203. *Polyfluoroalkyl Compounds of Silicon. Part II.* Free-radical Reaction of Dialkylsilanes with Fluoro-olefins.*†

By A. M. Geyer and R. N. Haszeldine.

A dialkylsilane R_2SiH_2 reacts with tetrafluoroethylene to give

$R_2SiH\cdot[CF_2\cdot CF_2]_n\cdot H$

Secondary reactions produce compounds of the type

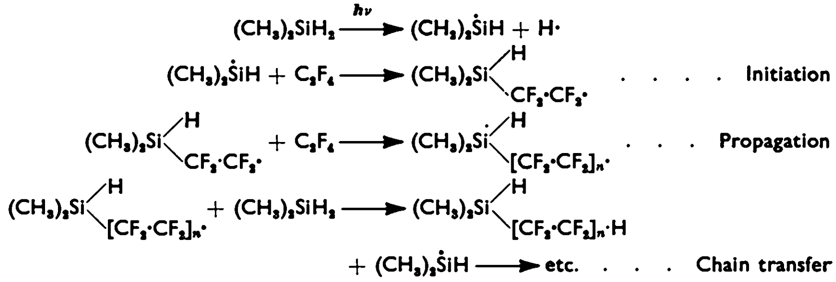
$H\cdot[CF_2\cdot CF_2]_x\cdot SiR_2\cdot[CF_2\cdot CF_2]_y\cdot H$

Radical-chain mechanisms are proposed for these reactions. The value of n is determined by the reactant ratio, and yields of $Me_2SiH(CF_2\cdot CF_2H)$ as high as 83% have been obtained from dimethylsilane. The SiH bond is reactive and further reaction with tetrafluoroethylene gives $Me_2Si(CF_2\cdot CF_2H)_2$. The polyfluoroalkyl silicon compounds are stable to water but with aqueous alkali liberate the polyfluoroalkyl group quantitatively as $H\cdot[CF_2\cdot CF_2]_n\cdot H$. Variations in the Si–H infrared frequency are discussed.

A clear idea of the reactivity and reactions of the $SiCl_3$ radical derived from trichlorosilane [1] can be gained from the study [2] of perfluoroalkyl radicals such as CF_3, and the convenient synthesis of compounds $H\cdot[CF_2\cdot CF_2]_n\cdot SiCl_3$ by reaction of trichlorosilane with tetrafluoroethylene was thus clearly predictable. Much less predictable, however, are the properties and reactivities of inorganic radicals derived from silanes such as $CH_3\cdot SiH_3$, $(CH_3)_2SiH_2$, or SiH_4 or in general $RSiH_3$, R_2SiH_2 ($R = H$, alkyl, aryl, etc.), containing more than one hydrogen atom linked directly to silicon. We now record the beginning of a general investigation [3] of the reaction of free radicals derived from inorganic covalent hydrides with olefins which are sensitive to free-radical attack, *e.g.*, fluoro-olefins, and, specifically, the reaction of dimethylsilane with tetrafluoroethylene.

Dimethylsilane and tetrafluoroethylene fail to react in the dark even during four months. Exposure to light of wavelength <3000 Å initiates an extremely rapid chain reaction; liquid products, formed in the vapour phase as a mist, appear immediately and the reaction, which is soon complete, is thus considerably faster than the corresponding reaction of trichlorosilane described in Part I. The products are all of the types (I)—(III). Hydrogen is not detectable, and all of the tetrafluoroethylene is consumed. The reaction can be effected with equal facility at room temperature in sealed silica tubes at super-atmospheric pressure, or in the apparatus described earlier [4] for photochemical reactions on approximately 1 molar scale at less than atmospheric pressure.

The main factor influencing the ratio of the products (I), (II), and (III) is the mole-ratio of dimethylsilane to tetrafluoroethylene used, and this reveals the facility of the chain-transfer step in the radical-chain reaction :



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* Part I, *J.*, 1956, 962.

† For a preliminary communication see *Nature*, 1956, **178**, 808.

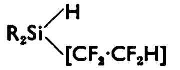
[1] Haszeldine and Marklow, *J.*, 1956, 962.

[2] *E.g.*, see Haszeldine and Osborne, *J.*, 1956, 61, and preceding papers.

[3] Geyer and Haszeldine, *Nature*, 1956, **178**, 808.

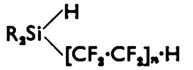
[4] Barr and Haszeldine, *J.*, 1955, 1881.

