901. *Polyfluoroalkyl Compounds of Silicon. Part IV.* Polyfluoroalkyl-silanes, -silicones, and -polysiloxanes derived from Perfluoroalkylethylenes or Vinylsilanes.*†

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Two methods of synthesis of polyfluoroalkylsilicon compounds are employed: (*a*) free-radical reaction of a compound containing an Si–H bond, *e.g.*, $SiHCl_3$, SiH_2Cl_2, $SiHMeCl_2$, $SiHMe(OEt)_2$, with a fluoro-olefin, *e.g.*, $CF_3\cdot CH\colon CH_2$; (*b*) free-radical addition of a polyfluoroalkyl iodide or bromide, *e.g.*, CF_3I, $CF_2Cl\cdot CFClI$, CF_2Br_2, to an alkenylsilicon compound, *e.g.*, $CH_2\colon CH\cdot SiCl_3$. Silicones and polysiloxanes such as $[CF_3\cdot CH_2\cdot CH_2\cdot Si\cdot O_{1.5}]_n$, $[CF_3\cdot CH_2\cdot CH_2\cdot SiMe\cdot O]_n$, $[(CF_3\cdot CH_2\cdot CH_2)_2Si\cdot O]_n$, $[C_3F_7\cdot CH_2\cdot CH_2\cdot SiMe\cdot O]_n$, $[CF_3\cdot CHMe\cdot CH_2\cdot SiMe\cdot O]_n$, $[CF_3\cdot CH_2\cdot CHI\cdot Si\cdot O_{1.5}]_n$, $[CF_2Cl\cdot CFCl\cdot CH_2\cdot CHI\cdot Si\cdot O_{1.5}]_n$, and $[CF_2Cl\cdot CFCl\cdot CH_2\cdot CHI\cdot SiMe\cdot O]_n$ have been prepared; certain of them show good thermal stability. Reaction of an olefin with dichlorosilane provides a simple direct route to dialkyldichlorosilanes and thence the silicone. The unsaturated compounds $CF_2Br\cdot CH\colon CH\cdot SiMe_3$, $CF_2Cl\cdot CFCl\cdot CH\colon CH\cdot SiMe_3$, and $CF_2\colon CF\cdot CH\colon CH\cdot SiMe_3$, have been isolated. Polymerisation of the diene $CF_2\colon CF\cdot CH\colon CH_2$ to give a rubber is mainly 1 : 4-, but is accompanied by 1 : 2-polymerisation involving only the $CH\colon CH_2$ group; polymerisation of $CF_2\colon CF\cdot CH\colon CH\cdot SiMe_3$ occurs similarly.

The first paper[1] in this series summarised the methods developed for the synthesis of polyfluoroalkyl compounds of silicon. Two of the main methods are exemplified in the present communication: (*a*) reaction of a compound containing an Si–H bond with a fluoro-olefin, (*b*) reaction of a polyfluoroalkyl iodide or bromide with an alkenylsilicon compound. Both involve free radicals as intermediates.

3 : 3 : 3-Trifluoropropene reacts smoothly with trichlorosilane on exposure to ultraviolet light:

$$\mathrm{SiHCl_3 \xrightarrow{h\nu} \cdot SiCl_3 + H\cdot}$$

$$\mathrm{\cdot SiCl_3 + CF_3\cdot CH\colon CH_2 \longrightarrow CF_3\cdot \dot{C}H\cdot CH_2\cdot SiCl_3}$$

$$\mathrm{CF_3\cdot \dot{C}H\cdot CH_2\cdot SiCl_3 + SiHCl_3 \longrightarrow \underset{(I)}{CF_3\cdot CH_2\cdot CH_2\cdot SiCl_3} + \cdot SiCl_3\ (Chain\ transfer)}$$

Unlike the reaction between tetrafluoroethylene and trichlorosilane,[1] there is no need to use a large excess of the chain-transfer agent to obtain good yields of the 1 : 1 adduct, since trifluoropropene polymerises with itself only with difficulty. There was no indication of the formation of material of b. p. higher than that of the 1 : 1 adduct even when approximately equimolar quantities of reactants were used.

The 1 : 1 adduct (91% yield) is assigned structure (I) rather than the alternative $CH_2I\cdot CH(CF_3)\cdot SiCl_3$, since earlier studies[2] have shown that free radicals attack the CH_2 group of compounds $R\cdot CH\colon CH_2$ exclusively no matter what the nature of R. Proof of structure is afforded by the synthesis of compound (I) from 3 : 3 : 3-trifluoropropylmagnesium iodide and silicon tetrachloride. Presence of three fluorine atoms decreases the b. p. by approximately 10° relative to trichloro-*n*-propylsilane. The trichloro-compound (I) rapidly yields the trimethoxy-compound (II) with methanol. Aqueous hydrolysis affords the white solid polysiloxane (III).

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* Part III, *J.*, 1957, 3925.

† Presented in part at the Amer. Chem. Soc. Meeting, Minneapolis, 1955, Abstracts, p. 43M.

[1] Haszeldine and Marklow, *J.*, 1956, 962.

[2] Haszeldine and Steele, *J.*, 1955, 3005, and preceding papers; Haszeldine, *J.*, 1952, 2504.

