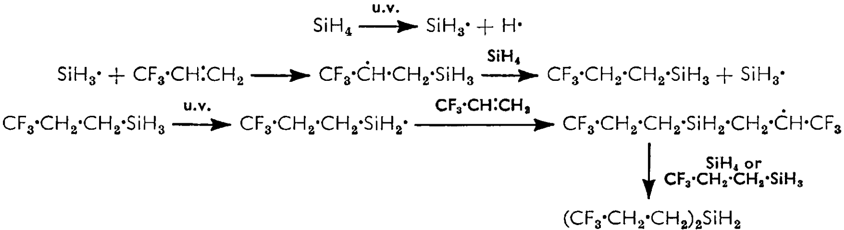
375. *Polyfluoroalkyl Compounds of Silicon. Part VI.*[1] *Reaction of 3,3,3-Trifluoropropene with Silane, and the Conversion of the Products into Silicones and Polysiloxanes*

By R. N. Haszeldine, M. J. Newlands, and J. B. Plumb

Photochemical reaction of silane with 3,3,3-trifluoropropene yields the compounds $(CF_3{\cdot}CH_2{\cdot}CH_2)_nSiH_{4-n}$, where $n = 1$—4. Thermal reaction of the compounds where $n = 1$—3 with chlorine, or photochemical reaction with phosgene, gives the compounds $(CF_3{\cdot}CH_2{\cdot}CH_2)_nSiCl_{4-n}$, and these can be converted into the corresponding Si–O–Si compounds by aqueous alkaline hydrolysis followed by acidification. Silane similarly reacts with tetrafluoroethylene to give the compound $CHF_2{\cdot}CF_2{\cdot}SiH_3$, also prepared from 1,1,2,2-tetrafluoroethyltrichlorosilane. Methylsilane can be converted into the compounds $CH_3{\cdot}SiH_2Cl$, $CH_3{\cdot}SiHCl_2$, and $CH_3{\cdot}SiCl_3$ by photochemical reactions with phosgene or carbon tetrachloride. Reaction of the compounds $(CF_3{\cdot}CH_2{\cdot}CH_2)_nSiH_{4-n}$, where $n = 1$—3, with aqueous alkali yields, on acidification, the corresponding polysiloxane $[RSi{\cdot}O_{1\cdot5}]_n$, the silicone $[R_2Si{\cdot}O]_n$, or the disiloxane $(R_3Si)_2O$ directly, and without need to form the chlorosilanes.

The methods most frequently used for the preparation of polyfluoroalkyl silicon compounds[2,3] are (*a*) photochemical reaction between a compound containing an Si–H bond and an olefin, or (*b*) the reaction of a polyfluoroalkyl Grignard compound with a compound containing Si–Cl bonds. To prepare a precursor of a silicone, R_2SiCl_2, method (*a*) requires dichlorosilane,[3] which is difficult to prepare in quantity, and method (*b*) gives a mixture of all the possible products, usually containing only a small quantity of the required dichloro-compound.

The free-radical reaction of silane with an olefin was investigated some years ago as a route to compounds difficult to obtain by other methods. The photochemical chain reaction of silane with 3,3,3-trifluoropropene:



$$SiH_4 \xrightarrow{\text{u.v.}} SiH_3\cdot + H\cdot$$

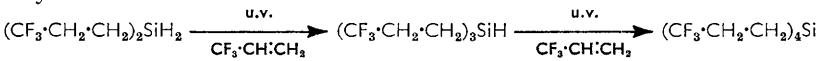
$$SiH_3\cdot + CF_3{\cdot}CH{:}CH_2 \longrightarrow CF_3{\cdot}\dot{C}H{\cdot}CH_2{\cdot}SiH_3 \xrightarrow{SiH_4} CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}SiH_3 + SiH_3\cdot$$

$$CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}SiH_3 \xrightarrow{\text{u.v.}} CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}SiH_2\cdot \xrightarrow{CF_3{\cdot}CH{:}CH_2} CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}SiH_2{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CF_3$$

$$\Big\downarrow{\scriptstyle SiH_4 \text{ or } CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}SiH_3}$$

$$(CF_3{\cdot}CH_2{\cdot}CH_2)_2SiH_2$$

and similarly



$$(CF_3{\cdot}CH_2{\cdot}CH_2)_2SiH_2 \xrightarrow[CF_3{\cdot}CH{:}CH_2]{\text{u.v.}} (CF_3{\cdot}CH_2{\cdot}CH_2)_3SiH \xrightarrow[CF_3{\cdot}CH{:}CH_2]{\text{u.v.}} (CF_3{\cdot}CH_2{\cdot}CH_2)_4Si$$

proceeds smoothly, since silane is such an excellent chain-transfer agent that telomerisation reactions are unimportant even when only a slight excess of silane over olefin is used. Irradiation of a 2 : 1 mixture of 3,3,3-trifluoropropene and silane thus gives mainly tris- and tetrakis-3,3,3-trifluoropropylsilane, and use of a 1 : 2 mixture gives mainly the mono- (26%), bis- (12%), and tris-compounds (10%).

