

202. Polyfluoroalkyl Compounds of Silicon. Part I. Reaction of Trichlorosilane with Tetrafluoroethylene.*

By R. N. HASZELDINE and R. J. MARKLOW.

The photochemical reaction of trichlorosilane with tetrafluoroethylene yields $\text{H} \cdot [\text{CF}_2 \cdot \text{CF}_2]_n \cdot \text{SiCl}_3$, where $n = 1, 2, 3$, etc. The reaction can be controlled to give mainly the compound with $n = 1$. Aqueous-alkaline hydrolysis of the silicon compounds yields the series $\text{H} \cdot [\text{CF}_2 \cdot \text{CF}_2]_n \cdot \text{H}$. The pyrolysis, hydrolysis, methanolysis, and chlorination of certain polyfluoroalkyl silicon compounds are described, and their infrared spectra are presented.

THE thermal and chemical stability of the fluorocarbons and many of their derivatives is now well established. As alkyl-silicon compounds and silicones are also stable thermally and chemically, we thought that a combination of the two types of compound to give polyfluoroalkyl-silicon compounds and polyfluoroalkyl-silicones would be worthy of investigation, since such compounds might show high thermal, and possibly chemical, stability.

Five methods have been found to be of general use for the preparation of polyfluoroalkyl silicon compounds: (a) reaction of a silicon tetrahalide with a polyfluoroalkyl Grignard compound, (b) reaction of a sodium or lithium polyfluoroalkyl with a silicon tetrahalide, (c) reaction of a polyfluoroalkyl bromide or iodide with silicon in presence of a catalyst, usually copper, (d) addition of a silicon compound to an unsaturated linkage in a polyfluoro-compound, and (e) addition of a polyfluoroalkyl iodide or bromide to an unsaturated linkage in an alkene-silicon compound. A sixth possible general approach can be visualised, namely, replacement of chlorine, bromine, or iodine in a polyhalogenoalkyl-silicon compound by fluorine. The initial results of a study of methods (a), (b), and (c) have already been briefly reported¹ and will be recorded in subsequent Parts of this series. The present Part illustrates method (d) by reaction of trichlorosilane with tetrafluoroethylene, and method (e) has been reported recently.²

Tetrafluoroethylene is a convenient, readily-available olefin whose polymerisation can often be controlled³ to give short-chain polymers; this often constitutes a relatively easy route to a homologous series of compounds which possess a reactive functional group at one end of the chain. Sommer, Pietrusza, and Whitmore⁴ showed that trichlorosilane reacted by addition with unsubstituted olefins. It seemed probable, from what is now known of

* Presented at Amer. Chem. Soc. Meeting, Minneapolis, 1955.

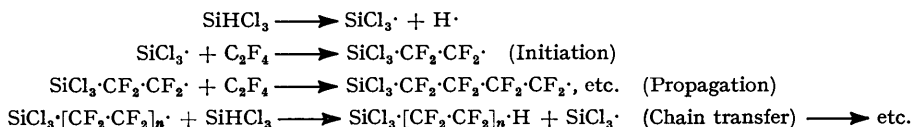
¹ Haszeldine, Amer. Chem. Soc. Meetings, New York, 1951; Atlantic City, 1952; New York, 1954; *Nature*, 1951, **168**, 1028; *Angew. Chem.*, 1954, **66**, 693.

² Haszeldine and Marklow, Amer. Chem. Soc. Meeting, Minneapolis, 1955.

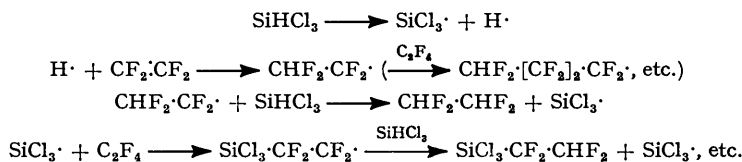
³ See, e.g., Haszeldine, *J.*, 1953, 3761.

⁴ Sommer, Pietrusza, and Whitmore, *J. Amer. Chem. Soc.*, 1945, **67**, 188; 1948, **70**, 484.

polyfluoroalkyl radical reactions, that trichlorosilane would react similarly with tetrafluoroethylene by a suitably initiated free-radical reaction :