The polyfluoroalkylsilicone (IV) was synthesised in good yield by photochemical addition of methyldichlorosilane to 3 : 3 : 3-trifluoropropene to give methyl-3 : 3 : 3-trifluoropropyldichlorosilane (V), followed by aqueous hydrolysis. Replacement of a chlorine in compound (I) by methyl raises the b. p. by approximately 10°. The dichloro-compound (V) with methanol gives the corresponding dimethoxy-compound which, when treated with water, also yielded silicone (IV).

$$\underset{\text{(II)}}{CF_3\cdot CH_2\cdot CH_2\cdot Si(OMe)_3} \qquad \underset{\text{(III)}}{[CF_3\cdot CH_2\cdot CH_2\cdot Si\cdot O_{1\cdot 5}]_n} \qquad \underset{\text{(IV)}}{[CF_3\cdot CH_2\cdot CH_2\cdot SiMe\cdot O]_n}$$

$$\underset{\text{(V)}}{CF_3\cdot CH_2\cdot CH_2\cdot SiMeCl_2}$$

A second route to polyfluoroalkyl silicones with fluorine in the γ-position to silicon utilises dichlorosilane in the free-radical addition reactions:

$$SiH_2Cl_2 \xrightarrow{h\nu} \cdot SiHCl_2 + H\cdot$$

$$\cdot SiHCl_2 + CF_3\cdot CH{:}CH_2 \longrightarrow CF_3\cdot\dot{C}H\cdot CH_2\cdot SiHCl_2 \xrightarrow{SiH_2Cl_2} \underset{\text{(VI)}}{CF_3\cdot CH_2\cdot CH_2\cdot SiHCl_2} + \cdot SiHCl_2$$

$$CF_3\cdot CH_2\cdot CH_2\cdot SiHCl_2 \xrightarrow{h\nu} CF_3\cdot CH_2\cdot CH_2\cdot SiCl_2\cdot + H\cdot$$

$$\begin{tikzcd} CF_3\cdot CH_2\cdot CH_2\cdot SiCl_2\cdot + CF_3\cdot CH{:}CH_2 \arrow[r] & CF_3\cdot\dot{C}H\cdot CH_2\cdot SiCl_2\cdot CH_2\cdot CH_2\cdot CF_3 \arrow[d, "CF_3\cdot CH_2\cdot CH_2\cdot SiHCl_2"] \\ & \text{(VII)}\ (CF_3\cdot CH_2\cdot CH_2)_2SiCl_2 + CF_3\cdot CH_2\cdot CH_2\cdot SiCl_2\cdot \end{tikzcd}$$

$$(CF_3\cdot CH_2\cdot CH_2)_2SiCl_2 \xrightarrow{H_2O} [(CF_3\cdot CH_2\cdot CH_2)_2Si\cdot O]_n \quad \text{(VIII)}$$

This route is particularly useful with olefins such as 3 : 3 : 3-trifluoropropene since chain propagation to give $CF_3\cdot CH(CH_2\cdot CH_2\cdot CF_3)\cdot CH_2\cdot SiHCl_2$ does not occur. The 1 : 1 adduct (VI) contains an Si–H bond and, unless an excess of dichlorosilane is used as chain-transfer agent, a secondary reaction sets in whereby the product (VI) reacts with more trifluoropropene to give dichlorodi-(3 : 3 : 3-trifluoropropyl)silane (VII). Isolation of the product (VI) in good yield thus requires an excess of dichlorosilane. If only the precursor (VII) of the silicone (VIII) is required, however, it is readily obtained by reaction of dichlorosilane with an excess of trifluoropropene. Conversion of the dichloro-compound (VII) into the corresponding dimethoxy-compound followed by aqueous hydrolysis, or hydrolysis of the dichloro-compound itself, gives the silicone (VIII).

Silicones containing heptafluoropropyl or trifluoro*iso*propyl groups were similarly obtained:

$$\begin{tikzcd} C_3F_7\cdot CH{:}CH_2 + CH_3\cdot SiHCl_2 \arrow[r, "h\nu"] & C_3F_7\cdot CH_2\cdot CH_2\cdot SiMeCl_2 \arrow[dd, "EtOH"'] \arrow[dr, "H_2O"] & \\ & & {[C_3F_7\cdot CH_2\cdot CH_2\cdot SiMe\cdot O]_n} \\ C_3F_7\cdot CH{:}CH_2 + CH_3\cdot SiH(OEt)_2 \arrow[r, "h\nu"] & C_3F_7\cdot CH_2\cdot CH_2\cdot SiMe(OEt)_2 \arrow[ur, "H_2O"'] & \end{tikzcd}$$

$$CF_3\cdot CMe{:}CH_2 + CH_3\cdot SiHCl_2 \xrightarrow{h\nu} CF_3\cdot CHMe\cdot CH_2\cdot SiMeCl_2 \xrightarrow{H_2O} [CF_3\cdot CHMe\cdot CH_2\cdot SiMe\cdot O]_n$$

Both silicones were colourless viscous oils. That containing the trifluoro*iso*propyl group was partially volatile at 100—200°/10^{-1} mm., suggesting that cyclic siloxanes were present.

The monomers (I), (VII), $C_3F_7\cdot CH_2\cdot CH_2\cdot SiMeCl_2$, and $CF_3\cdot CHMe\cdot CH_2\cdot SiMeCl_2$, the polysiloxane (III), and the silicones (IV), (VIII), and $[C_3F_7{\cdot}CH_2{\cdot}CH_2{\cdot}SiMe{\cdot}O]_n$ are stable at 250° and break down only slowly at 300°.

The second general method used for the synthesis of polyfluoroalkylsilicon compounds involves free-radical addition of polyhalogenoalkyl iodides or bromides, *e.g.*, CF_3I, CF_2Br_2, $CF_2Cl{\cdot}CFClI$, or CCl_3Br, to alkenylsilanes, *e.g.*, $CH_2{:}CH{\cdot}SiX_3$ (X = Cl or alkyl). The reaction follows the general scheme:

$$CF_3I \xrightarrow{h\nu} CF_3{\cdot} + I{\cdot}$$

$$CF_3{\cdot} + CH_2{:}CH{\cdot}SiX_3 \longrightarrow CF_3{\cdot}CH_2{\cdot}\dot{C}H{\cdot}SiX_3 \xrightarrow{CF_3I} CF_3{\cdot}CH_2{\cdot}CHI{\cdot}SiX_3$$

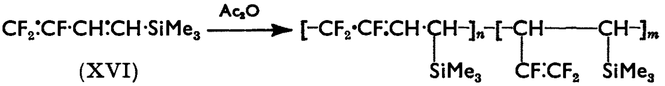
The direction of free-radical attack on the vinylsilane can be predicted with certainty from earlier studies.[2] Vinylsilanes do not homopolymerise *via* the ethylenic link readily, and the chain propagation reaction

$$CF_3{\cdot}CH_2{\cdot}\dot{C}H{\cdot}SiX_3 + CH_2{:}CH{\cdot}SiX_3 \longrightarrow CF_3{\cdot}CH_2{\cdot}CH(SiX_3){\cdot}CH_2{\cdot}\dot{C}H{\cdot}SiX_3$$

is thus insignificant, with consequent high yields of 1 : 1 adducts. The compounds so prepared are shown in the annexed Table.

