Organosilicon Chemistry. Part XV.[1] Thermal Reactions of Trifluoro(1,1,2,2-tetrafluoroethyl)silane and Silicon Tetrafluoride with Methoxotrimethylsilane, Hexamethyldisilazane, and Trimethylsilanol

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Trifluoro(1,1,2,2-tetrafluoroethyl)silane reacts thermally with methoxotrimethylsilane, hexamethyldisilazane, or trimethylsilanol, possibly *via* co-ordination of the silicon atom of the SiF_3 group with the nitrogen or oxygen atom of the other reactant, to give fluorotrimethylsilane and trimethoxo(1,1,2,2-tetrafluoroethyl)silane, tar, or polymeric material possibly the silsesquioxane $(CHF_2\cdot CF_2\cdot Si\cdot O_{1.5})_n$, respectively. Silicon tetrafluoride under the same conditions similarly reacts with the disilazane or the methoxosilane to give fluorotrimethylsilane and 1,1,1-trifluoro-3,3,3-trimethyldisilazane or fluorotrimethoxosilane, respectively.

THE thermal decomposition of trifluoro(1,1,2,2-tetrafluoroethyl)silane, $CHF_2\cdot CF_2\cdot SiF_3$ (I), at *ca.* 150 °C results in quantitative formation of silicon tetrafluoride and 1,2,2-trifluoroethylidene, $CHF_2\cdot\ddot{C}F$.[2,3]

In the present work the thermal reactions of silane (I) with the compounds Me_3SiOMe, $(Me_3Si)_2NH$, and

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[1] Part XIV, R. N. Haszeldine, A. E. Tipping, and R. O'B. Watts, *J.C.S. Perkin I*, 1975, 966.

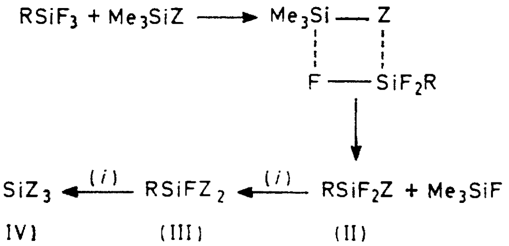
[2] W. I. Bevan, R. N. Haszeldine, and J. C. Young, *Chem. and Ind.*, 1961, 789; R. N. Haszeldine, P. J. Robinson, and R. F. Simmons, *J. Chem. Soc.*, 1964, 1890.

[3] G. Fishwick, R. N. Haszeldine, C. Parkinson, P. J. Robinson, and R. F. Simmons, *Chem. Comm.*, 1965, 382.

Me_3SiOH have been investigated and on the basis of the results obtained the thermal reactions of silicon tetrafluoride with the former two silicon compounds were also carried out.

RESULTS AND DISCUSSION

The products obtained can be explained by the general reaction scheme:



(*i*), Me_3SiZ; R = $CHF_2\cdot CF_2$ or F and Z = OMe, $HN\cdot SiMe_3$, or OH.

The products when R = $CHF_2\cdot CF_2$ and Z = OMe (1 : 3 molar ratio) at 100 or 150 °C were unchanged methoxotrimethylsilane (4% recovered), fluorotrimethylsilane (95% based on 3 F available in $RSiF_3$), trimethoxo-(1,1,2,2-tetrafluoroethyl)silane, $CHF_2\cdot CF_2\cdot Si(OMe)_3$ (IVa) (90%), and fluorodimethoxo(1,1,2,2-tetrafluoroethyl)-silane, $CHF_2\cdot CF_2\cdot SiF(OMe)_2$ (IIIa) (6%), and, when R = F and Z = OMe (1 : 3 molar ratio), were unchanged methoxotrimethylsilane (7%), fluorotrimethylsilane (71% based on 4 F available in SiF_4), fluorotrimethoxosilane, $FSi(OMe)_3$ (IVb) (80%), difluorodimethoxosilane, $F_2Si(OMe)_2$ (IIIb) (11%), trifluoro(methoxo)silane, F_3SiOMe (IIb) (*ca.* 1%), and tetramethoxosilane (*ca.* 1%).

The products when R = $CHF_2\cdot CF_2$ and Z = $HN\cdot SiMe_3$ (1 : 3 molar ratio) at 150 °C were unchanged disilazane (60%), silicon tetrafluoride (15%), fluorotrimethylsilane (36%), and a dark viscous residue, while at 100 °C the products were unchanged disilazane (47%), fluorotrimethylsilane (42%), and a dark viscous tar. However, when R = F and Z = $HN\cdot SiMe_3$ the compound $Me_3Si\cdot NH\cdot SiF_3$ (IIc) (63%) was isolated together with fluorotrimethylsilane (45%) and unidentified higher-boiling material. The products when R = $CHF_2\cdot CF_2$ and Z = OH (1 : 3 molar ratio) at 150 °C were unchanged silanol (3% recovered), fluorotrimethylsilane (96%), a small amount of liquid low polymer, and solid polymer (>90%) (m.p. >310 °C).