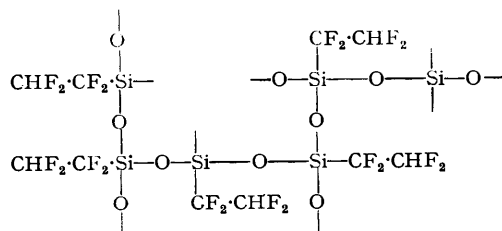


This has proved to be the case. The Si-H bond appears to be essential for formation of the SiCl_3 radical which initiates the reaction, since attempts to use silicon tetrachloride instead of trichlorosilane failed. The failure to achieve homolytic fission of the polar Si-Cl bond by use of heat, light, or peroxide initiators has been noted by previous workers.^{4, 5} The purely thermal reaction of trichlorosilane with tetrafluoroethylene yields products of the type $\text{H}\cdot[\text{CF}_2\cdot\text{CF}_2]_n\cdot\text{SiCl}_3$, but the reaction is not as convenient on a laboratory scale as is a photochemical reaction, since some tetrafluoroethylene is lost by its conversion into perfluorocyclobutane. Photochemical initiation causes a smooth, fast reaction, and light of wavelength $> 2200 \text{ \AA}$ gives an essentially quantitative yield and conversion of tetrafluoroethylene into the compounds $\text{H}\cdot[\text{CF}_2\cdot\text{CF}_2]_n\cdot\text{SiCl}_3$. The value of n can be controlled particularly easily in this reaction by the ratio of C_2F_4 to SiHCl_3 ; thus a ratio of 1 : 4 gives the compound with $n = 1$ in *ca.* 60% yield, whereas with a ratio of 1 : 1.2 the yield of the compound with $n = 1$ falls to *ca.* 35% with a 65% yield of products where $n > 1$. Trichlorosilane is thus an efficient chain-transfer reagent, and the speed of reaction shows that the SiCl_3 radical is reactive towards tetrafluoroethylene. The absence of even traces of free hydrogen in the reaction products shows that hydrogen-atom combination does not occur, nor does hydrogen formation occur by attack of a hydrogen atom on trichlorosilane to generate the SiCl_3 radical. The hydrogen atoms formed initially must thus react with tetrafluoroethylene, but the subsequent stages in the reaction so initiated are similar to those initiated by the SiCl_3 radical :



Small amounts of tetrafluoroethane cannot be detected with the same ease as hydrogen.

Trichloro-(1 : 1 : 2 : 2-tetrafluoroethyl)silane, the compound where $n = 1$, was examined as typical of the series. It reacts rapidly and quantitatively with ice-water to give an ether-soluble polysiloxane $(\text{CHF}_2\cdot\text{CF}_2\cdot\text{SiO}_{1.5})_n$ as a white solid which does not melt below 330° . The polysiloxane is clearly formed by conversion of the SiCl_3 group into $\text{Si}(\text{OH})_3$, followed by a 3-dimensional condensation to give a product of the type

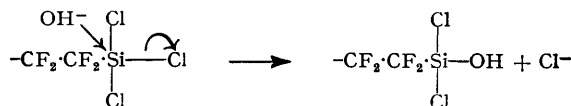


The polysiloxane is stable to water and aqueous acid, but is decomposed rapidly by cold aqueous sodium hydroxide to liberate 1 : 1 : 2 : 2-tetrafluoroethane and silicate quantitatively. Trichloro-(1 : 1 : 2 : 2-tetrafluoroethyl)silane similarly reacts with cold aqueous alkali to yield 1 : 1 : 2 : 2-tetrafluoroethane and silicate quantitatively. The compounds $\text{CF}_3\cdot\text{SiCl}_3$ and $(\text{CF}_3)_2\text{SiCl}_2$ also liberate fluoroform with aqueous alkali though not with

* Barry, DePree, Gilbey, and Hook, *J. Amer. Chem. Soc.*, 1947, **69**, 2916.

water.⁶ By contrast, trichloro(trichloromethyl)silane is hydrolysed to chloroform and silicate merely by reaction with water at room temperature,⁷ so that a polysiloxane cannot be obtained from this compound.

Both members of the series $\text{H}\cdot[\text{CF}_2\cdot\text{CF}_2]_n\cdot\text{SiCl}_3$ where $n = 2$ or 3 are hydrolysed by aqueous sodium hydroxide to give quantitative yields of $\text{H}\cdot[\text{CF}_2\cdot\text{CF}_2]_n\cdot\text{H}$ ($n = 2$ or 3), and the reaction of trichlorosilane with tetrafluoroethylene followed by hydrolysis in this way constitutes a general method for the preparation of the compounds $\text{H}\cdot[\text{CF}_2\cdot\text{CF}_2]_n\cdot\text{H}$, which are otherwise somewhat difficult to obtain. Hydrolysis of the silicon compounds where $n = 2$ or 3 is slower than that of trichloro-(1 : 1 : 2 : 2-tetrafluoroethyl)silane. The increase in the ease of hydrolytic attack



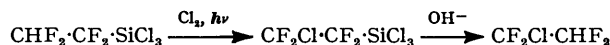
attributed to the increased positive character of silicon when a polyfluoroalkyl group is attached to it is clearly offset to some extent by some other factor in the longer-chain compounds, probably since the polysiloxanes generated initially are only partly soluble in water and are protected by the liberated polyfluorocarbon $\text{H}\cdot[\text{CF}_2\cdot\text{CF}_2]_n\cdot\text{H}$ which tends to form a film around the solid polymer. In the latter case, the use of higher temperatures for the hydrolysis might serve to volatilise the polyfluorocarbon.

The marked increase in boiling point on replacement of terminal fluorine atoms in a fluorocarbon by hydrogen is shown below :

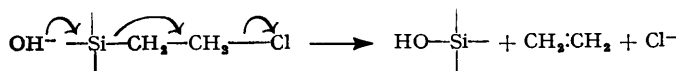
Compound	B. p.	Compound	B. p.	Compound	B. p.
$\text{CF}_3\cdot\text{CF}_3$	-79°	$\text{CF}_3\cdot\text{CHF}_2$	-48°	$\text{CHF}_2\cdot\text{CHF}_2$	-20°
$\text{CF}_3\cdot[\text{CF}_2]_2\cdot\text{CF}_3$	-5	$\text{CF}_3\cdot[\text{CF}_2]_2\cdot\text{CHF}_2$	14	$\text{H}\cdot[\text{CF}_2]_4\cdot\text{H}$	43
$\text{CF}_3\cdot[\text{CF}_2]_4\cdot\text{CF}_3$	55	$\text{CF}_3\cdot[\text{CF}_2]_4\cdot\text{CHF}_2$	70	$\text{H}\cdot[\text{CF}_2]_6\cdot\text{H}$	87