The compound $CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}SiH_3$ was also obtained by reaction of 3,3,3-trifluoropropyltrichlorosilane[3] with lithium aluminium hydride, thus establishing the structure. Further reaction of 3,3,3-trifluoropropylsilane with trifluoropropene can be used to prepare more of the silicone precursor, $(CF_3{\cdot}CH_2{\cdot}CH_2)_2SiH_2$.

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[1] Part V, R. N. Haszeldine and J. C. Young, *J.*, 1960, 4503.

[2] R. N. Haszeldine and R. J. Marklow, *J.*, 1956, 962; A. M. Geyer and R. N. Haszeldine, *J.*, 1957, 1038, 3925.

[3] A. M. Geyer, R. N. Haszeldine, K. Leedham, and R. J. Marklow, *J.*, 1957, 4472.

Silane reacts similarly with tetrafluoroethylene to give the compound $CHF_2{\cdot}CF_2{\cdot}SiH_3$ in 61% yield, so that the reaction appears to be of general application for fluoro-olefins. The 2 : 1 adducts $(CHF_2{\cdot}CF_2)_2SiH_2$ and $CHF_2{\cdot}(CF_2)_3{\cdot}SiH_3$, arising respectively by further photochemical reaction of the tetrafluoroethylsilane with tetrafluoroethylene and by telomerisation:

$$CHF_2{\cdot}CF_2{\cdot}SiH_3 \longrightarrow CHF_2{\cdot}CF_2{\cdot}SiH_2{\cdot} \xrightarrow{C_2F_4} CHF_2{\cdot}CF_2{\cdot}SiH_2{\cdot}CF_2{\cdot}CF_2{\cdot} \xrightarrow{SiH_4} (CHF_2{\cdot}CF_2)_2SiH_2$$

$$\cdot CF_2{\cdot}CF_2{\cdot}SiH_3 \xrightarrow{C_2F_4} \cdot CF_2{\cdot}(CF_2)_3{\cdot}SiH_3 \xrightarrow{SiH_4} CHF_2{\cdot}(CF_2)_3{\cdot}SiH_3$$

were obtained in 30% yield. Lithium aluminium hydride reduction of 1,1,2,2-tetrafluoroethyltrichlorosilane gives a 78% yield of 1,1,2,2-tetrafluoroethylsilane, but some C–Si fission occurs, even under the mild conditions used, to give silane (22%).

Conversion of $\geqslant$Si–H *into* $\geqslant$Si–Cl *compounds.* Polysiloxanes, silicones, or disiloxanes are usually prepared by hydrolysis of the compounds $RSiCl_3$, R_2SiCl_2, or R_3SiCl, respectively, and methods were thus sought for the conversion of the compounds $RSiH_3$, R_2SiH_2, or R_3SiH into the corresponding chloro-compounds. Thermal reaction with chlorine, photochemical reaction with phosgene, and photochemical reaction with carbon tetrachloride were found to be satisfactory.

The direct reaction of chlorine with the trifluoropropylsilanes occurs smoothly on a small scale, provided that the reaction vessel is allowed to warm from –196° to room temperature only slowly to prevent carbonisation or explosion. The compounds $(CF_3{\cdot}CH_2{\cdot}CH_2)_nSiCl_{4-n}$, where $n = 1$—3, were thus prepared in high yield. Use of a solvent for the chlorine (*e.g.*, carbon tetrachloride) moderates the vigour of the reaction and enables the chlorination to be carried out on a larger scale; the small amount of Si–H compound which remains unchanged when room temperature has been reached can be removed by then raising the temperature to 100°:

$$CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}SiH_3 \xrightarrow{Cl_2} CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}SiCl_3 \quad 82\%$$

$$(CF_3{\cdot}CH_2{\cdot}CH_2)_2SiH_2 \xrightarrow{Cl_2} (CF_3{\cdot}CH_2{\cdot}CH_2)_2SiCl_2 \quad 67\%$$

$$(CF_3{\cdot}CH_2{\cdot}CH_2)_3SiH \xrightarrow{Cl_2} (CF_3{\cdot}CH_2{\cdot}CH_2)_3SiCl \quad 76\%$$

