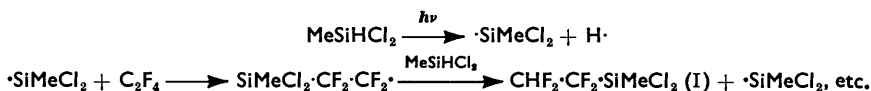


### 779. Polyfluoroalkyl Compounds of Silicon. Part III.<sup>1</sup> A Polyfluoroalkyl Silicone.

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Liquid-phase photochemical reaction of methylchlorosilane with tetrafluoroethylene gives the compound  $\text{CHF}_2\cdot\text{CF}_2\cdot\text{SiMeCl}_2$  quantitatively; reaction in the vapour phase yields mainly  $\text{CHF}_2\cdot\text{CF}_2\cdot[\text{CF}_2\cdot\text{CF}_2]_n\cdot\text{SiMeCl}_2$ . Aqueous hydrolysis of the 1 : 1 adduct gives the polyfluoroalkyl silicone  $[(\text{CHF}_2\cdot\text{CF}_2)\text{SiMe}\cdot\text{O}]_n$ . Thermal decomposition of the unfractionated silicone begins at 200° but is incomplete at 320°; trifluoroethylene is the main volatile product. Aqueous alkaline hydrolysis of methyl-1 : 1 : 2 : 2-tetrafluoroethylchlorosilane, or of the silicone derived from it, gives 1 : 1 : 2 : 2-tetrafluoroethane.

A FLUORO-OLEFIN such as tetrafluoroethylene is sensitive to attack by silicon radicals such as  $\cdot\text{SiCl}_3$  or  $\cdot\text{SiHMe}_2$  which thus initiate a chain reaction.<sup>1,2</sup> Chain transfer by abstraction of hydrogen from an  $\text{>SiH}$  group by a  $-\text{CF}_2\cdot\text{CF}_2\cdot$  radical occurs readily so that polyfluoroalkylsilicon compounds  $\text{CHF}_2\cdot\text{CF}_2\cdot\text{Si}<$  can be obtained in good yield.<sup>1,2</sup> This type of reaction has now been extended to the synthesis of methyl-1 : 1 : 2 : 2-tetrafluoroethylchlorosilane, the precursor of a polyfluoroalkylsilicone:



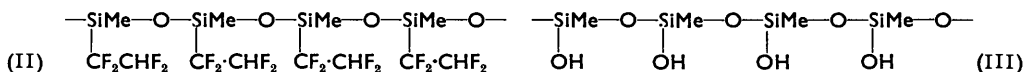
Exposure of a solution of tetrafluoroethylene in methylchlorosilane to ultraviolet light of wavelength  $>2200 \text{ \AA}$  causes rapid reaction to give methyl-1 : 1 : 2 : 2-tetrafluoroethylchlorosilane (I) essentially quantitatively within a few hours. The propagation reaction,



is prevented by use of a 200% excess of methylchlorosilane as solvent. It is noteworthy that hydrogen is not a product, indicating that the hydrogen atoms react preferentially with tetrafluoroethylene.<sup>1</sup>

Photochemical reaction of an excess of methylchlorosilane with tetrafluoroethylene in the vapour phase is extremely fast. The propagation step is not prevented as easily as for the liquid-phase reaction, and methyl 1 : 1 : 2 : 2-tetrafluoroethylchlorosilane is formed in only 20% yield, with the compounds  $\text{CHF}_2\cdot\text{CF}_2\cdot[\text{CF}_2\cdot\text{CF}_2]_n\cdot\text{SiMeCl}_2$  as the main product, although increase in the ratio of methylchlorosilane to tetrafluoroethylene would doubtless improve the yield of the 1 : 1 adduct.

Aqueous hydrolysis of methyl-1 : 1 : 2 : 2-tetrafluoroethylchlorosilane gives the polyfluoroalkylsilicone (II) quantitatively. This is a colourless viscous ether-soluble liquid of b. p.  $>200^\circ$ . It is stable to water and acids, but is readily cleaved by aqueous sodium hydroxide to give 1 : 1 : 2 : 2-tetrafluoroethane quantitatively, together with the polysiloxane  $[\text{CH}_3\cdot\text{SiO}_{1.5}]_n$  formed by cross-linking of the intermediate polysilanol (III).



Methyl-1 : 1 : 2 : 2-tetrafluoroethylchlorosilane similarly yields 1 : 1 : 2 : 2-tetrafluoroethane with aqueous alkali. The electron-releasing methyl group thus does not offset the

<sup>1</sup> Part II, Geyer and Haszeldine, *J.*, 1957, 1038.