Use of a 5 : 1 ratio of dimethylsilane to tetrafluoroethylene gives the compounds (I; R = Me), (II; R = Me, $n = 2$), and (III; R = Me, $x = y = 1$) in 83, 7, and 2% yield respectively. The main reaction involved in the formation of compounds containing more than



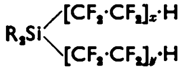
$R_2Si\begin{smallmatrix}H\\ [CF_2\cdot CF_2H]\end{smallmatrix}$

(I)



$R_2Si\begin{smallmatrix}H\\ [CF_2\cdot CF_2]_n\cdot H\end{smallmatrix}$

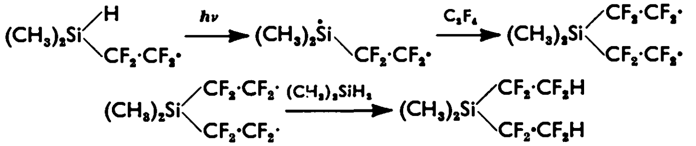
(II)



$R_2Si\begin{smallmatrix}[CF_2\cdot CF_2]_x\cdot H\\ [CF_2\cdot CF_2]_y\cdot H\end{smallmatrix}$

(III)

one C_2F_4 unit per silicon atom is thus the chain-propagation mentioned above rather than the formation of mixed silyl alkyl diradicals; *e. g.*,



$$(CH_3)_2Si\begin{smallmatrix}H\\ CF_2\cdot CF_2\cdot\end{smallmatrix} \xrightarrow{h\nu} (CH_3)_2\dot{S}i\begin{smallmatrix}\\ CF_2\cdot CF_2\cdot\end{smallmatrix} \xrightarrow{C_2F_4} (CH_3)_2Si\begin{smallmatrix}CF_2\cdot CF_2\cdot\\ CF_2\cdot CF_2\cdot\end{smallmatrix}$$

$$(CH_3)_2Si\begin{smallmatrix}CF_2\cdot CF_2\cdot\\ CF_2\cdot CF_2\cdot\end{smallmatrix} \xrightarrow{(CH_3)_2SiH_2} (CH_3)_2Si\begin{smallmatrix}CF_2\cdot CF_2H\\ CF_2\cdot CF_2H\end{smallmatrix}$$

The compound (III; R = Me, $x = y = 1$) is formed by the further reaction of (I; R = Me) with tetrafluoroethylene as described below. The predominance of the propagation step with tetrafluoroethylene again illustrates the ease of free-radical polymerisation of this olefin and the necessity for a highly efficient chain-transfer agent if the chain length of the polymer is to be controlled.[5]

The absence of even traces of hydrogen from the reaction products suggests [1,6] that attack by hydrogen atoms on the olefin occurs to give a polyfluoroalkyl radical which generates a dimethylsilyl radical from dimethylsilane and is thereby converted into 1 : 1 : 2 : 2-tetrafluoroethane:

$$(CH_3)_2SiH_2 \xrightarrow{h\nu} (CH_3)_2\dot{S}iH + H\cdot$$

$$H\cdot + C_2F_4 \longrightarrow CHF_2\cdot CF_2\cdot \xrightarrow{(CH_3)_2SiH_2} CHF_2\cdot CHF_2 + (CH_3)_2\dot{S}iH$$

A dimethylsilane : tetrafluoroethylene ratio of *ca.* 1·5 : 1 gives dimethyl-(1 : 1 : 2 : 2-tetrafluoroethyl)silane (I; R = Me) in *ca.* 50% yield, and the amount of product containing more than one C_2F_4 unit per silicon atom is correspondingly increased. The material containing two C_2F_4 units per silicon atom is an isomeric mixture of dimethyl-(1 : 1 : 2 : 2 : 3 : 3 : 4 : 4-octafluorobutyl)silane (II; R = Me, $n = 2$) formed in 20% yield, and dimethyldi-(1 : 1 : 2 : 2-tetrafluoroethyl)silane (III; R = Me, $x = y = 1$) formed in 7% yield. The material containing three C_2F_4 units per silicon atom is similarly an isomeric mixture of (1 : 1 : 2 : 2 : 3 : 3 : 4 : 4 : 5 : 5 : 6 : 6-dodecafluorohexyl)dimethylsilane (II; R = Me, $n = 3$) and dimethyl-(1 : 1 : 2 : 2 : 3 : 3 : 4 : 4-octafluorobutyl)-(1 : 1 : 2 : 2-tetrafluoroethyl)silane (III; R = Me, $x = 1, y = 2$) formed in 0·5 and 8% yields respectively. Material of even higher molecular weight is also present. These products arise by a primary initiation, propagation, and chain-transfer as outlined above, followed by secondary reactions of the products which contain Si–H bonds with tetrafluoroethylene as shown in the scheme on page 1040.