Polyhalogenoalkane	Vinylsilane	1 : 1 Adduct
CF_3I	$CH_2{:}CH{\cdot}SiMe_3$	$CF_3{\cdot}CH_2{\cdot}CHI{\cdot}SiMe_3$ (IX)
CF_2Br_2	,,	$CF_2Br{\cdot}CH_2{\cdot}CHBr{\cdot}SiMe_3$ (X)
$CF_2Cl{\cdot}CFClI$	,,	$CF_2Cl{\cdot}CFCl{\cdot}CH_2{\cdot}CHI{\cdot}SiMe_3$ (XI)
CF_3I	$CH_2{:}CH{\cdot}SiCl_3$	$CF_3{\cdot}CH_2{\cdot}CHI{\cdot}SiCl_3$ (XII)
$CF_2Cl{\cdot}CFClI$	,,	$CF_2Cl{\cdot}CFCl{\cdot}CH_2{\cdot}CHI{\cdot}SiCl_3$ (XIII)
CCl_3Br	,,	$CCl_3{\cdot}CH_2{\cdot}CHBr{\cdot}SiCl_3$ (XIV)
$CF_2Cl{\cdot}CFClI$	$CH_2{:}CH{\cdot}SiMeCl_2$	$CF_2Cl{\cdot}CFCl{\cdot}CH_2{\cdot}CHI{\cdot}SiMeCl_2$ (XV)

Dehydroiodination of trimethyl-(3 : 3 : 3-trifluoro-1-iodopropyl)silane (IX) by hot quinoline gave the trifluoropropenylsilane but not analytically pure. Dehydrobromination of 1 : 3-dibromo-3 : 3-difluoropropyltrimethylsilane (X) gave, however, the pure propenylsilane $CF_2Br{\cdot}CH{:}CH{\cdot}SiMe_3$. Ethanolic potassium hydroxide removed hydrogen iodide from the adduct (XI) to give the olefin $CF_2Cl{\cdot}CFCl{\cdot}CH{:}CH{\cdot}SiMe_3$, and mild treatment of this in ether with zinc gave trimethyl-(3 : 4 : 4-trifluorobuta-1 : 3-dienyl)silane (XVI). In presence of acetyl peroxide this compound readily gave a polymer containing both $-CF_2{\cdot}CF{:}CH{\cdot}CH-$ and $CF_2{:}CF-$ units as shown by C:C infrared absorption at 5·80 and 5·57 μ, respectively:



$$\underset{\text{(XVI)}}{CF_2{:}CF{\cdot}CH{:}CH{\cdot}SiMe_3} \xrightarrow{Ac_2O} [-CF_2{\cdot}CF{:}CH{\cdot}\underset{SiMe_3}{CH}-]_n-[-\underset{CF{:}CF_2}{CH}-\underset{SiMe_3}{CH}-]_m$$

Polymerisation has thus involved both 1 : 4- and 1 : 2- (on the $-CH{:}CH-$ group) addition, but not 3 : 4-addition, since there was no indication of the presence of a $CH{:}CH-$ band in the spectrum.

Trichloro-(3 : 3 : 3-trifluoro-1-iodopropyl)silane (XII) showed C–I absorption at 275 mμ in light petroleum, and the related compound $CF_3{\cdot}CH_2{\cdot}CHI{\cdot}Si(OEt)_3$ showed maximum absorption at 267 mμ in ethanol. There is thus a shift of the peak to the red compared with a secondary iodide such as *iso*propyl iodide[3] ($\lambda_{max.}$ 261 mμ in light petroleum and in ethanol), or 1 : 1 : 1-trifluoro-3-iodobutane[4] ($\lambda_{max.}$ 264 mμ in ethanol), associated with the presence of silicon α to the $>CHI$ group. The trichloro-compound (XII) is hydrolysed to the glass-like polysiloxane $[CF_3{\cdot}CH_2{\cdot}CHI{\cdot}Si{\cdot}O_{1{\cdot}5}]_n$ which also shows C–I absorption in ethanol at 267 mμ. Reaction of this polysiloxane with dilute aqueous alkali gave the unsaturated polysiloxane $[CF_2{\cdot}CH{:}CH{\cdot}Si{\cdot}O_{1{\cdot}5}]_n$ but not analytically pure.

Attempts to deiodochlorinate trichloro-(3: 3 : 3-trifluoro-1-iodopropyl)silane (XII) to

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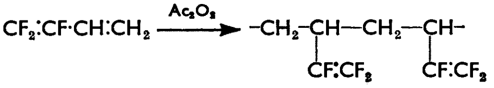
[3] Haszeldine, *J.*, 1953, 1764.