<sup>2</sup> Haszeldine and Marklow, *J.*, 1956, 962.

inductive pull of the polyfluoroalkyl group, which has pseudohalogen character and makes the silicon atom sensitive to nucleophilic attack.<sup>2</sup>

The infrared spectra of compounds (I) and (II) are very similar, but the latter shows a new strong band at 1156  $\text{cm}^{-1}$  which is attributed to the  $-\text{Si}-\text{O}-\text{Si}-$  vibration. The C-F stretching vibration is at 1110  $\text{cm}^{-1}$ .

A preliminary investigation has been made of the thermal stability of the silicone (II). Partial decomposition of the unfractionated (by distillation or solvent-extraction) silicone occurred at 200° *in vacuo*, and further decomposition set in when the temperature was raised to 260°, then 320°. The gaseous product at each temperature was a mixture of trifluoroethylene and compounds (*e.g.*, silicon tetrafluoride) soluble in aqueous alkali. The total yield of trifluoroethylene was 47%. Pyrolysis of the silicone thus involves abstraction of  $\beta$ -fluorine by silicon with fission of the Si-CF<sub>2</sub> bond. The compounds CF<sub>2</sub>Cl·CF<sub>2</sub>·SiCl<sub>3</sub> and CHF<sub>2</sub>·CF<sub>2</sub>·SiCl<sub>3</sub> similarly yield chlorotrifluoroethylene and trifluoroethylene respectively on pyrolysis.<sup>2</sup> Thermal degradation of the silicon (II) is not complete at any one temperature, however, and some of the silicone distills out of the pyrolysis furnace. These observations suggest that the unfractionated silicone is a mixture of polymers of different chain length and cyclic siloxanes. The general problem of the effect of structure on the thermal stability of polyfluoroalkylsilicon compounds is now under investigation, using suitable reference compounds and fractionated polyfluoroalkyl-silicones and polysiloxanes.

#### EXPERIMENTAL

*Reaction of Methylchlorosilane with Tetrafluoroethylene.*—(a) *In silica apparatus.* Methylchlorosilane (12.25 g., 106.5 mmoles), freshly distilled *in vacuo* with precautions to remove traces of air (Found: *M*, 115. Calc. for CH<sub>3</sub>Cl<sub>2</sub>Si: *M*, 115) and tetrafluoroethylene (3.55 g., 35.5 mmoles) (ratio C<sub>2</sub>F<sub>4</sub> : CH<sub>3</sub>SiHCl<sub>2</sub> = 1 : 3) in a sealed 200-ml. silica tube were exposed to ultraviolet light from a Hanovia S 250 arc for 64 hr. The main reaction is over within a few hours. Both liquid and vapour phase were irradiated. No hydrogen could be detected when the tube was connected to an apparatus for the manipulation of gases and opened; even traces would have been detected by the sensitive techniques available. Distillation gave unchanged methylchlorosilane (8.2 g., 77%) and methyl-1 : 1 : 2 : 2-tetrafluoroethylchlorosilane (7.5 g., 34.9 mmoles, 98%) (Found: C, 17.0; H, 2.0. C<sub>3</sub>H<sub>4</sub>Cl<sub>2</sub>F<sub>4</sub>Si requires C, 16.7; H, 1.9%), b. p. 95.5—96.0°/770 mm. Only a very small amount of liquid of higher b. p., probably CHF<sub>2</sub>·[CF<sub>2</sub>]<sub>3</sub>·SiMeCl<sub>2</sub>, remained.

(b) *In a 20-l. flask.* The apparatus described earlier<sup>3</sup> for photochemical reactions on a molar scale was used. The reaction of methylchlorosilane (50.6 g., 440 mmoles) with tetrafluoroethylene (17.0 g., 170 mmoles) (ratio C<sub>2</sub>F<sub>4</sub> : MeSiHCl<sub>2</sub> = 1 : 2.59) in the vapour phase was very rapid and globules of product formed as a mist as soon as the ultraviolet light was turned on. Reaction was complete after 5—6 hr., and irradiation was continued for a total of 42 hr. without further change. Distillation gave unchanged methylchlorosilane (31.0 g., 61%), methyl-1 : 1 : 2 : 2-tetrafluoroethylchlorosilane (7.28 g., 20%), b. p. 96°, a fraction (18.2 g.) of b. p. 98—158°, and a still residue (3.0 g.). The 20-l. flask contained 5 g. of a viscous oil which could not be removed by distillation *in vacuo*. Redistillation of the material of b. p. 98—158° gave a fraction, b. p. 140—144°, which is probably CHF<sub>2</sub>·[CF<sub>2</sub>]<sub>3</sub>·SiMeCl<sub>2</sub>, since when hydrolysed with 10% aqueous sodium hydroxide it liberated 1 : 1 : 2 : 2 : 3 : 3 : 4 : 4-octafluorobutane (Found: *M*, 197. Calc. for C<sub>4</sub>H<sub>2</sub>F<sub>8</sub>: *M*, 202), identified by means of its infrared spectrum.<sup>1</sup>