Thus the reactions between the fluorosilane (I) or silicon tetrafluoride and the methoxosilane go essentially to completion to afford compounds of type (IV) as the major products; the small amount of tetramethoxosilane isolated in the silicon tetrafluoride reaction indicates that some disproportionation of intermediate fluoromethoxosilanes is taking place. In the reaction with silane (I) at 150 °C products expected from decomposition of the silane by α elimination, *i.e.* silicon tetrafluoride, trifluoroethylene, and the cyclopropanes *cis*- and *trans*-$CHF_2\cdot\overline{CF\cdot CF_2\cdot C}HF$, were not detected. This indicates that carbene formation *via* α elimination from silane (I) does not compete successfully with reaction between (I) and the methoxosilane. Furthermore, reaction at 100 °C, at which temperature silane (I) does not decompose to give a carbene,[3] gave an identical product distribution to that observed for reaction at 150 °C.

However, silicon tetrafluoride (15%) was isolated from reaction between silane (I) and the disilazane at 150 °C, which indicates that (I) reacts at a slower rate with the disilazane than with the methoxosilane, thus allowing the α-elimination process to compete to some extent. In an analogous reaction carried out at 100 °C silicon tetrafluoride was not detected in the products. The low yields of fluorotrimethylsilane (36 and 42%, respectively) and the corresponding high recoveries of disilazane (60 and 47%, respectively) from these reactions indicate that the major intermediate product is of type (II), *i.e.* $CHF_2\cdot CF_2\cdot SiF_2\cdot NH\cdot SiMe_3$ (theoretical yield of Me_3SiF, 33%), but attempts to isolate this compound or its subsequent decomposition products were unsuccessful. In support of this it was observed that reaction between silicon tetrafluoride and the disilazane gave 1,1,1-trifluoro-3,3,3-trimethyldisilazane, (IIc) (63%). The disilazane (IIc) decomposed slowly at room temperature giving fluorotrimethylsilane and an involatile tar and it was therefore identified by n.m.r. spectroscopy [^{19}F δ 69·0 p.p.m. (SiF_3) and ^1H τ 2·6 (1 H, broad, NH) and 9·80 (9 H, s, $SiMe_3$)] and mass spectrometry (*m*/*e* 159 $[M - C_2H_5]^+$ and 85 $[SiF_3]^+$).

The high yield of fluorotrimethylsilane (96%) obtained from the reaction of silane (I) with trimethylsilanol indicates that reaction goes nearly to completion, as observed with methoxotrimethylsilane. It would then be expected that the other major product would be of type (IV), *i.e.* the silanetriol $CHF_2\cdot CF_2\cdot Si(OH)_3$. However, polymeric material containing Si–O–Si linkages (i.r.) is formed which suggests that condensation reactions involving Si–OH groups have taken place. If such condensation reactions went to completion the ultimate product would be the silsesquioxane $(CHF_2\cdot CF_2\cdot Si\cdot O_{1.5})_n$, which has previously been prepared by aqueous hydrolysis of the silane $CHF_2\cdot CF_2\cdot SiCl_3$.[4]

The reactions are all postulated to occur *via* four-centre transition states which possibly involve initial co-ordination between the silicon atom in silane (I) or silicon tetrafluoride and the oxygen or nitrogen atom in the methoxosilane, silanol, or disilazane. In this respect it has been reported that a five-co-ordinate complex is formed between the silane $CHF_2\cdot CF_2\cdot SiH_3$ and triethylamine [5] and earlier reports also indicate that silicon tetrafluoride forms co-ordination complexes with electron donors such as amines, *e.g.* $F_4Si\cdot 2NH_3$ [6] and $F_4Si\cdot 2NMe_3$.[7]

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[4] R. N. Haszeldine and R. J. Marklow, *J. Chem. Soc.*, 1956, 962.

[5] D. I. Cook, R. Fields, M. Green, R. N. Haszeldine, B. R. Iles, A. Jones, and M. J. Newlands, *J. Chem. Soc.* (*A*), 1966, 887.

[6] T. S. Piper and E. G. Rochow, *J. Amer. Chem. Soc.*, 1954, **76**, 4318; D. B. Miller and H. H. Sisler, *ibid.*, 1955, **77**, 4998.

[7] J. E. Ferguson, D. K. Grant, R. H. Hickford, and C. J. Wilkins, *J. Chem. Soc.*, 1959, 99; C. J. Wilkins and D. K. Grant, *ibid.*, 1953, 927.