[4] Haszeldine, Leedham, and Steele, *J.*, 1954, 2040.

give the compound $CF_3{\cdot}CH_2{\cdot}CH{:}SiCl_2$ led only to iodine-free material of high molecular weight, suggesting that the monomer, if produced at all, soon polymerised. Trichloro-(3 : 4-dichloro-3 : 4 : 4-trifluoro-1-iodobutyl)silane (XIII) was produced only slowly photochemically, probably because both reactants had only a low vapour pressure. It, and its triethoxy-analogue, showed ultraviolet absorption in light petroleum or ethanol typical of the $-CX_2{\cdot}CH_2{\cdot}CHI{\cdot}Si\lessgtr$ system. Aqueous sodium hydroxide at 100° converted the pentachloride (XIII) into 3 : 4-dichloro-3 : 4 : 4-trifluorobutene and silicate. Hydrolytic carbon–silicon fission thus occurs, somewhat surprisingly, even when the fluorine is as far removed as the γ-carbon atom and with only a weakly electronegative element such as iodine on the α-carbon atom. If $CF_2Cl{\cdot}CFCl{\cdot}CH_2{\cdot}CH_2I$, which can also be obtained by photochemical reaction of 1 : 2-dichloro-1 : 2 : 2-trifluoro-1-iodoethane with ethylene, were the intermediate hydrolysis product, it would be dehydroiodinated by the aqueous base to give the butene. Alternatively, initial dehydroiodination to $CF_2Cl{\cdot}CFCl{\cdot}CH{:}CH{\cdot}Si\lessgtr$ would enable the inductive effect of the $CF_2Cl{\cdot}CFCl-$ group to be relayed to the silicon, so promoting nucleophilic attack on that atom.[1] Aqueous hydrolysis of the halide (XIII) yields the polysiloxane, which also shows C–I absorption in ethanolic solution. The polysiloxane is also cleaved hydrolytically by aqueous base at 100° to give 3 : 4-dichloro-3 : 4 : 4-trifluorobutene.

This olefin shows the C:C stretching vibration as a weak band at 6·03 μ, the position typical of a polyfluoroalkylethylene of type $R{\cdot}CH{:}CH_2$. The out-of-plane C–H vibrations are at 10·19 and 10·38 μ (cf. 10·10, 10·99 μ when R is a hydrocarbon group). Zinc and ether dechlorinate the olefin to the diene $CF_2{:}CF{\cdot}CH{:}CH_2$. This readily polymerises, and study of the infrared spectra of the polymers shows that both 1 : 2- and (predominantly) 1 : 4-addition occur. It was pointed out earlier [5] that perfluorobutadiene behaves in some ways as if conjugation between the double bonds was poor, *i.e.*, as if the double bonds were isolated. Of the two types of double bond in 1 : 1 : 2-trifluorobuta-1 : 3-diene, the $-CH{:}CH_2$ type will certainly be more sensitive to free-radical attack than the $-CF{:}CF_2$ type.[2] It is not unexpected therefore to find a band in the infrared spectrum of the polymer produced with acetyl peroxide at 5·58 μ typical of the $-CF{:}CF_2$ group, *i.e.*, polymerisation involving 1 : 2-addition occurs in part:



$$CF_2{:}CF{\cdot}CH{:}CH_2 \xrightarrow{Ac_2O_2} -CH_2-\underset{CF:CF_2}{\underset{|}{CH}}-CH_2-\underset{CF:CF_2}{\underset{|}{CH}}-$$

There is no band in the region typical of $-CH{:}CH_2$ group absorption, *i.e.*, 1 : 2-polymerisation involving the $-CF{:}CF_2$ group does not occur. The main C:C band is at 5·80 μ, typical of the $-CF_2{\cdot}CF{:}CH{\cdot}CH_2-$ group produced by 1 : 4-polymerisation:

$$CH_2{:}CH{\cdot}CF{:}CF_2 \xrightarrow{Ac_2O_2} -CH_2{\cdot}CH{:}CF{\cdot}CF_2{\cdot}CH_2{\cdot}CH{:}CF{\cdot}CF_2-$$

Benzoyl peroxide converts the diene into a polymer containing mainly $-CH_2{\cdot}CH{:}CF{\cdot}CF_2-$ units. The double bonds in the diene thus show appreciable, though incomplete, conjugation.

1 : 2-Dichloro-1 : 2 : 2-trifluoro-1-iodoethane reacted readily with dichloromethylvinylsilane to give the 1 : 1 adduct (XV) which, on aqueous hydrolysis, gave the silicone $[CF_2Cl{\cdot}CFCl{\cdot}CH_2{\cdot}CHI{\cdot}SiMe{\cdot}O]_n$.

The polysiloxane $[CCl_3{\cdot}CH_2{\cdot}CHBr{\cdot}Si{\cdot}O_{1\cdot5}]_n$, obtained by aqueous hydrolysis of (1-bromo-3 : 3 : 3-trichloropropyl)trichlorosilane (XIV), contains a terminal CCl_3 group; when this was treated with concentrated sulphuric acid hydrolysis occurred to give the polysiloxane $[HO_2C{\cdot}CH_2{\cdot}CHBr{\cdot}Si{\cdot}O_{1\cdot5}]_n$.

The above results show that the free-radical addition approach for the synthesis of polyfluoroalkyl silicon compounds is convenient and sufficiently versatile to enable

[5] Haszeldine, *J.*, 1952, 4423.

silicones and polysiloxanes to be prepared with the fluorine atoms attached to carbon in the α- or γ-position relative to silicon. The site of the fluorine has a profound influence on the thermal and hydrolytic stability of such compounds, as will be shown in a later paper.

EXPERIMENTAL

Reactions were carried out in sealed tubes which were filled by use of a conventional apparatus for manipulation of volatile compounds. Air and moisture were thus excluded, and the tubes were sealed *in vacuo*.

Reaction of 3 : 3 : 3-*Trifluoropropene with Trichlorosilane*.—The olefin (60 mmoles) and trichlorosilane (62 mmoles), sealed in a 200-ml. silica tube and shaken whilst exposed to ultraviolet light for 96 hr., gave unchanged olefin (5%), trichlorosilane (6%), and *trichloro*-(3 : 3 : 3-*trifluoropropyl*)*silane* (91%) (Found: C, 15·6; H, 1·6. $C_3H_4Cl_3F_3Si$ requires C, 15·6; H, 1·7%), b. p. 113°.

This silane (1·1 g.), added dropwise to an excess of anhydrous methanol (4 ml.), then shaken for 1 hr., gave, on distillation, *trimethoxy*-(3 : 3 : 3-*trifluoropropyl*)*silane* (79%) (Found: C, 33·1; H, 6·1. $C_6H_{13}O_3F_3Si$ requires C, 33·0; H, 6·0%), b. p. 144°/760 mm., 84°/90 mm.

