimethyl*-2,4-*disilapentane with Magnesium.*—The disilapentane (7·1 g, 23·1 mmol) in diethyl ether (10 cm^3) was slowly added to magnesium turnings (0·85 g, 0·035 g-atoms) activated by iodine (two crystals) in diethyl ether (50 cm^3) and the reaction mixture heated under reflux (1 h), cooled, and poured onto crushed ice (50 g). The organic layer was separated, washed with ice–water (3 × 10 cm^3), dried ($MgSO_4$), and the solvent removed by fractionation to afford a high-boiling residue (5·0 g) which was shown (i.r.) to be polymeric with linear $SiCH_2$ chains.

Hydrolysis of Acetato(2,4-*dimethyl*-2,4-*diphenyl*-5-*oxa*-2,4-*disilaheptyl*)*mercury.*—The mercury compound (2·5 g, 4·35 mmol) dissolved in ethanol (50 cm^3) was shaken with aqueous sodium hydrogencarbonate (5% w/v, 30 cm^3) and the resulting solution extracted with diethyl ether (3 × 10 cm^3). The ether extract was dried ($MgSO_4$) and the solvent removed *in vacuo* to afford a yellow oil (2·0 g; *M*, 2 400) the i.r. spectrum of which showed that (*i*) the acetate group was absent, (*ii*) the Si–OEt group had been cleaved, and (*iii*) the material was polymeric with linear $SiCH_2$ groups.

Hydrolysis of Acetato(2,2,4,4-*tetraphenyl*-5-*oxa*-2,4-*disilaheptyl*)*mercury.*—The mercury compound (2·5 g, 3·6 mmol) in ethanol (50 cm^3) was shaken with aqueous sodium hydrogencarbonate (5% w/v, 30 cm^3) and the product worked-up as in the previous experiment to afford a mixture (2·3 g) of a solid and a viscous oil. The mixture was shown (i.r.) to be mainly polymeric and could not be separated by chromatography on a neutral alumina column (50 cm) using chloroform and methanol as the eluants or by attempted low-temperature crystallisation from light petroleum (b.p. 30—40 °C).

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