The thermal reaction of a phosphine RPH_2 with phosgene has been used successfully to prepare the chloro-compound $RPCl_2$.[4] Photochemical reaction with phosgene is more successful than a thermal reaction in the silicon field. Thus, although methylsilane does not react with phosgene at 220° during 6 hr., the photochemical reaction with phosgene proceeds cleanly and rapidly, presumably by the radical chain mechanism:

$$COCl_2 \longrightarrow \cdot COCl + Cl\cdot$$

$$\cdot COCl \longrightarrow CO + Cl\cdot$$

$$Cl\cdot + RSiH_3 \longrightarrow RSiH_2\cdot + HCl$$

$$\begin{tikzcd} RSiH_2\cdot + COCl_2 \arrow[r] & RSiH_2Cl \arrow[d, "Cl\cdot"] + \cdot COCl \arrow[r] & CO + Cl\cdot \\ & \text{etc.} & \end{tikzcd}$$

e.g.,

$$(CF_3{\cdot}CH_2{\cdot}CH_2)_2SiH_2 \xrightarrow{COCl_2,\ u.v.} (CF_3{\cdot}CH_2{\cdot}CH_2)_2SiCl_2\ [+\ (CF_3{\cdot}CH_2{\cdot}CH_2)_2SiHCl]$$

$$CH_3{\cdot}SiH_3 \xrightarrow{COCl_2,\ u.v.} CH_3{\cdot}SiCl_3 \quad (76\%)$$

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[4] G. M. Burch, H. Goldwhite, and R. N. Haszeldine, *J.*, 1963, 1083.

Carbon tetrachloride can also be used to convert Si–H into Si–Cl compounds, and is particularly useful if compounds containing both hydrogen and chlorine on silicon are required, *e.g.*,

$$CH_3{\cdot}SiH_3 \xrightarrow{\text{u.v.}} CH_3{\cdot}SiH_2{\cdot} \xrightarrow{CCl_4} CH_3{\cdot}SiH_2Cl + CCl_3{\cdot}$$

$$CCl_3{\cdot} + CH_3{\cdot}SiH_3 \longrightarrow CHCl_3 + CH_3{\cdot}SiH_2{\cdot} \xrightarrow{CCl_4} \text{etc.}$$

or

$$\begin{tikzcd} CCl_4 \arrow[r, "\text{u.v.}"] & CCl_3{\cdot} \arrow[r, "CH_3{\cdot}SiH_3"] \arrow[d] & \text{etc.} \\ & C_2Cl_6 & \end{tikzcd}$$

$$CH_3{\cdot}SiH_2Cl \xrightarrow{CCl_4,\ \text{u.v.}} CH_3{\cdot}SiHCl_2 \xrightarrow{CCl_4,\ \text{u.v.}} CH_3{\cdot}SiCl_3$$

Methylchlorosilane was thus prepared from methylsilane in 26% yield, and further reaction gave methyldichlorosilane and methyltrichlorosilane. The abstraction of halogen by alkylsilyl radicals has been described earlier.[1]

Conversion of $\geqslant$Si–H *into* $\geqslant$Si–O–Si$\leqslant$ *compounds.* Reaction of the mono-, bis-, and tris-3,3,3-trifluoropropylsilanes with aqueous sodium hydroxide liberates hydrogen, and the compounds $(CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}Si{\cdot}O_{1{\cdot}5})_n$, $[(CF_3{\cdot}CH_2{\cdot}CH_2)_2Si{\cdot}O]_n$, and $[(CF_3{\cdot}CH_2{\cdot}CH_2)_3Si]_2O$ can thus be prepared directly, after acidification, etc., without need to form the chloro-compounds. Tristrifluoropropylsilane needs to be heated to 100° with aqueous alkali to complete the hydrolysis. This method works satisfactorily for fluoroalkyl silicon compounds where the fluorine is γ to silicon; α- or β-fluoroalkylsilicon compounds usually undergo C–Si fission with aqueous alkali.[5]

Hydrolysis of either the silane $(CF_3{\cdot}CH_2{\cdot}CH_2)_2SiH_2$ or the corresponding dichloro-compound under alkaline conditions apparently gave mainly the cyclotetrasiloxane, whereas hydrolysis of the dichloro-compound under acidic conditions apparently gave the cyclotrisiloxane and the linear polymer. Hydrolysis of a 1 : 1 mixture of the compounds $(CF_3{\cdot}CH_2{\cdot}CH_2)_3SiCl$ and $(CF_3{\cdot}CH_2{\cdot}CH_2)_2SiCl_2$ gave an end-stopped linear silicone which had an analysis corresponding to the following average composition $(CF_3{\cdot}CH_2{\cdot}CH_2)_3Si{\cdot}O[(CF_3{\cdot}CH_2{\cdot}CH_2)_2{\cdot}Si{\cdot}O]_4{\cdot}Si(CH_2{\cdot}CH_2{\cdot}CF_3)_3$.

EXPERIMENTAL

Reactions were usually carried out *in vacuo* in sealed glass or silica tubes filled by means of an apparatus for manipulation of volatile compounds. The ultraviolet lamp was a Hanovia 500w.