An ethereal solution of trichloro-(3 : 3 : 3-trifluoropropyl)silane (2·1 g. in 10 ml.) was shaken with water (10 ml.) for 30 min. The ether was evaporated at room temperature from the dried (Na_2SO_4) extract to give the *polysiloxane* $[CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}Si{\cdot}O_{1.5}]_n$ (93%) (Found: C, 24·0; H, 2·9. $C_3H_4O_{1.5}F_3Si$ requires C, 24·2; H, 2·7%) as a white, free-running solid.

Reaction of ethereal 3 : 3 : 3-trifluoropropylmagnesium iodide (0·16 mole) with silicon tetrachloride (0·51 mole) at 20—30° for 24 hr. gave trichloro-(3 : 3 : 3-trifluoropropyl)silane, b. p. 113—114°, in 23% yield.

Reaction of 3 : 3 : 3-*Trifluoropropene with Methyldichlorosilane*.—The olefin (53 mmoles) and methyldichlorosilane (55 mmoles), exposed to ultraviolet light in a sealed 200-ml. silica tube for 82 hr., gave *methyl*-3 : 3 : 3-*trifluoropropyldichlorosilane* (92%) (Found: C, 22·8; H, 3·2. $C_4H_7Cl_2F_3Si$ requires C, 22·8; H, 3·3%), b. p. 125°. No unchanged olefin was detected.

Methyl-3 : 3 : 3-trifluoropropyldichlorosilane (1·7 g.), added slowly with shaking to anhydrous methanol, gave *dimethoxy-methyl*-3 : 3 : 3-*trifluoropropylsilane* (71%) (Found: C, 35·4; H, 6·4. $C_6H_{13}O_2F_3Si$ requires C, 35·6; H, 6·4%), b. p. 85°/150 mm., 100°/283 mm.

Methyl-3 : 3 : 3-trifluoropropyldichlorosilane (3·1 g.) was added slowly to a stirred mixture of ether (10 ml.) and water (10 ml.). The ethereal extract was dried (Na_2SO_4) and removal of the ether on a water-bath left the *silicone* $[(CF_3{\cdot}CH_2{\cdot}CH_2)(CH_3)Si{\cdot}O]_n$ (90%) (Found: C, 30·7; H, 4·4. $C_4H_7OF_3Si$ requires C, 30·8; H, 4·5%) as a clear, colourless, viscous oil. A similar viscous silicone was obtained by aqueous hydrolysis of the dimethoxy-compound.

Reaction of 3 : 3 : 3-*Trifluoropropene with Dichlorosilane*.—The olefin (40 mmoles) and dichlorosilane (100 mmoles) were sealed in a 200-ml. silica tube and exposed to ultraviolet light for 64 hr. Distillation *in vacuo* gave unchanged dichlorosilane (51%), unchanged olefin (3%), trichlorosilane (2%), *dichloro*-3 : 3 : 3-*trifluoropropylsilane* (83%) (Found: C, 18·2; H, 2·4. $C_3H_5Cl_2F_3Si$ requires C, 18·3; H, 2·5%), b. p. 90—91°, and a small amount of liquid of higher b. p., probably $(CF_3{\cdot}CH_2{\cdot}CH_2)_2SiCl_2$ (see below).

Dichloro-3 : 3 : 3-trifluoropropylsilane (70 mmoles; prepared as above) and 3 : 3 : 3-trifluoropropene (65 mmoles), irradiated for 80 hr. in a silica tube, gave unchanged reactants (8%) and *dichlorodi*-(3 : 3 : 3-*trifluoropropyl*)*silane* (85%) (Found: C, 24·4; H, 2·5. $C_6H_8Cl_2F_6Si$ requires C, 24·6; H, 2·7%), b. p. 162—163°.

Dichlorosilane (35 mmoles) and 3 : 3 : 3-trifluoropropene (102 mmoles), irradiated for 107 hr. in a silica tube, gave unchanged olefin, dichloro-3 : 3 : 3-trifluoropropylsilane (9%), and dichlorodi-(3 : 3 : 3-trifluoropropyl)silane (77%), b. p. 162—163°. Yields are based on dichlorosilane.

Reaction of dichlorodi-(3 : 3 : 3-trifluoropropyl)silane (2·9 g.) with a 10% excess of anhydrous methanol gave *dimethoxydi*-(3 : 3 : 3-*trifluoropropyl*)*silane* (88%) (Found: C, 33·5; H, 4·9. $C_8H_{14}O_2F_6Si$ requires C, 33·8; H, 4·9%), b. p. 175—176°/760 mm., 96°/60 mm.

To dichlorodi-(3 : 3 : 3-trifluoropropyl)silane (2·7 g.) and ether (5 ml.) was slowly added a saturated solution of water in ether (20 ml.). The solution was then poured with stirring into an excess of water (10 ml.). Removal of the ether from the dried ethereal extract gave the *silicone* $[(CF_3{\cdot}CH_2{\cdot}CH_2)_2Si{\cdot}O]_n$ (91%) (Found: C, 30·1; H, 3·5. $C_6H_8OF_6Si$ requires C, 30·3; H, 3·4%) as a colourless oil with negligible volatility at 200°. A similar oil was obtained by aqueous hydrolysis of the ethereal dimethoxy-compound.

Reaction of 3 : 3 : 4 : 4 : 5 : 5 : 5-*Heptafluoropentene with Methyldichlorosilane or Methyldiethoxysilane.*—The olefin (50 mmoles) and methyldichlorosilane (60 mmoles) were sealed in a 200-ml. silica tube which was shaken vigorously whilst horizontal so as to disperse the reactants as a liquid film over the whole surface of the tube. Smooth reaction ensued on irradiation and after 88 hr. distillation gave *dichloro*-3 : 3 : 4 : 4 : 5 : 5 : 5-*heptafluoropentylmethylsilane* (73%) (Found: C, 23·0; H, 2·1. $C_6H_7Cl_2F_7Si$ requires C, 23·2; H, 2·3%), b. p. 72°/70 mm., 147°/760 mm.