The chlorine atoms in trichloro-(1 : 1 : 2 : 2-tetrafluoroethyl)silane are readily replaced by alkoxy-groups; *e.g.*, the compound $\text{CHF}_2\cdot\text{CF}_2\cdot\text{Si}(\text{OMe})_3$ was easily prepared by reaction with anhydrous methanol. Aqueous hydrolysis of the trimethoxy-compound gave a polysiloxane very similar to that obtained from the trichloro-compound, and very probably formed from the same intermediate, $\text{CHF}_2\cdot\text{CF}_2\cdot\text{Si}(\text{OH})_3$; reaction of the trimethoxy-compound or its polysiloxane with aqueous sodium hydroxide again liberated tetrafluoroethane quantitatively.

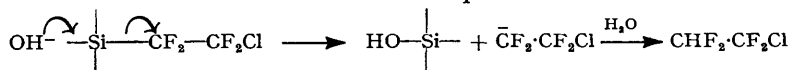
Trichloro-(1 : 1 : 2 : 2-tetrafluoroethyl)silane is stable at 150° in glass apparatus, and thermal chlorination at this temperature readily yields trichloro-(2-chlorotetrafluoroethyl)silane. The same compound is obtained almost quantitatively by photochemical chlorination, and fission of the carbon-silicon bond cannot be detected. Aqueous alkaline hydrolysis of the chlorinated material yields 1-chloro-1 : 1 : 2 : 2-tetrafluoroethane quantitatively :



This forms an interesting comparison with the aqueous-alkaline hydrolysis of trichloro-(2-chloroethyl)silane which yields ethylene,⁸ probably by a concerted mechanism :



which is prevented in the case of the fluorine compound by the fluorine atoms' stabilising the chlorine atom towards anion elimination in an aqueous medium :

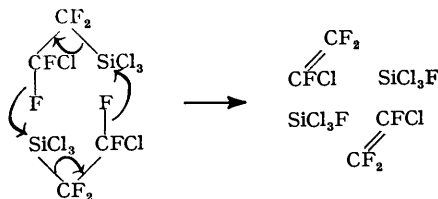


⁶ Haszeldine, ref. 1 and later Parts of this series.

⁷ Di Giorgio, Sommer, and Whitmore, *J. Amer. Chem. Soc.*, 1948, **70**, 3512.

⁸ Sommer, Goldberg, Dorfman, and Whitmore, *ibid.*, 1946, **68**, 1083.

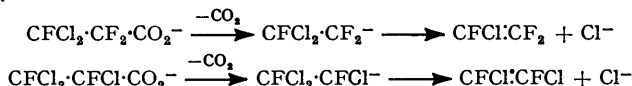
The pyrolysis of trichloro-(2-chloro-1 : 1 : 2 : 2-tetrafluoroethyl)silane was investigated to determine the mode of breakdown of polyfluoroalkyl-silicon compounds. Chlorotrifluoroethylene was the only organic compound obtained at 220°, and this novel reaction is best visualised as a process in which fluoride is transferred to silicon, probably *via* a cyclic intermediate :



The trichlorofluorosilane formed initially could then disproportionate. A mechanism of the type postulated earlier⁹ for the formation of polyfluoro-olefins by pyrolysis of alkali-metal salts of polyfluorocarboxylic acids, *i.e.*, halide elimination from a fluoro-carbanion :



is unlikely, since elimination of chloride rather than of fluoride occurs with polychloro-fluoro-acids, *e.g.* :

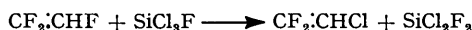


Pyrolysis of the silicon compound resulted exclusively in elimination of fluoride, and tetrafluoroethylene was not a reaction product. A free-radical mechanism following initial homolytic fission of the C-Si bond also seems unlikely, since expulsion of a fluorine atom from $\text{CF}_2\text{Cl}\cdot\text{CF}_2\cdot$ would be involved.

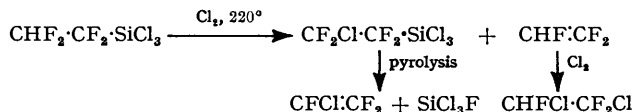
Pyrolysis of trichloro-(1 : 1 : 2 : 2-tetrafluoroethyl)silane at 220° gave approximately equimolar amounts of trifluoroethylene and 1-chloro-2 : 2-difluoroethylene. The first olefin is that expected by analogy with the pyrolysis of trichloro-(2-chloro-1 : 1 : 2 : 2-trifluoroethyl)silane, being formed thus :



but the second olefin was unexpected. Its formation can be attributed to the replacement by chlorine of the lone fluorine atom in trifluoroethylene by reaction with silicon chlorofluorides, *e.g.*,



Thermal chlorination of trichloro-(1 : 1 : 2 : 2-tetrafluoroethyl)silane at temperatures higher than the 150° mentioned earlier gives a mixture of products. At 225°, for example, both chlorination and pyrolysis of the silicon compound occur, to give trichloro-(2-chloro-1 : 1 : 2 : 2-tetrafluoroethyl)silane and trifluoroethylene respectively. The olefin so produced then reacts with chlorine to give 1 : 2-dichlorotrifluoroethane, and the trichloro-(2-chloro-1 : 1 : 2 : 2-tetrafluoroethyl)silane is pyrolysed to give chlorotrifluoroethylene :