Reaction of 3,3,3-*Trifluoropropene with Silane.*—The olefin (2·57 g., 26·8 mmoles) and silane (1·72 g., 53·5 mmoles), sealed in a 360 ml. silica tube and exposed to ultraviolet light for 96 hr., gave unreacted silane (1·20 g., 70%) but no unreacted olefin. The less-volatile products from four tubes were fractionally distilled under nitrogen to give 3,3,3-*trifluoropropylsilane* (3·57 g., 27·9 mmoles, 26%) (Found: C, 28·3; H, 5·3. $C_3H_7F_3Si$ requires C, 28·1; H, 5·5%) b. p. 30—31°, and *bis*-3,3,3-*trifluoropropylsilane* (1·45 g., 6·45 mmoles, 12%) (Found: C, 32·4; H, 4·6. $C_6H_{10}F_6Si$ requires C, 32·1; H, 4·5%) b. p. 129—130°.

The high-boiling residues from a number of such irradiations were combined and distilled under reduced pressure to give *tris*-3,3,3-*trifluoropropylsilane* (10%) (Found: C, 33·9; H, 4·2. $C_9H_{13}F_9Si$ requires C, 33·8; H, 4·1%) b. p. 148—152°/100 mm., 72—74°/7·5 mm., and a fraction (4·0 g.) distilling at 290—330°/760 mm. The infrared spectrum of the last fraction revealed Si–H bonds (band at 4·6 μ) although the elemental analysis agreed with that for $(CF_3{\cdot}CH_2{\cdot}CH_2)_4Si$. This material was therefore treated with boiling 20% aqueous sodium hydroxide, acidified with hydrochloric acid, and extracted with ether. The ethereal solution was dried (K_2CO_3), the ether removed and the residual liquid distilled to give *tetrakis*-3,3,3-*trifluoropropylsilane* (*ca.* 3%) (Found: C, 34·8; H, 4·1. $C_{12}H_{16}F_{12}Si$ requires C, 34·6, H, 3·8%) b. p. 134—160°/1 mm., as a colourless oil showing no Si–H bands in the infrared.

In experiments using an excess of the olefin, several silica tubes containing silane (1·15 g.

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[5] T. N. Bell, R. N. Haszeldine, M. J. Newlands, and J. B. Plumb, Part VII, following Paper.

total, 35·0 mmole), 3,3,3-trifluoropropene (6·89 g. total, 70·0 mmoles), and a few drops of dimethyl azobisisobutyrate were irradiated (Hanovia 250w lamp) for 3 days to give silane (0·905 g., 28·3 mmoles, 80%), trifluoropropene (5·71 g., 59·5 mmoles, 85%), and relatively involatile materials with an overall silane : trifluoropropene ratio of 1 : 4 (1·40 g.). About 60% of this material consisted of the tris- and tetrakis-products.

Reaction of 3,3,3-*Trifluoropropylsilane with* 3,3,3-*Trifluoropropene*.—The olefin (4·46 g., 46·5 mmoles) and 3,3,3-trifluoropropylsilane (6·70 g., 52 mmoles) exposed to ultraviolet light in a 60 ml. silica tube for 168 hr., gave hydrogen (2·5 mmoles, 2% conversion, 7% yield, based on 3,3,3-trifluoropropylsilane), unchanged 3,3,3-trifluoropropylsilane (1·8 g., 14·1 mmoles, 27%), bis-3,3,3-trifluoropropylsilane (2·8 g., 12·5 mmoles, 24% conversion, 32% yield) and higher-boiling materials (5·1 g.). No unchanged olefin was detected.

Reaction of 3,3,3-*Trifluoropropyltrichlorosilane with Lithium Aluminium Hydride*.—The chlorosilane (27·3 g., 118 mmoles) in tetrahydrofuran (40 ml.) was added dropwise (1 hr.) to a stirred suspension of lithium aluminium hydride (5·3 g., 140 mmoles) in tetrahydrofuran (45 ml.) at 0°. The temperature was raised to reflux and maintained there for 1 hr. The volatile materials were fractionated at atmospheric pressure to give 3,3,3-trifluoropropylsilane (4·60 g., 36·2 mmoles, 31%) identical with that obtained by reaction of trifluoropropene with silane.