A portion of this product (1·8 g.) in ether (5 ml.) was added slowly to a stirred mixture of water (5 ml.) and ether (10 ml.). Removal of the ether from the dried ethereal extracts left the *silicone* $[C_3F_7\cdot CH_2\cdot CH_2\cdot SiMe\cdot O]_n$ (87%) (Found: C, 27·9; H, 2·7. $C_6H_7OF_7Si$ requires C, 28·1; H, 2·7%) as a colourless viscous liquid.

To a second portion of dichloro-3 : 3 : 4 : 4 : 5 : 5 : 5-heptafluoropentylmethylsilane (3·2 g.) was added a 10% excess of anhydrous ethanol. After being heated at 50° for 2 hr. the solution was distilled to give *diethoxy*-3 : 3 : 4 : 4 : 5 : 5 : 5-*heptafluoropentylmethylsilane* (67%) (Found: C, 36·4; H, 5·2. $C_{10}H_{17}O_2F_7Si$ requires C, 36·6; H, 5·2%), b. p. 82—83°/28 mm. Addition of water to a shaken ethereal solution of the diethoxy-compound and removal of ether from the dried ethereal extract gave the silicone $[C_3F_7\cdot CH_2\cdot CH_2\cdot SiMe\cdot O]_n$ (91%) (Found: C, 28·0; H, 2·6%).

Methyldiethoxysilane (30 mmoles) and 3 : 3 : 4 : 4 : 5 : 5 : 5-heptafluoropentene (30 mmoles), shaken and exposed to ultraviolet light for 3 days, gave diethoxy-3 : 3 : 4 : 4 : 5 : 5 : 5-heptafluoropentylmethylsilane (79%) (Found: C, 36·6; H, 5·0%), b. p. 82—84°/28 mm., identical with the material described above.

Reaction of 3 : 3 : 3-*Trifluoro*-2-*methylpropene with Methyldichlorosilane.*—3 : 3 : 3-Trifluoro-2-methylpropene (56 mmoles) and methyldichlorosilane (61 mmoles) in a 200-ml. silica tube were shaken and exposed to ultraviolet light for 98 hr. Distillation gave *methyl*-(3 : 3 : 3-*trifluoro*-2-*methylpropyl*)*dichlorosilane* (63%) (Found: C, 26·5; H, 4·1. $C_5H_9Cl_2F_3Si$ requires C, 26·7; H, 4·0%), b. p. 139°.

To a stirred solution of the dichloro-compound (2·6 g.) in ether (8 ml.) was slowly added wet ether (10 ml.), then water (5 ml.) dropwise. Removal of ether from the dried ethereal extract gave the *silicone* $[CF_3\cdot CHMe\cdot CH_2\cdot SiMe\cdot O]_n$ (Found: C, 35·0; H, 5·4. $C_5H_9OF_3Si$ requires C, 35·3; H, 5·3%) as a mobile oil. Approximately 10% of the oil distilled when it was heated from 100° to 200°/10^{-1} mm. in a short-path still, indicating the presence of cyclic polysiloxanes.

Thermal Stability of Certain Fluoroalkylsilicon Compounds.—Preliminary information was obtained about thermal stability by heating samples (1·0—1·5 g.) in 20-ml., sealed, evacuated, silica tubes for 24 hr. The compounds $CF_3\cdot CH_2\cdot CH_2\cdot SiCl_3$, $(CF_3\cdot CH_2\cdot CH_2)_2SiCl_2$, $C_3F_7\cdot CH_2\cdot CH_2\cdot SiMeCl_2$, and $CF_3\cdot CHMe\cdot CH_2\cdot SiMeCl_2$ failed to give volatile breakdown products at 200° or 250°, and were partially decomposed (15—20%) at 300° after 6 hr. The polysiloxane, $[CF_3\cdot CH_2\cdot CH_2\cdot Si\cdot O_{1\cdot 5}]_n$, and the silicones, $[CF_3\cdot CH_2\cdot CH_2\cdot SiMe\cdot O]_n$, $[(CF_3\cdot CH_2\cdot CH_2)_2Si\cdot O]_n$, and $[C_3F_7\cdot CH_2\cdot CH_2\cdot SiMe\cdot O]_n$, were unaffected at 250° and gave only a low yield (10—15%) of volatile product after 6 hr. at 300°.

Reaction of Vinyltrimethylsilane with Trifluoroiodomethane.—The olefin (75 mmoles) and trifluoroiodomethane (67 mmoles), sealed in a 200-ml. silica tube and shaken whilst exposed to ultraviolet light for 102 hr., gave unchanged olefin (12%), only a trace of trifluoroiodomethane, and *trimethyl*-(3 : 3 : 3-*trifluoro*-1-*iodopropyl*)*silane* (79%) (Found: C, 24·3; H, 4·2. $C_6H_{12}F_3ISi$ requires C, 24·3; H, 4·1%), b. p. 72°/20 mm.

Dehydroiodination occurred when the compound (2·1 g.) was heated to 120° with quinoline, but final purification of the trimethyltrifluoropropenylsilane (Found: *M*, 162. Calc. for $C_6H_{11}F_3Si$: *M*, 168) could not be effected on the scale used.

Reaction of Vinyltrimethylsilane with Dibromodifluoromethane.—The bromo-compound (69 mmoles) and the olefin (70 mmoles), irradiated in a 200-ml. silica tube for 120 hr., gave unchanged olefin (23%) and dibromodifluoromethane (21%) and 1 : 3-*dibromo*-3 : 3-*difluoropropyltrimethylsilane* (79% based on bromo-compound consumed) (Found: C, 23·0; H, 4·1. $C_6H_{12}Br_2F_2Si$ requires C, 23·2; H, 3·9%), b. p. 95°/25 mm.