The hydrogen chloride liberated during the chlorination reaction does not react with the other products provided that an excess of chlorine is present. Anhydrous hydrogen chloride alone reacts with trichloro-(1 : 1 : 2 : 2-tetrafluoroethyl)silane at 205°, however, to

⁹ Haszeldine, *Nature*, 1951, **163**, 1028; *J.*, 1952, 4259; 1954, 4026; 1955, 4291, 4302.

give 1 : 1 : 2 : 2-tetrafluoroethane ($\text{CHF}_2 \cdot \text{CF}_2 \cdot \text{SiCl}_3 \longrightarrow \text{CHF}_2 \cdot \text{CHF}_2 + \text{SiCl}_4$) as well as products formed by pyrolysis of the silicon compound.

The reaction of trichlorosilane with tetrafluoroethylene thus provides a simple and convenient route to polyfluoroalkylsilanes, and the extension of the reaction to other fluoro-olefins will be described later.

The present work thus answers, at least in part, the questions of whether polyfluoroalkyl silicon compounds which contain a $\text{CF}_2 \cdot \text{Si}$ group are stable (a) to heat, (b) to hydrolysis by water, acid, or base, and (c) to oxygen; it also gives a clear indication of the types of structure which must be sought if maximum stability is to be obtained in such compounds. The stability of the $\text{Si}-\text{CF}_2$ bond in polyfluoroalkyl-silicon compounds clearly depends to an appreciable extent on the nature of the atom or group also attached to the silicon. Thus the compounds $\text{CHF}_2 \cdot \text{CF}_2 \cdot \text{SiCl}_3$ and $\text{CF}_2\text{Cl} \cdot \text{CF}_2 \cdot \text{SiCl}_3$ decompose at 220° , whereas the polysiloxane $(\text{CHF}_2 \cdot \text{CF}_2 \cdot \text{SiO}_{1.5})_n$ is stable up to at least 330° . Chlorine is bonded to silicon in the first type of compound, and the relatively weak $\cdot\text{CF}_2 \cdot \text{Si}-\text{X}$ bond ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$), and particularly the tendency for silicon tetrahalide formation by the β -halogen elimination discussed above, leads to thermal instability. The polysiloxane contains a strong $\cdot\text{CF}_2 \cdot \text{Si}-\text{O} \cdot$ bond and there is no tendency for the β -elimination reaction; such a structure must be sought to attain high thermal stability. The stability of the polyfluoroalkyl-silicon compounds to oxygen and to aqueous or acid hydrolysis is good, and there is little doubt that the stability to alkaline hydrolysis can be improved or made complete by modifying the molecule so that the polyfluoroalkyl group is in a suitable position relative to silicon without loss of the thermal stability found for the $\cdot\text{CF}_2 \cdot \text{Si}-\text{O} \cdot$ system.

The analysis of polyfluoroalkyl-silicon compounds of the type described above presents some problems, since the compounds are sensitive to moisture, yet thermally stable, and the presence of fluorine and ultimately of fluoride makes estimation of silicon by conventional methods difficult. Jewsbury's method,¹⁰ modified to fit our requirements, was found to be most suitable for determination of silicon as silicate. The silicon in the polyfluoroalkyl-silicon compound was obtained as silicate (a) by removal of the polyfluoroalkyl group by hydrolysis with aqueous alkali, or (b) by fusion of the compound with sodium in a nickel bomb. Method (b) introduced fluoride into the silicate solution, but the procedure adopted was satisfactory in both cases. Many polyfluoroalkyl silicon compounds are hydrolysed quantitatively by aqueous alkali, whereby the silicon compound $\text{R}_F\text{Si}-$ is converted into R_FH and silicate ($\text{R}_F = \text{polyfluoroalkyl}$). If R_FH is sufficiently volatile it can be transferred quantitatively to a vacuum-apparatus and measured, and this constitutes a convenient analytical method.

EXPERIMENTAL

Reactions were carried out in sealed Pyrex or silica tubes which were filled by use of a vacuum-apparatus; moisture, air, etc., were carefully excluded. Trichlorosilane was a commercial sample, redistilled before use. The tetrafluoroethylene was spectroscopically pure and was refractionated *in vacuo*. Reaction products were identified by infrared spectroscopy whenever possible.

Analytical Methods.—(a) *Determination of silicon.* The silicon compound (ca. 0.2 g.) was weighed in a Polythene container fitted with a tight stopper, which was then opened under 100 ml. of 10% aqueous "AnalaR" sodium hydroxide in a Polythene beaker. After reaction had ceased, the solution was neutralised (phenolphthalein) with 3N-sulphuric acid, and ca. 10 g. of "AnalaR" boric acid were added. After being stirred for 5–10 min., the filtered solution was made up to 250 ml.

Compounds resistant to aqueous alkaline hydrolysis were weighed in a gelatin capsule and heated in a nickel bomb with an excess of sodium at 600° (2 hr.). The excess of sodium was removed by reaction with ethanol, then water, and the contents of the bomb were transferred to a platinum crucible. "AnalaR" sodium hydroxide (2 g.) was added, and the mixture digested for 1–2 hr. After transfer to a Polythene beaker, the mixture was treated as before.