Reaction of 3,3,3-*Trifluoropropylmagnesium Iodide with Trichlorosilane* (with B. R. ILES).—The Grignard reagent was prepared from 3,3,3-trifluoropropyl iodide (78·4 g., 0·35 mole) in 300 ml. of dry diethyl ether in a 1-litre flask flushed with nitrogen. Trichlorosilane (11·0 g., 0·095 mole) in dry ether (50 ml.) was added to the ice-cooled flask over 30 min. with rapid stirring. The temperature of the mixture was then allowed to rise to room temperature, the mixture was heated under reflux for 24 hr., then hydrolysed with hydrochloric acid–ice. The ethereal layer was washed with water, dried (Na_2SO_4), and distilled to give tris-3,3,3-trifluoropropylsilane (22·0 g., 0·069 mole, 85%) (Found: C, 34·3; H, 4·1: Calc. for $C_9H_{13}F_9Si$: C, 33·8; H, 4·1%) b. p. 80°/10 mm., d_4^{20} 1·292, n_D^{20} 1·355.

Reaction of Tris-3,3,3-*trifluoropropylsilane with* 3,3,3-*Trifluoropropene* (with B. R. ILES).—Tris-3,3,3-trifluoropropylsilane (7·30 g., 0·023 mole) and 3,3,3-trifluoropropene (21·5 g., 0·025 mole), sealed *in vacuo* in a 300 ml. silica tube with mercury (1 ml.) and irradiated for 675 hr. gave trifluoropropene (1·72 g., 0·020 mole), tris-3,3,3-trifluoropropylsilane (5·40 g., 0·017 mole), and tetrakis-3,3,3-trifluoropropylsilane (1·80 g., 0·004 mole, 26% conversion, 67% yield) (Found: C, 34·5; H, 3·9%; *M*, 421. Calc. for $C_{12}H_{16}F_{12}Si$: C, 34·6; H, 3·8%; *M*, 416), b. p. 120°/10^{-2} mm., d_4^{20} 1·404, n_D^{20} 1·370.

Reaction of the 3,3,3-*Trifluoropropylsilanes with Chlorine*.—(*a*) 3,3,3-*Trifluoropropylsilane*. The silane (1·40 g., 11·0 mmoles) and chlorine (2·34 g., 33·0 mmoles), sealed *in vacuo* in a 440 ml. tube at −196°, then transferred to a bath at −130° which was allowed to warm to room temperature during 24 hr., gave hydrogen chloride (1·17 g., 31·5 mmoles, 96%) and 3,3,3-trifluoropropyltrichlorosilane (2·07 g., 9·0 mmoles, 82%) (Found: C, 15·8; H, 1·8%. Calc. for $C_3H_4Cl_3F_3Si$: C, 15·5; H, 1·7%) b. p. 111—112° (lit.,[2,3] 113°).

(*b*) *Bis*-3,3,3-*trifluoropropylsilane*. The silane (3·53 g., 15·7 mmoles) and chlorine (2·23 g., 31·4 mmoles), sealed *in vacuo* in a 440 ml. tube and treated as in (*a*) above, gave hydrogen chloride (1·00 g., 26·1 mmoles, 83%), unchanged bis-3,3,3-trifluoropropylsilane (0·92 g., 4·08 mmoles, 26%), and dichlorobis-3,3,3-trifluoropropylsilane (2·31 g., 7·90 mmoles, 50% conversion, 68% yield) (Found: C, 26·1; H, 3·4. Calc. for $C_6H_8Cl_2F_6Si$: C, 24·6; H, 2·7%), b. p. 160—165° (lit.,[3] 162—163°). The infrared spectrum of this last material showed that traces of material containing Si–H bonds were still present.

The need to control the reaction temperature is demonstrated by an experiment in which bis-3,3,3-trifluoropropylsilane (4·13 g., 18·5 mmoles) and chlorine (3·60 g., 50·5 mmoles), sealed as above, were allowed to warm rapidly from −196° to room temperature. Examination after 3 hr. showed that the tube was coated with carbon, and that the only products were hydrogen (0·29 g., 8·0 mmoles), chlorine (0·28 g., 4·0 mmoles), and a mixture of silicon tetrafluoride and hydrogen chloride (109 mmoles). The vigorous exothermic reaction had caused complete decomposition of the starting material.

In a third experiment bis-3,3,3-trifluoropropylsilane (2·00 g., 8·9 mmoles), dry carbon tetrachloride (10 ml.) and chlorine (1·27 g., 17·8 mmoles) were sealed *in vacuo* in a 440 ml. tube at −196°. The tube was transferred to a bath at −130° which was allowed to warm slowly to room temperature. A faint chlorine colour remained, so the tube was heated to 100° (30 min.). Distillation gave hydrogen chloride (0·64 g., 17·4 mmoles, 98%), unchanged solvent, and dichlorobis-3,3,3-trifluoropropylsilane (1·47 g., 5·0 mmoles, 56%) (Found: C, 24·4; H, 2·7. Calc. for $C_6H_8Cl_2F_6Si$: C, 24·6; H, 2·7%) b. p. 158—164°.