Reaction of this product (4·1 g.) with quinoline (8 g.) at 120° in a sealed tube for 10 hr. gave unchanged starting material (37%) and 3-*bromo*-3 : 3-*difluoropropenyltrimethylsilane* (48% based on starting material consumed) (Found: C, 31·8; H, 4·8. $C_6H_{11}BrF_2Si$ requires C, 31·5; H, 4·8%), b. p. 66—68°/52 mm. The compound gave a dibromide when exposed to ultraviolet light with bromine for 30 min.

Reaction of Vinyltrimethylsilane with 1 : 2-*Dichloro*-1-*iodotrifluoroethane*.—The same quantities and conditions were used as for the dibromodifluoromethane reaction above. Distillation gave unchanged olefin (10%) and 3 : 4-*dichloro*-3 : 4 : 4-*trifluoro*-1-*iodobutyltrimethylsilane* (66%) (Found: C, 22·1; H, 3·2. $C_7H_{12}Cl_2F_3ISi$ requires C, 22·2; H, 3·2%), b. p. 99—100°/9 mm.

To this compound (3·9 g.), dissolved in ethanol (5 ml.), was added dropwise with stirring a 10% excess of 10% ethanolic potassium hydroxide at 0° during 3 hr. Addition of an excess of water (400 ml.), separation of the lower layer, drying, and distillation gave 3 : 4-*dichloro*-3 : 4 : 4-*trifluorobutenyltrimethylsilane* (57%) (Found: C, 33·3; H, 4·5. $C_7H_{11}Cl_2F_3Si$ requires C, 33·5; H, 4·4%), b. p. 57—59°/15 mm. The presence of the double bond was confirmed by the rapid absorption of chlorine at room temperature in the dark.

3 : 4-Dichloro-3 : 4 : 4-trifluorobutenyltrimethylsilane (4·4 g.) in ether (5 ml.) was added dropwise to powdered zinc (4 g.) and ether (25 ml.) at 50°. Dehalogenation was complete after 4 hr. and treatment of the filtered solution with an excess of water, followed by distillation of the organic layer, gave *trimethyl*-(3 : 4 : 4-*trifluorobuta*-1 : 3-*dienyl*)*silane* (31%) (Found: C, 46·3; H, 6·0. $C_7H_{11}F_3Si$ requires C, 46·6; H, 6·1%), b. p. 25°/25 mm., approx. 110—113°/760 mm. When this was heated to 100° in a sealed tube with a small amount of acetyl peroxide, polymerisation occurred to give a white, stable solid showing $-CF{:}CF_2$ absorption at 5·57 μ, stronger $-CF_2{\cdot}CH{:}CF{\cdot}CH-$ absorption at 5·80 μ, and no band in the $-CH{:}CH-$ region (5·9—6·3 μ).

Reaction of Trifluoroiodomethane with Vinyltrichlorosilane.—The iodo-compound (22 mmoles) and vinyltrichlorosilane (27·5 mmoles) in a 200-ml. silica tube were irradiated for 9·5 days. Distillation gave unchanged reactants and *trichloro*-(3 : 3 : 3-*trifluoro*-1-*iodopropyl*)*silane* (35%) (Found: C, 10·1; H, 0·9; Si, 7·7. $C_3H_3Cl_3F_3ISi$ requires C, 10·1; H, 0·8; Si, 7·9%), b. p. 79°/25 mm. Ultraviolet absorption:

Solvent	$\lambda_{max.}$	ε	$\lambda_{min.}$	ε
Light petroleum	275	400	228	60
Dioxan	265	530	231	160
EtOH *	267	430	226	90

* Reacts with solute to give $CF_3{\cdot}CH_2{\cdot}CHI{\cdot}Si(OEt)_3$.

Trichloro-(3 : 3 : 3-trifluoro-1-iodopropyl)silane (2·27 mmoles), shaken with water (50 ml.) and ether (50 ml.), gave, on evaporation of the dried ethereal extract, the *polysiloxane* $[CF_3{\cdot}CH_2{\cdot}CHI{\cdot}Si{\cdot}O_{1.5}]_n$ (88%) (Found: C, 13·1; H, 1·5. $C_3H_3F_3ISiO_{1.5}$ requires C, 13·1; H, 1·1%) as a colourless glass. Ultraviolet absorption in EtOH: $\lambda_{max.}$ 267 (ε 420), $\lambda_{min.}$ 232 (ε 135).

The polysiloxane (0·8 mmole) was shaken with 2% aqueous sodium hydroxide (15 ml.) for 10 min., then kept overnight at 20°. The aqueous solution gave a strong positive test for iodide. There were no volatile products. Acidification and extraction with ether (50 ml.) gave a white powder, m. p. >250°, probably the polysiloxane $[CF_3{\cdot}CH{:}CH{\cdot}Si{\cdot}O_{1.5}]_n$ but not analytically pure.

Trichloro-(3 : 3 : 3-trifluoro-1-iodopropyl)silane (3·48 mmoles), anhydrous tetrahydrofuran (3 ml.), and zinc powder (0·6 g.) were shaken in a sealed tube at 75° for 14 hr. Only polymeric material was isolated from the organic phase after removal of solid products by centrifuging. The iodo-compound (4·35 mmoles) failed to react with zinc in presence of light petroleum during 15 hr. at 20°. The iodo-compound (4·25 mmoles), zinc (0·73 g.), and anhydrous ether (4 ml.), shaken at 20° for 12 hr. in a sealed tube, gave only polymer on examination of the ethereal phase.

Reaction of 1 : 2-*Dichloro*-1-*iodotrifluoroethane with Vinyltrichloro*)*silane*.—The iodo-compound (75 mmoles) and vinyltrichlorosilane (41 mmoles), exposed to ultraviolet light for 9 days, gave unchanged reactants and *trichloro*-(3 : 4-*dichloro*-3 : 4 : 4-*trifluoro*-1-*iodobutyl*)*silane* (26%) (Found: C, 10·9; H, 0·7. $C_4H_3Cl_5F_3ISi$ requires C, 10·9; H, 0·7%), b. p. 124°/*ca.* 1 mm. Ultraviolet spectra:

Solvent	$\lambda_{max.}$	ε	$\lambda_{min.}$	ε
Light petroleum	275·5	400	231	100
Dioxan	264	485	231	140
EtOH *	267·5	440	223	50

* Reacts with solute to give $CF_2Cl{\cdot}CFCl{\cdot}CH_2{\cdot}CHI{\cdot}Si(OEt)_3$.