*Hydrolysis of Methyl-1 : 1 : 2 : 2-tetrafluoroethylchlorosilane.*—(a) *Aqueous hydrolysis.* The silane (0.310 g., 1.44 mmoles) was shaken for 30 min. with water (10 ml.) in a 500-ml. bulb in absence of air. No volatile products were detected. Extraction of the solution with ether and removal of the ether from the dried (Na<sub>2</sub>SO<sub>4</sub>) extract at room temperature gave the silicone (II) (0.225 g., 1.40 mmoles, 98%) (Found: C, 22.6; H, 2.5. C<sub>3</sub>H<sub>4</sub>F<sub>4</sub>O<sub>2</sub>Si requires C, 22.5; H, 2.5%) as a clear, colourless, viscous oil.

On a larger scale methyl-1 : 1 : 2 : 2-tetrafluoroethylchlorosilane (6.28 g., 29.2 mmoles) was slowly added to a stirred mixture of water (20 ml.) and ether (20 ml.) at 15—20°. The hydrolysis is exothermic. The ethereal solution was dried (Na<sub>2</sub>SO<sub>4</sub>) and the ether removed by distillation,

\* Barr and Haszeldine, *J.*, 1955, 1881.

to leave the silicone (3.91 g., 84%). The oil was heated to 180° without decomposition or signs of distillation.

(b) *Aqueous alkaline hydrolysis.* Methyl-1 : 1 : 2 : 2-tetrafluoroethyldichlorosilane (0.0893 g., 0.415 mmole) and 10% aqueous sodium hydroxide (10 ml.), shaken at 20° for 10 min., gave 1 : 1 : 2 : 2-tetrafluoroethane (0.405 mmole, 98%) (Found: *M*, 100. Calc. for  $C_2H_2F_4$ : *M*, 102), identified by means of its infrared spectrum.

*Reactions of the Silicone (II).*—(a) *With aqueous alkali.* The silicone (0.1996 g., 1.25 mmoles) reacted at room temperature with 10% aqueous sodium hydroxide (10 ml.), but the hydrolysis was expedited by heating the mixture at 100° for 10 hr. Distillation of the volatile product gave 1 : 1 : 2 : 2-tetrafluoroethane (1.2 mmoles, 96%) (Found: *M*, 102. Calc. for  $C_2H_2F_4$ : *M*, 102), identified spectroscopically. The polysiloxane  $[CH_3SiO_{1.5}]_n$  remaining was identified spectroscopically.

(b) *Thermal decomposition.* The silicone (0.660 g., 4.1 mmoles) in a platinum crucible was heated at 200° *in vacuo* in a platinum tube for 1 hr. The gaseous product (0.15 mmole) was removed as formed by condensation in a trap cooled in liquid oxygen. The temperature was next raised to 260° for 2 hr., a further amount (0.9 mmole) of gas being collected in a cooled trap. Finally, the temperature was raised to 320° for 1 hr.; further breakdown occurred to give gaseous product (0.6 mmole). The same gaseous product was produced at each temperature, and the combined material (1.65 mmoles) was washed with aqueous sodium hydroxide to remove silicon tetrafluoride and fractionated to give trifluoroethylene (1.2 mmoles, 47% based on the silicone destroyed) (Found: *M*, 84. Calc. for  $C_2HF_3$ : *M*, 82), identified by means of its infrared spectrum. Distillation of the more volatile polymer occurred also to some extent during the pyrolysis, and this material (0.254 g., 1.59 mmoles, 39%), a thin colourless oil, condensed in the cooler parts of the pyrolysis tube.

*Infrared Spectra.*—Recorded on a Perkin-Elmer Model 21 with sodium chloride optics, these were:

$CHF_2 \cdot CF_2 \cdot SiMeCl_2$  (vapour), 2980 (m), 1410 (w), 1379 (s), 1345 (m), 1272 (s), 1200 (s), 1110 (vs), 1062 (s), 1027 (s), 847 (w), 805 (s), 762 (s), 650 (w)  $cm^{-1}$ .

Silicone (II) (film), 2975 (m), 1393, 1381 (m, doublet), 1345 (m), 1276 (s), 1204 (w), 1156 (vs), 1100 (vs, broad), 1017 (w), 785 (s), 646 (w)  $cm^{-1}$ .

(w = weak, m = medium, s = strong, vs = very strong.)

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