(*c*) *Tris*-3,3,3-*trifluoropropylsilane.* The silane (4·61 g., 14·4 mmoles) and chlorine (1·07 g., 15·1 mmoles), treated as in (*a*) above, gave hydrogen chloride (0·50 g., 13·7 mmoles, 95%) and chlorotris-3,3,3-trifluoropropylsilane (3·88 g., 10·9 mmoles, 76%) which showed Si–H bands in the infrared. Retreatment with chlorine gave pure *chlorotris*-3,3,3-*trifluoropropylsilane* (Found: C, 30·4; H, 3·6; Cl, 9·9. $C_9H_{12}ClF_9Si$ requires: C, 30·4; H, 3·6; Cl, 10·0%) b. p. 82—85°/7·5 mm., 77—80°/5 mm.

In a second experiment, tris-3,3,3-trifluoropropylsilane (2·34 g., 7·3 mmoles) in dry carbon tetrachloride (10 ml.), sealed with chlorine (0·52 g., 7·3 mmoles) as in (*b*) above, gave hydrogen chloride (0·25 g., 6·8 mmoles, 93%), unchanged solvent, and chlorotris-3,3,3-trifluoropropylsilane (2·00 g., 5·6 mmoles, 77%) (Found: C, 30·6; H, 3·5%).

Reaction of Bis-3,3,3-*trifluoropropylsilane with Phosgene.*—The silane (2·61 g., 11·6 mmoles) and phosgene (2·68 g., 23·2 mmoles), sealed *in vacuo* in a 360 ml. silica tube, were shaken and exposed to ultraviolet light (3 hr.) to give carbon monoxide (0·38 g., 13·7 mmoles, 59% conversion, 80% yield, based on phosgene), hydrogen chloride (0·51 g., 14·0 mmoles, 60% conversion, 80% yield), unreacted phosgene (0·75 g., 6·5 mmoles, 28%), a fraction (0·69 g.) b. p. 125—169° [a mixture of the compounds $(CF_3{\cdot}CH_2{\cdot}CH_2)_2SiH_2$ and $(CF_3{\cdot}CH_2{\cdot}CH_2)_2SiHCl$], and dichlorobis-3,3,3-trifluoropropylsilane (0·64 g., 2·18 mmoles, 19%) (Found: C, 24·8; H, 2·8%) b. p. 159—160°, shown by infrared spectroscopy to be free from Si–H bonds.

Reaction of Methylsilane with Phosgene.—The silane (0·20 g., 4·5 mmoles) and phosgene (1·32 g., 13·5 mmoles) in a 440 ml. tube, were unchanged after being heated to 220° (6 hr.). The reactants were transferred to a sealed 360 ml. silica tube and exposed to ultraviolet light (2 hr.) to give carbon monoxide (0·35 g., 12·5 mmoles, 92%), hydrogen chloride (0·47 g., 13·0 mmoles, 97%), and methyltrichlorosilane (0·51 g., 3·4 mmoles, 76%) (Found: *M*, 147. Calc. for CH_3SiCl_3: *M*, 150), identified by means of its infrared spectrum. No unreacted phosgene was detected.

Reaction of Methylsilane with Carbon Tetrachloride.—Methylsilane (1·62 g., 35·2 mmoles), shaken and irradiated with carbon tetrachloride (16·3 g., 106 mmoles) in a sealed 360 ml. silica tube (168 hr.), gave methylsilane (0·89 g., 19·4 mmoles, 55%), methylchlorosilane (0·72 g., 9·0 mmoles, 26%) (Found: *M*, 81. Calc. for CH_5ClSi: *M*, 81), and methyldichlorosilane which was identified by its infrared spectrum, but on the scale used could not be obtained free from methyltrichlorosilane, carbon tetrachloride, and possibly chloroform, by distillation. The brown residue in the reaction tube was dissolved in chloroform and the red-brown solid obtained on evaporation of the filtered chloroform solution was sublimed at 182—184° to give hexachloroethane (0·40 g., 1·7 mmoles, 2%) (Found: C, 10·7; Cl, 88·7%. Calc. for C_2Cl_6: C, 10·1; Cl, 89·9%).

Reaction of the 3,3,3-*Trifluoropropylsilanes with Aqueous Base.* (*a*) 3,3,3-*Trifluoropropylsilane.* The silane (0·188 g., 1·47 mmoles), and 20% aqueous sodium hydroxide (20 ml.) sealed and shaken *in vacuo* in a 150 ml. silica tube for 1 hr. gave hydrogen (8·4 mg., 4·20 mmoles) equivalent to 2·9 mol. hydrogen (theory predicts 3 mol.). The aqueous solution was acidified, extracted with ether (3 × 20 ml.) and the ethereal extracts dried (Na_2SO_4). After removal of the ether the residue was heated at 200° *in vacuo* (3 hr.) to give 3,3,3-trifluoropropylpolysiloxane [3] (0·197 g., 1·3 mmoles, 90%) (Found: C, 22·9; H, 2·7%. Calc. for $C_3H_4F_3O_{1\cdot5}Si$: C, 24·2; H, 2·7%).