An aliquot part of the neutralised solution containing 0.5–1 mg. of silicon was transferred to a 50-ml. standard flask and made up to ca. 40 ml. by addition of 4% "AnalaR" boric acid solution

¹⁰ Jewsbury, *Analyst*, 1950, **75**, 256.

(to form a complex with the fluoride) and 2 ml. of 5N-nitric acid. This was followed by 5 ml. of 10% ammonium molybdate solution, and the solution was then made up to 50 ml. with water. The above procedure converts silicate into yellow silicomolybdic acid. The intensity of the yellow colour was next measured by use of a Unicam Ultraviolet Spectrophotometer at a definite wavelength rather than by use of a Spekker instrument with a specific filter as described by Jewsbury. The optical density of the solution obtained as described above was measured, 5 min. after the solution had been prepared, in 1-cm. Pyrex cells at 420 μ , with water in the reference cell. The slit width was 0.03 mm. There is no maximum in the absorption curve for the silicomolybdic acid, and 420 μ is the wavelength where the acid absorbs strongly but the reagents' absorption (unlike that at, e.g., 390 μ) is negligible.

A standard graph of optical density against silicon content was prepared by use of a standard silicate solution (0.1295 g. of SiO_2 per 100 ml.) which was analysed gravimetrically. This solution was diluted four times to give solution *A*, portions of which were put through the routine described above, the resultant optical density being measured. The results are shown in the annexed Table.

Solution <i>A</i> (ml.) ...	0	0.5	1.0	1.5	2.02	2.5	3.0	3.5
Si (mg.)	0	0.162	0.324	0.486	0.654	0.810	0.972	1.134
Optical density ...	0	0.140	0.281	0.420	0.586	0.720	0.858	0.995

(b) *Determination of polyfluoroalkyl groups by hydrolysis.* A weighed amount of a volatile polyfluoroalkyl-silicon compound was transferred *in vacuo* to the cold finger of an evacuated 500-ml. bulb fitted with vacuum tap and taper joint. An excess of aqueous alkali was then added to the bulb by filling the taper joint above the tap with the solution and drawing it into the bulb by momentarily opening the tap. After being vigorously shaken, the volatile product (e.g., $\text{CHF}_2 \cdot \text{CHF}_2$ from $\text{CHF}_2 \cdot \text{CF}_2 \cdot \text{SiCl}_3$) was transferred to an apparatus for the vacuum-manipulation of gases, where its volume and molecular weight were measured. Polyfluoroalkanes with b. p.s up to 100° can be transferred quantitatively in this way. Less volatile polyfluoroalkyl-silicon compounds (e.g., polysiloxanes) were weighed into a fragile tube which was sealed, then inserted into a larger tube (50 ml.) containing aqueous sodium hydroxide. The larger tube was sealed, then the inner tube broken by shaking. When reaction was complete the volatile products were transferred to the vacuum-apparatus in the usual way.

Photochemical Reaction of Trichlorosilane with Tetrafluoroethylene.—Trichlorosilane (15.2 g., 110 mmoles) and tetrafluoroethylene (6.85 g., 68.5 mmoles), shaken and irradiated in a sealed 200-ml. silica tube (24 hr.), gave liquid products, which were distilled through a small column to give (a) unchanged trichlorosilane, b. p. 32°, (b) *trichloro*-(1 : 1 : 2 : 2-tetrafluoroethyl)silane (7.1 g., 44%), b. p. 84.5—85.0°, n_D^{20} 1.367 (Found : C, 10.3; H, 0.8; Cl, 45.5, 45.2; Si, 11.8, 11.7%; *M*, 236. $\text{C}_2\text{HCl}_3\text{F}_4\text{Si}$ requires C, 10.2; H, 0.4; Cl, 45.4; Si, 11.9%; *M*, 235.5), and (c) a residue of higher b. p. (4.0 g.). There are no products other than $\text{H} \cdot [\text{CF}_2 \cdot \text{CF}_2]_m \cdot \text{SiCl}_3$ formed during this reaction.

The trichloro-(1 : 1 : 2 : 2-tetrafluoroethyl)silane was redistilled through a packed column to remove trichlorosilane, and was checked by infrared spectroscopy before analysis. Chlorine and silicon were determined (a) by hydrolysis and (b) by sodium fusion. The b. p. of the silicon compound measured by use of an isoteniscope is 84.2°.

The above experiment was repeated with variation in reactant ratio. The effect on the yield of trichloro-(1 : 1 : 2 : 2-tetrafluoroethyl)silane is shown in the annexed Table, where $\text{H} \cdot [\text{CF}_2 \cdot \text{CF}_2]_m \cdot \text{SiCl}_3$ refers to the polymer containing more than two carbon atoms per molecule. In all cases a small amount of solid formed on the walls of the silica tube.