EXPERIMENTAL

Reactants and products were manipulated, where possible, in a conventional vacuum system to avoid contamination with air or moisture. The thermal reactions were carried out in Pyrex bulbs (*ca.* 5 l unless stated to the contrary) fitted with a side arm and at maximum pressures of *ca.* 0·8 atm.[*] Pure compounds were isolated by repeated fractional condensation *in vacuo* or by preparative-scale gas–liquid chromatography [g.l.c., Pye 105 or Perkin-Elmer 452 instruments with columns (4 or 8 m) packed with Silicone MS 550 oil on Celite], i.r. spectroscopy (Perkin-Elmer spectrophotometer model 452 with sodium chloride optics), mass spectrometry (A.E.I. MS/2 instrument), and n.m.r. spectroscopy (Perkin-Elmer R10 instrument operating at 60·0 MHz for ^{1}H and 56·46 MHz for ^{19}F with internal tetramethylsilane and external trifluoroacetic acid as the respective references).

Hexamethyldisilazane[8] was prepared (70%) by the reaction of ammonia with chlorotrimethylsilane, trimethylsilanol (73%) by reaction of ammonium fluoride with a mixture of hexamethyldisiloxane and concentrated sulphuric acid, methoxotrimethylsilane[9] (84%) by reaction of chlorotrimethylsilane with methanol in pyridine, silicon tetrafluoride (60%) by fluorination *in vacuo* of silicon tetrachloride with antimony trifluoride containing a small amount of antimony pentachloride (5% by weight), and trifluoro(1,1,2,2-tetrafluoroethyl)silane by photochemical addition of trichlorosilane to tetrafluoroethylene followed by fluorination (SbF_3–$SbCl_5$) of the resulting 1 : 1 adduct.[2,3]

All reactants were carefully purified before use.

Reactions of Trifluoro(1,1,2,2-*tetrafluoroethyl*)*silane*.—(a) *With hexamethyldisilazane.* A mixture of the trifluorosilane (5·58 g, 30·0 mmol) and hexamethyldisilazane (14·5 g, 90·0 mmol), pyrolysed at 150 °C (6 h), gave (*i*) silicon tetrafluoride (0·47 g, 4·5 mmol, 15%), (*ii*) fluorotrimethylsilane (3·02 g, 32·8 mmol, 36%), (*iii*) unchanged disilazane (8·70 g, 54·0 mmol, 60%), and (*iv*) a viscous tar (*ca.* 8·0 g) which was not examined further. In a second experiment a mixture of the trifluorosilane (2·23 g, 12·0 mmol) and the disilazane (5·82 g, 36·0 mmol), sealed in a Pyrex bulb (*ca.* 2 l) and heated at 100 °C (6 h), gave (*i*) fluorotrimethylsilane (1·41 g, 15·3 mmol, 42%), (*ii*) unchanged hexamethyldisilazane (2·72 g, 16·9 mmol, 47%), and (*iii*) a viscous tar (*ca.* 3·9 g) which was not examined further.

(b) *With methoxotrimethylsilane.* A mixture of the trifluorosilane (5·58 g, 30·0 mmol) and methoxotrimethylsilane (9·35 g, 90·0 mmol), pyrolysed at 150 °C (6 h), gave (*i*) fluorotrimethylsilane (7·80 g, 85·0 mmol, 95%), (*ii*) unchanged methoxotrimethylsilane (0·52 g, 5·0 mmol, 5%), and (*iii*) a mixture (6·42 g, 29·0 mmol, 96%) which was separated by g.l.c. (8 m column at 130 °C) into its two components, present in the ratio 2 : 27, which were identified as fluorodimethoxo(1,1,2,2-tetrafluoroethyl)silane (0·42 g, 2·0 mmol, 6%), with ^{19}F n.m.r. bands (50% solution in $CFCl_3$) at 54·5 [dmult., 2 F, CF_2, $J(F_3{-}H_1)$ 6·0], 58·0 [dmult., 2 F, CHF_2, $J(F_2{-}H_1)$ 56·0], and 70·5 p.p.m. [tmult., 1 F, SiF, $J(F_4{-}F_3)$ 3·0 Hz] and ^{1}H n.m.r. bands at τ 4·24 [tt, 1 H, CHF_2, $J(H_1{-}F_2)$, $J(H_1{-}F_3)$] and 6·21 (d, 6 H, 2 OMe), and trimethoxo(1,1,2,2-tetrafluoroethyl)silane (6·0 g, 27·0 mmol, 90%) (Found: C, 27·3; H, 4·8; F, 34·2. Calc. for $C_5H_{10}F_3O_3Si$: C, 27·0; H, 4·5; F, 34·3%), b.p. 136 °C (lit.,[4] 98 °C at 190 mmHg), with ^{19}F n.m.r. bands at 54·0 [dt, 2 F, CF_2, $J(F_3{-}H_1)$ 6·0, $J(F_3{-}F_2)$ 3·5] and 59·0 p.p.m. [dt, 2 F, CHF_2, $J(F_2{-}H_1)$ 56·5 Hz, $J(F_2{-}F_3)$], ^{1}H n.m.r. bands at τ 4·27 [tt, 1 H, CHF_2, $J(H_1{-}F_2)$, $J(H_1{-}F_3)$] and 6·38 (s, 9 H, 3 OMe), and *m*/*e* 140 {12, $[FSi(OMe)_3]^+$}, 139 (25, $[C_3H_8FO_3Si]^+$), 121 {100, $[Si(OMe)_3]^+$}, 109 {50, $[FSi(OMe)_2]^+$}, and 97 (5%, $[F_2SiOMe]^+$). A small amount (*ca.* 0·2 g) of non-volatile material was also isolated. A second experiment using the same amounts of reactants and carried out at 100 °C (6 h) gave identical results.