(*b*) *Bis*-3,3,3-*trifluoropropylsilane.* Bis-3,3,3-trifluoropropylsilane (0·372 g., 1·65 mmoles), treated with 10% aqueous sodium hydroxide (20 ml.) for 3 hr. at 20°, gave hydrogen (7·0 mg., 3·5 mmoles, 2·1 mol.) (Calc. 2·0 mol.). The silicone [3] $[(CF_3{\cdot}CH_2{\cdot}CH_2)_2SiO]_n$ was obtained on acidification.

(*c*) *Tris*-3,3,3-*trifluoropropylsilane.* The silane (1·34 g., 4·16 mmoles), treated with 10% aqueous sodium hydroxide (15 ml.) at 70—80° for 1 hr., gave hydrogen (8·2 mg., 4·1 mmoles, 49%). Ether extraction of the acidified aqueous solution, drying (Na_2SO_4), and removal of the ether gave a viscous residue the infrared spectrum of which showed both Si–H and Si–OH groups.

In a second experiment tris-3,3,3-trifluoropropylsilane (1·54 g., 4·81 mmoles), treated with 10% aqueous sodium hydroxide (15 ml.) at 100° for 5 hr., gave hydrogen (9·4 mg., 4·7 mmoles, 0·97 mol.) (Calc. 1·00 mol.) and, after acidification, the disiloxane $[(CF_3{\cdot}CH_2{\cdot}CH_2)_3Si]_2O$ free from Si–H bonds.

Hexakis-3,3,3-*trifluoropropyldisiloxane*.—Tris-3,3,3-trifluoropropylsilane (3·00 g., 9·5 mmoles), was refluxed with 20% aqueous sodium hydroxide (20 ml.) for 5 hr., then cooled, acidified (conc. hydrochloric acid), and heated under reflux for 1 hr. The solution was extracted with ether (3 × 20 ml.) and the extract was washed free from acid, dried (Na_2SO_4), and the ether removed *in vacuo*, to leave a solid residue which recrystallised from benzene to give *hexakis*-3,3,3-*trifluoropropyldisiloxane* (1·80 g., 2·8 mmoles, 60%) (Found: C, 32·8; H, 3·7. $C_{18}H_{24}F_{18}OSi_2$ requires: C, 33·0; H, 3·7%), m. p. 140°.

Attempts to make the same compound by hydrolysis of chlorotris-3,3,3-trifluoropropylsilane (2·66 g., 7·50 mmoles) gave a mixture of the silanol and the disiloxane (Found: C, 32·8; H, 3·9. Calc. for $C_9H_{13}F_9OSi$: C, 32·2; H, 3·9; Calc. for $C_{18}H_{24}F_{18}OSi_2$: C, 33·0; H, 3·7%). The mixture had infrared bands at 2·78 and 2·95 μ (Si–OH groups). After being kept for 10 months this mixture (1·03 g.) deposited crystals of the disiloxane (0·354 g., 1·03 mmoles, overall yield 14%) (Found: C, 33·2; H, 3·6. Calc. for $C_{18}H_{24}F_{18}OSi_2$: C, 33·0; H, 3·7%), m. p. 138·5—140·5° (from benzene).

3,3,3-*Trifluoropropylsilicones*.—(*a*) *The cyclotetrasiloxane*. When 20% aqueous sodium hydroxide (20 ml.) was slowly added to bis-3,3,3-trifluoropropylsilane (2·22 g., 9·9 mmoles), then the mixture was heated slowly to reflux and boiled for 45 min., a white solid separated. The cooled mixture was acidified (10% hydrochloric acid) and heated under reflux (10 min.). The crystals which deposited on cooling were removed and washed with water, the filtrate was extracted with ether (4 × 20 ml.), the crystals were dissolved in the ether, and the dried (K_2CO_3) ethereal solution was evaporated until crystallisation began, to give *octakis*-3,3,3-*trifluoropropylcyclotetrasiloxane* (1·35 g., 5·2 mmoles, 53%) (Found: C, 30·2; H, 3·5. $C_{24}H_{32}F_{24}O_4Si_4$ requires C, 30·2; H, 3·4%), m. p. 140—141°, with $\nu_{max.}$ 9·2 μ (Si–O).[6]

(*b*) *The trisiloxane*. Dichlorobis-3,3,3-trifluoropropylsilane (1·38 g., 4·7 mmoles) was hydrolysed with distilled water (15 ml.) at reflux temperature for 2 hr. The cold mixture was extracted with ether (4 × 10 ml.), the ethereal solution was dried (K_2CO_3), and concentrated to crystallisation point to give hexakis-3,3,3-trifluoropropylcyclotrisiloxane (0·21 g., 0·92 mmole, 19%) (Found: C, 31·7; H, 3·6. Calc. for $C_{18}H_{24}F_{18}O_3Si_3$: C, 30·2; H, 3·4%), m. p. 114·5—115°, $\nu_{max.}$ 9·82 μ (Si–O).