Trichloro-(3 : 4-dichloro-3 : 4 : 4-trifluoro-1-iodobutyl)silane (1·43 mmoles) and 10% aqueous sodium hydroxide (20 ml.), heated at 100° (6 hr.), gave 3 : *4-dichloro-*3 : 4 : *4-trifluorobutene* (58%) (Found: C, 27·1; H, 1·9%; *M*, 179. $C_4H_3Cl_2F_3$ requires C, 26·8; H, 1·7%; *M*, 179), b. p. 79° (isoteniscope).

Hydrolysis by shaking a solution of the iodo-compound (3·57 mmoles) in ether (50 ml.) with water (50 ml.) for 1 hr. gave, on removal of the ether, the impure polysiloxane $[CF_2Cl{\cdot}CFCl{\cdot}CH_2{\cdot}CHI{\cdot}Si{\cdot}O_{1.5})_n$, m. p. 48°, which could not be purified to give satisfactory analytical figures. Absorption spectrum in EtOH: $\lambda_{max.}$ 268 (ε 395), $\lambda_{min.}$ 233 (ε 165). Hydrolysis of the polysiloxane with 10% aqueous sodium hydroxide at 100° gave 3 : 4-dichloro-3 : 4 : 4-trifluorobutene (50%), identified by means of its infrared spectrum.

Polymerisation of 1 : 1 : 2-*Trifluorobuta*-1 : 3-*diene*.—3 : 4-Dichloro-3 : 4 : 4-trifluorobutene (30 mmoles) in dry ether (10 ml.) was added dropwise to zinc dust (4 g.) and refluxing ether (20 ml.) during 6 hr. The volatile product, removed through a reflux condenser kept at 10°, was transferred to an apparatus for manipulation of volatile compounds and distilled to give 1 : 1 : 2-trifluorobuta-1 : 3-diene (61%) (Found: *M*, 108. Calc. for $C_4H_3F_3$: *M*, 108), b. p. 8° (isoteniscope). Tarrant and Lilyquist [6] report b. p. 7·8° for this compound.

The diene (1·1 g.) and acetyl peroxide (5 mg.), heated in an evacuated, sealed, silica tube at 100° for 2 hr., gave a white rubber which was dissolved in chloroform and washed with dilute aqueous sodium hydroxide to remove traces of acetic acid, etc. The gum-rubber obtained on evaporation of the chloroform solution hardened if kept in air. A sample of the gum-rubber was softened by chloroform until it could be pressed into a thin film between two sodium chloride plates. Examination of its infrared spectrum revealed C⁚C band at 5·58 and 5·80 μ, with the former one-fifth of the intensity of the second. There was no absorption at 6·0—6·3 μ. A second elastomer was obtained from the diene (1·0 g.) and benzoyl peroxide (5 mg.) at 100° for 6 hr. This was swollen by, but did not dissolve in, chloroform. Examination of the infrared spectrum of a thin film of this polymer revealed a strong C⁚C band at 5·80, a weak band at 5·5—5·75, and absence of a band at 6·0—6·3 μ.

Reaction of Bromotrichloromethane with Vinyltrichlorosilane.—The bromo-compound (53 mmoles) and vinyltrichlorosilane (55 mmoles), sealed and shaken in a 200-ml. silica tube and exposed to ultraviolet light for 90 hr., gave (*1-bromo*-3 : 3 : *3-trichloropropyl)trichlorosilane* (79%) (Found: C, 10·1; H, 0·9. $C_3H_3BrCl_6Si$ requires C, 10·0; H, 0·8%), b. p. 145°/35 mm. A solution of the product (1·3 g.) in ether (5 ml.) poured into stirred ice-water (10 ml.) gave, on evaporation of the dried ethereal solution, the *polysiloxane* $[CCl_3{\cdot}CH_2{\cdot}CHBr{\cdot}Si{\cdot}O_{1.5}]_n$ (89%) (Found: C, 12·8; H, 1·2. $C_3H_3BrCl_3SiO_{1.5}$ requires C, 13·0; H, 1·1%) as a white solid. The polysiloxane liberated hydrogen chloride when heated with concentrated sulphuric acid at 100°. After being washed with water the polysiloxane showed a distinct acid reaction and titration with alkali indicated the presence of $[HO_2C{\cdot}CH_2{\cdot}CHBr{\cdot}Si{\cdot}O_{1.5}]_n$, although an analytically pure sample could not be obtained; infrared spectroscopic examination showed the presence of the carboxyl group by its broad absorption at 5·85 μ.

Reaction of 1 : 2-*Dichloro*-1-*iodotrifluoroethane with Methylvinyldichlorosilane*.—The iodo-compound (63 mmoles) and the olefin (65 mmoles) were exposed to ultraviolet light for 89 hr. to give unchanged olefin (27%) and *dichloro*-(3 : *4-dichloro*-3 : 4 : *4-trifluoro*-1-*iodobutyl)methylsilane* (58%) (Found: C, 14·1; H, 1·2. $C_5H_6Cl_4F_3ISi$ requires C, 14·3; H, 1·4%), b. p. 108°/25 mm. Hydrolysis of the product with water as described above gave the *silicone* $[CF_2Cl{\cdot}CFCl{\cdot}CH_2{\cdot}CHI{\cdot}SiMe{\cdot}O]_n$ (81%) (Found: C, 16·2; H, 1·6. $C_5H_6Cl_2F_3ISiO$ requires C, 16·4; H, 1·6%) as a colourless viscous liquid.

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[6] Tarrant and Lilyquist, *J. Amer. Chem. Soc.*, 1955, **77**, 3640.