(c) *With trimethylsilanol.* A mixture of the trifluorosilane (5·58 g, 30·0 mmol) and the silanol (8·10 g, 90·0 mmol), pyrolysed at 150 °C (6 h), gave (*i*) fluorotrimethylsilane (7·95 g, 86·4 mmol, 96%), (*ii*) unchanged trimethylsilanol (0·33 g, 3·0 mmol, 3%), (*iii*) water (trace), (*iv*) a viscous liquid (*ca.* 0·6 g), the i.r. spectrum of which showed a strong band at 9·5 μm (Si–O–Si str.), and (*v*) solid polymeric material (*ca.* 4·5 g), m.p. >310 °C, which also showed i.r. absorption due to Si–O–Si linkages.

Reactions of Silicon Tetrafluoride.—(a) *With hexamethyldisilazane.* A mixture of silicon tetrafluoride (1·24 g, 11·9 mmol) and the disilazane (5·82 g, 36·0 mmol), heated in a Pyrex bulb (*ca.* 2 l) at 100 °C (6 h), gave (*i*) fluorotrimethylsilane (2·0 g, 21·7 mmol, 45%), (*ii*) 1,1,1-trifluoro-3,3,3-trimethyldisilazane (*ca.* 1·3 g, *ca.* 7·5 mmol), with a ^{19}F n.m.r. band at 69·0 p.p.m. (s), ^{1}H n.m.r. bands at τ 2·6 (broad, 1 H, NH) and 9·80 (s, 9 H, $SiMe_3$), and *m*/*e* 159 (4, $[CH_5F_3NSi_2]^+$), 85 (15, $[SiF_3]^+$), 78 (14, $[C_2H_7FSi]^+$), 77 (100, $[Me_2SiF]^+$), 63 (10, $[MeSiHF]^+$), and 47 (33%, $[FSi]^+$), (*iii*) unchanged hexamethyldisilazane (2·0 g, 12·4 mmol, 34%), and (*iv*) a viscous tar (*ca.* 1·7 g) which was not examined further. The trifluorotrimethyldisilazane slowly decomposed at room temperature to give fluorotrimethylsilane and viscous tar.

(b) *With methoxotrimethylsilane.* A mixture of the methoxosilane (5·62 g, 54·0 mmol) and silicon tetrafluoride (1·87 g, 18·0 mmol), sealed in a Pyrex bulb (*ca.* 3 l) and heated at 100 °C (6 h), gave fluorotrimethylsilane (4·70 g, 51·0 mmol, 71%) and a higher-boiling fraction (2·50 g) which was shown by g.l.c. (4 m column at 50 °C) and n.m.r. spectroscopy to consist of (*i*) unchanged methoxotrimethylsilane (0·41 g, 4·0 mmol, 7%), (*ii*) fluorotrimethoxosilane (2·00 g, 14·4 mmol, 80%) (^{1}H n.m.r. band at τ 6·35), (*iii*) difluorodimethoxosilane (0·39 g, 3·0 mmol, 11%) (^{1}H n.m.r. band at τ 6·45), and (*iv*) small amounts of trifluoro(methoxo)silane (^{1}H n.m.r. band at τ 6·80), and tetramethoxosilane.

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[*] 1 atm = 101 325 Pa.

[8] R. O. Sauer, *J. Amer. Chem. Soc.*, 1944, **66**, 1707.

[9] S. H. Langer, S. Connell, and I. Wender, *J. Org. Chem.*, 1958, **23**, 50.