(*c*) *Linear silicone*. The residual ethereal solution from (*b*) was evaporated to minimum bulk and distilled to give poly(bis-3,3,3-trifluoropropylsiloxane)[3] (0·65 g., 2·7 mmoles, 58%) (Found: C, 30·0; H, 3·3. Calc. for $C_6H_8F_6OSi$: C, 30·2; H, 3·4%) b. p. 195—220°/<1 mm. with Si–O stretching absorptions at 9·33 and 9·74 μ.

(*d*) *End-stopped linear silicone*. A mixture of the compounds $(CF_3{\cdot}CH_2{\cdot}CH_2)_2SiCl_2$ and $(CF_3{\cdot}CH_2{\cdot}CH_2)_3SiCl$ (1·28 g., 4·35 mmoles, and 1·77 g., 5·00 mmoles, respectively), hydrolysed with an excess of water, liberated 96% of the theoretical amount of hydrochloric acid. Extraction with ether (4 × 20 ml.), drying (K_2CO_3), and distillation of the ethereal solutions gave a product boiling over the range 104°/7·5 mm. to 180°/1 mm. (1·64 g., 61%); crystals of hexakis-3,3,3-trifluoropropyldisiloxane (0·19 g., 12%) m. p. 141° (mixed m. p. 139—140°) deposited on standing. The residual liquid had composition approximately corresponding to $(CF_3{\cdot}CH_2{\cdot}CH_2)_3{\cdot}Si{\cdot}O{\cdot}[(CF_3{\cdot}CH_2{\cdot}CH_2)_2Si{\cdot}O]_4{\cdot}Si(CH_2{\cdot}CH_2{\cdot}CF_3)_3$ (Found: C, 31·2; H, 3·6. Calc. for $C_6H_8F_6OSi$: C, 30·2; H, 3·4. Calc. for $C_{18}H_{24}F_{18}OSi_2$: C, 33·0; H, 3·7. Calc. for $C_{42}H_{56}F_{42}Si_6O_5$: C, 31·4; H, 3·50).

Reaction of Silane with Tetrafluoroethylene (with J. C. Young).—Silane (1·71 g., 53·4 mmoles) and tetrafluoroethylene (2·67 g., 26·7 mmoles) divided between two 250 ml. silica tubes and irradiated (18 hr.) gave unchanged silane (0·96 g., 30 mmoles, 56%), tetrafluoroethylene (0·80 g., 8·0 mmoles, 30%), 1,1,2,2-*tetrafluoroethylsilane* (1·50 g., 11·4 mmoles, 61%) (Found: C, 18·3; H, 3·1. $C_2H_4F_4Si$ requires C, 18·2; H, 3·0%) b. p. 1·2° (isoteniscope), and a mixture (0·66 g., 2·85 mmoles, 30%) of the 2 : 1 adducts of tetrafluoroethylene and silane, $(CHF_2{\cdot}CF_2)_2SiH_2$ and $CHF_2{\cdot}(CF_2)_3{\cdot}SiH_3$. Hydrolysis of the last mixture with an excess of 10% aqueous sodium hydroxide gave hydrogen, and a mixture of 1,1,2,2-tetrafluoroethane and 1,1,2,2,3,3,4,4-octafluorobutane (Found: *M*, 156. Calc. for $C_2H_2F_4$: *M*, 102. Calc. for $C_4H_2F_8$: *M*, 202). The composition of the mixture of 2 : 1 adducts was thus $(CHF_2{\cdot}CF_2)_2SiH_2$ 30% and $CHF_2{\cdot}(CF_2)_3{\cdot}SiH_3$ 70%, consistent with infrared-spectroscopic examination.

Reaction of 1,1,2,2-*Tetrafluoroethyltrichlorosilane with Lithium Aluminium Hydride*.—The chloro-compound (56·0 g., 0·23 mole) in di-n-butyl ether (50 ml.) was added during 2 hr. to a

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[6] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 2nd edn., 1958, p. 338.

stirred, ice-cold suspension of lithium aluminium hydride (16·0 g., 0·42 mole) in di-n-butyl ether (100 ml.) under nitrogen. The mixture was warmed slowly to 70°, and the gaseous products, collected in traps cooled in liquid nitrogen, were fractionated to give silane (1·6 g., 0·05 mole, 22%) and 1,1,2,2-tetrafluoroethylsilane (31·5 g., 0·18 mole, 78%), identical with the compound obtained by reaction of silane with tetrafluoroethylene.

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