SiHCl_3 (mmoles)	C_2F_4 (mmoles)	Mole ratio $\text{SiHCl}_3 : \text{C}_2\text{F}_4$	$\text{CHF}_2 \cdot \text{CF}_2 \cdot \text{SiCl}_3$ Wt. (g.)	Yield (%)	$\text{H} \cdot [\text{CF}_2 \cdot \text{CF}_2]_m \cdot \text{SiCl}_3$ (g.)
82.5	68.5	1.5	5.4	34	4.8
110	"	2.0	7.1	44	4.0
220	"	4.0	9.8	58	3.1
275	"	5.0	10.1	61	3.0

The material of b. p. higher than that of the compound where $m = 1$, which accumulated during several experiments, was combined and distilled under reduced pressure in a nitrogen atmosphere to give (a) *trichloro*-(1 : 1 : 2 : 2 : 3 : 3 : 4 : 4-octafluorobutyl)silane (8.35 g.), b. p. 90°/195 mm. (Found : C, 14.2; H, 0.4; Cl, 31.6; Si, 8.3. $\text{C}_4\text{HF}_8\text{Cl}_3\text{Si}$ requires C, 14.3; H, 0.3; Cl, 31.8; Si, 8.4%), (b) *trichloro*-(1 : 1 : 2 : 2 : 3 : 3 : 4 : 4 : 5 : 5 : 6 : 6-dodecafluorohexyl)silane (4.2 g.), b. p. 128°/205 mm. (Found : C, 16.2; H, 0.4; Cl, 24.7; Si, 6.4. $\text{C}_6\text{HF}_{12}\text{Cl}_3\text{Si}$

requires C, 16.5; H, 0.2; Cl, 24.4; Si, 6.4%), and (c) a residue (2.0 g.) which set to a paste when cold.

Thermal Reaction of Trichlorosilane with Tetrafluoroethylene.—This was not examined in detail, but experiments showed that at 210° up to 80% of the tetrafluoroethylene was converted into perfluorocyclobutane; the compounds $H \cdot [CF_2 \cdot CF_2]_n \cdot SiCl_3$ were also produced and identified by infrared spectroscopy. Further examination of this reaction at temperatures below 200°, with peroxide or azo-compound initiators, would probably enable much better yields of the required silicon compounds to be obtained.

Attempted Reaction of Silicon Tetrachloride with Tetrafluoroethylene.—In a single experiment, silicon tetrachloride (50 mmoles) and tetrafluoroethylene (12.5 mmoles) were heated in presence of benzoyl peroxide (0.83 mmole) at 120° for 16 hr. The product was a thin gel suspended in silicon tetrachloride. Tetrafluoroethylene (40%) and silicon tetrachloride were recovered by distillation, which left a residue of a tetrafluoroethylene polymer and organic matter from the decomposed peroxide. Spectroscopic examination identified the polytetrafluoroethylene, and chemical examination showed that no carbon-silicon bonds were present.

In a single experiment silicon tetrachloride (42.5 mmoles) and tetrafluoroethylene (14.8 mmoles), heated at 230° (15 hr.) in a 20-ml. autoclave, gave only unchanged silicon tetrachloride, perfluorocyclobutane, and polytetrafluoroethylene. Polyfluoroalkyl-silicon compounds were not produced.

Alkaline Hydrolysis of Compounds $H \cdot [CF_2 \cdot CF_2]_n \cdot SiCl_3$.—(a) *Trichloro-(1 : 1 : 2 : 2-tetrafluoroethyl)silane.* The silicon compound (0.456 g., 1.94 mmoles), shaken with 10% aqueous sodium hydroxide (20 ml.) for 5 min., gave, on fractionation *in vacuo*, 1 : 1 : 2 : 2-tetrafluoroethane (1.92 mmoles, 99.2%), b. p. (isoteniscope) -20° (Found : C, 23.4; H, 2.1%; *M*, 103. Calc. for $C_2H_2F_4$: C, 23.5; H, 2.0%; *M*, 102). Henne and Renoll¹¹ report b. p. -23°. A similar experiment using 2% aqueous sodium hydroxide gave a 99.3% yield of tetrafluoroethane from trichloro-(1 : 1 : 2 : 2-tetrafluoroethyl)silane (0.323 g., 1.37 mmoles).

(b) *Trichloro-(1 : 1 : 2 : 2 : 3 : 3 : 4 : 4-octafluorobutyl)silane.* This compound appeared to react only slowly with aqueous alkali at room temperature. A sample (1.104 g., 3.0 mmoles) was sealed with 10% aqueous sodium hydroxide (10 ml.) and heated at 100° (4 hr.). Fractionation of the volatile products *in vacuo* followed by distillation at atmospheric pressure through a short column, gave 1 : 1 : 2 : 2 : 3 : 3 : 4 : 4-octafluorobutane (3.0 mmoles, 100%), b. p. (isoteniscope) 43° (Found : C, 23.8; H, 1.0%; *M*, 201. $C_4H_2F_8$ requires C, 23.8; H, 1.0%; *M*, 202).

(c) *Trichloro-(1 : 1 : 2 : 2 : 3 : 3 : 4 : 4 : 5 : 5 : 6 : 6-dodecafluorohexyl)silane.* The compound appeared to be incompletely hydrolysed under the conditions used for (a) above. A sample (1.028 g., 2.35 mmoles) and 10% aqueous sodium hydroxide (10 ml.), heated at 100° (7 hr.), gave, on fractionation of the volatile products *in vacuo*, followed by distillation at atmospheric pressure through a short column, 1 : 1 : 2 : 2 : 3 : 3 : 4 : 4 : 5 : 5 : 6 : 6-dodecafluorohexane (2.35 mmoles, 100%), b. p. (isoteniscope) 87° (Found : C, 23.6; H, 1.1%; *M*, 303. $C_6H_2F_{12}$ requires C, 23.8; H, 0.7%; *M*, 302).

Aqueous Hydrolysis of Trichloro-(1 : 1 : 2 : 2-tetrafluoroethyl)silane.—Reaction of the silane (0.266 g., 1.125 mmoles) with water (20 ml.) was immediate but gave no volatile products. An aqueous solution containing a fine suspension was obtained after 5 minutes' shaking. Addition of 10% aqueous sodium hydroxide (10 ml.) brought about immediate evolution of 1 : 1 : 2 : 2-tetrafluoroethane (1.12 mmoles, 99.7%).

Trichloro-(1 : 1 : 2 : 2-tetrafluoroethyl)silane (1.631 g.) was dissolved in anhydrous ether (100 ml.) then shaken (5 min.) with ice water (50 ml.). The ether layer and subsequent ethereal extracts (3 × 25 ml.) of the aqueous solution were combined. Evaporation of the ether gave a viscous oil, which when dried *in vacuo* (P_2O_5) yielded a brittle glass. This was treated with light petroleum (b. p. 60—80°) to remove traces of occluded organic matter. The residual material was a white solid *polysiloxane* of formula $[CHF_2 \cdot CF_2 \cdot SiO_{1.5}]_n$, (0.914 g., 92%) [Found : C, 15.9; H, 1.1; Si, 18.0. ($C_2HO_{1.5}F_4Si$)_n requires C, 15.6; H, 0.7; Si, 18.3%]. The polysiloxane was insoluble in water, benzene, carbon tetrachloride, and light petroleum, moderately soluble in acetone or ethanol, and readily soluble in ether. It did not melt below 330°.

Reaction of the polysiloxane (0.078 g.) with 10% aqueous sodium hydroxide (20 ml.) was rapid and yielded (5 min.) 1 : 1 : 2 : 2-tetrafluoroethane (0.52 g., 100%).

Trimethoxy-(1 : 1 : 2 : 2-tetrafluoroethyl)silane.—Trichloro-(1 : 1 : 2 : 2-tetrafluoroethyl)silane (3.103 g., 13.2 mmoles) was frozen in a tube with dry methanol (1.265 g., 39.6 mmoles) and a

¹¹ Henne and Renoll, *J. Amer. Chem. Soc.*, 1936, **58**, 887.

reflux condenser was attached to the tube. Reaction occurred as the tube warmed to room temperature, and evolution of hydrogen chloride was complete after the reactants had been heated on a water-bath (15 min.). The product was transferred to a distillation apparatus, and dry nitrogen was bubbled through the liquid for 1 hr. to remove hydrogen chloride. Distillation then gave only trimethoxy-(1 : 1 : 2 : 2-tetrafluoroethyl)silane (2.15 g., 74%), b. p. 98°/190 mm. (Found : C, 26.9; H, 4.2; Si, 12.6. $C_5H_{10}O_3F_4Si$ requires C, 27.0; H, 4.5; Si, 12.6%).

Reaction of the chloro-compound with the equivalent amount of methanol gives better results than use of an excess of methanol, which appears to form an azeotrope with the required product, and readily absorbs the hydrogen chloride liberated during the reaction.

Trimethoxy-(1 : 1 : 2 : 2-tetrafluoroethyl)silane (0.0762 g.) reacted with 10% aqueous sodium hydroxide (20 ml.) at room temperature to give 1 : 1 : 2 : 2-tetrafluoroethane (0.0349 g., 99.7%).

The trimethoxy-compound (0.710 g.) and water (0.4 ml.) were shaken at 0° to give a homogeneous solution (3 min.) which was kept at 0° for 1 hr. The aqueous methanol was removed *in vacuo* to give a white solid polysiloxane (0.458 g., 94%) of formula $(CHF_2 \cdot CF_2 \cdot SiO_{1.5})_n$, spectroscopically identical with the product described earlier. It showed similar characteristics when heated.

Trichloro-(2-chloro-1 : 1 : 2 : 2-tetrafluoroethyl)silane.—(a) *Photochemical chlorination.* Trichloro-(1 : 1 : 2 : 2-tetrafluoroethyl)silane (3.30 g., 14.0 mmoles) and chlorine (1.056 g., 14.8 mmoles), exposed to ultraviolet light in a silica tube (15 hr.), gave hydrogen chloride (Found : *M*, 37. Calc. for HCl : *M*, 36.5) and trichloro-(2-chloro-1 : 1 : 2 : 2-tetrafluoroethyl)silane (2.83 g., 75%), b. p. 102° (Found : C, 9.1; Cl, 39.9; Si, 10.2. $C_2Cl_4F_4Si$ requires C, 8.9; Cl, 39.5; Si, 10.4%).

(b) *Thermal chlorination.* Trichloro-(1 : 1 : 2 : 2-tetrafluoroethyl)silane (1.493 g., 6.3 mmoles) and chlorine (0.453 g., 6.4 mmoles) failed to react in a 50-ml. sealed tube heated at 100° or 125°, but the yellow colour began to fade at 150°. After 15 hr. at this temperature, distillation gave hydrogen chloride (5.5 mmoles) (Found : *M*, 36.5) and a liquid (1.4 g.) of higher b. p. which when redistilled yielded trichloro-(2-chloro-1 : 1 : 2 : 2-tetrafluoroethyl)silane (1.0 g., 59%), b. p. 102°. The yield based on the crude liquid is 83%.

Thermal chlorination at higher temperatures yielded more complex products. Trichloro-(1 : 1 : 2 : 2-tetrafluoroethyl)silane (0.89 g., 3.75 mmoles) and chlorine (0.288 g., 4.05 mmoles) gave mainly volatile products when heated in a 50-ml. tube at 225° (18 hr.). Fractionation *in vacuo*, followed by infrared spectroscopic examination and molecular-weight determinations on the fractions obtained, revealed the presence of chlorotrifluoroethylene, a chlorofluoroethane, and unidentified silicon compounds (not the tetrachloride or tetrafluoride). The silicon compounds were removed by reaction with water, and the olefin by reaction with chlorine. Redistillation of the chlorinated product and of the residual material, followed by spectroscopic analysis and molecular-weight determinations, showed that the original reaction had produced chlorotrifluoroethylene (2.35 mmoles, 63%) and 1 : 2-dichlorotrifluoroethane (1.85 mmoles, 49%). Small amounts of an unidentified olefin were also present.

Trichloro-(2-chloro-1 : 1 : 2 : 2-tetrafluoroethyl)silane (0.0941 g.) and 10% aqueous sodium hydroxide (20 ml.), shaken at room temperature (5 min.), gave 1-chlorotetrafluoroethane (0.0470 g., 99.5%), identified by infrared spectroscopy.

Pyrolysis of Trichloro-(2-chloro-1 : 1 : 2 : 2-tetrafluoroethyl)silane.—The compound (0.684 g., 2.51 mmoles), heated at 220° (15 hr.) in a 50-ml. Pyrex tube, gave chlorotrifluoroethylene (2.25 mmoles, 90%), identified spectroscopically. The silicon compounds produced are probably $SiCl_3F$, $SiCl_2F_2$, and SiF_3Cl , since spectroscopic examination showed that neither silicon tetrachloride nor the tetrafluoride was present in any quantity.

Pyrolysis of Trichloro-(1 : 1 : 2 : 2-tetrafluoroethyl)silane.—The compound (1.014 g., 4.25 mmoles), heated at 220° (15 hr.) in a 50-ml. Pyrex tube, gave trifluoroethylene (1.45 mmoles, 34%) and 1-chloro-2 : 2-difluoroethylene (2.05 mmoles, 49%), fractionated *in vacuo* and identified by infrared spectroscopy.

Reaction of Hydrogen Chloride with Trichloro-(1 : 1 : 2 : 2-tetrafluoroethyl)silane.—The silicon compound (1.149 g., 4.85 mmoles) and anhydrous hydrogen chloride (6.1 mmoles) failed to react in a sealed 50-ml. Pyrex tube at 185° (15 hr.). Reaction occurred at 205° (15 hr.) to give 1 : 1 : 2 : 2-tetrafluoroethane and 1-chloro-2 : 2-difluoroethylene (identified by infrared spectroscopy) as the main organic products. The silicon tetrahalides produced were removed by reaction with 10% aqueous sodium hydroxide, and reaction of the residual volatile products with chlorine removed the olefin present. Fractionation *in vacuo* and infrared spectroscopic examination showed the residual material to be 1 : 1 : 2 : 2-tetrafluoroethane (1.6 mmoles, 33%).

Infrared Spectra.—The infrared spectra of the following compounds obtained during the present work have been deposited with the Chemical Society:

Compound	C.S. No.	Compound	C.S. No.	Compound	C.S. No.
SiCl ₄	305	H·[CF ₂] ₆ ·SiCl ₃	309	H·[CF ₂] ₆ ·H.....	312
SiHCl ₃	306	CHF ₂ ·CHF ₂	310	CHF ₂ ·CF ₂ ·Si(OMe) ₃ ...	313
CHF ₂ ·CF ₂ ·SiCl ₃	307	H·[CF ₂] ₄ ·H.....	311	CF ₂ Cl·CF ₂ ·SiCl ₃	314
H·[CF ₂] ₄ ·SiCl ₃	308				

The Si-H stretching vibration in trichlorosilane is at 4·42, 4·45 μ (doublet) and the appreciable shift to shorter wavelength compared with the corresponding vibration in alkylsilanes (4·7—4·8 μ) is attributed to the inductive effect of chlorine. The C-H stretching vibration in compounds which contain the CHF₂ group is at 3·34 μ and appears as a single sharp band; the C-H deformation vibration appears as a sharp band in the 7·1—7·4 μ region. Both these bands are absent from the spectrum of trichloro-(2-chloro-1:1:2:2-tetrafluoroethyl)silane. The spectrum of the polysiloxane (CHF₂·CF₂·SiO_{1.5})_n shows the C-H stretching vibration at 3·38 μ . The C-F stretching vibrations appear, as usual, as strong bands in the 8·3—9·1 μ region, and are dwarfed only by the Si-O vibration at 9·10 μ in trimethoxy-(1:1:2:2-tetrafluoroethyl)silane; the last compound shows C-F absorption at 8·37 μ , C-H stretching vibrations at 3·40, 3·52 μ (doublet), and deformation vibrations at 6·85, 7·23 μ . The spectra of the compounds H·[CF₂]_n·H, where $n = 4$ or 6 , are sufficiently different to be used diagnostically.

One of the authors (R. J. M.) is indebted to the Department of Scientific and Industrial Research for a Maintenance Allowance.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

[Received, August 19th, 1955.]