The primary reaction, considered to be that shown on the main line of the scheme, yields a series of products of type (II; R = Me, $n = 1, 2, 3$ . . . . etc.) each containing an Si–H bond, with the value of n governed mainly by reactant ratio. As the concentration of the compound (I; R = Me) increases it eventually becomes comparable with that of the unconsumed dimethylsilane present at that time, and the secondary reaction of (I; R = Me) with tetrafluoroethylene becomes increasingly important; the relative amounts of the compounds (III; R = Me, $x = 1, y = 1, 2, 3$ . . . . etc.) produced by

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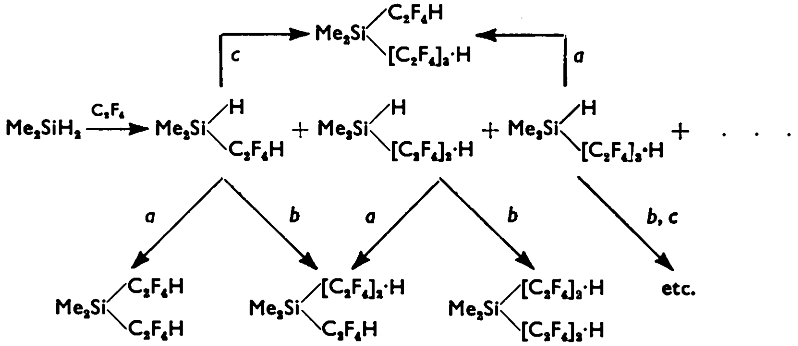
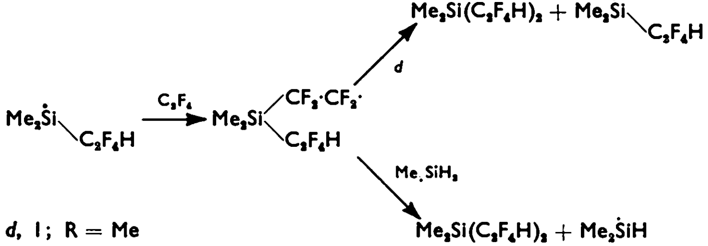
[5] Haszeldine, *J.*, 1953, 3761; 1955, 4291.

[6] Haszeldine and Steele, *J.*, 1954, 3747.

this secondary reaction at any given time will vary throughout the reaction, since the concentration of dimethylsilane and of (I; R = Me) will be changing. It should also be noted that the chain-transfer step in this secondary reaction occurring at a stage when an appreciable amount of dimethylsilane is present can occur by generation of dimethylsilyl radicals as well as of dimethyl-(1 : 1 : 2 : 2-tetrafluoroethyl)silyl radicals:



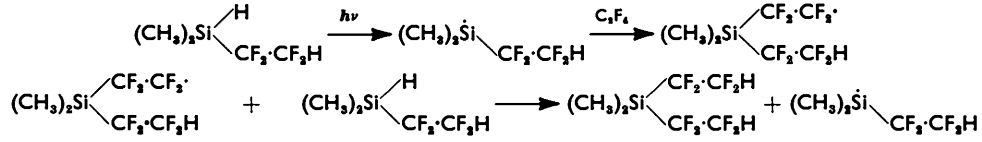
[a] Chain reaction with tetrafluoroethylene with absence of propagation step; *i.e.*, addition of one C_2F_4 unit.
[b] Chain reaction with tetrafluoroethylene with addition of two C_2F_4 units at propagation step.
[c] Chain reaction with tetrafluoroethylene with addition of three C_2F_4 units at propagation step.



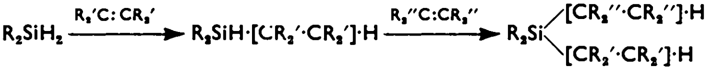
d, I; R = Me

and this will tend to produce mainly (III; R = Me, $x = y = 1$) from (I; R = Me). As the concentration of dimethylsilane decreases further, *i.e.*, towards the end of the primary reaction, the propagation reaction with (I; R = Me) will increase in importance. The secondary reaction of (II; R = Me, $n = 2$) with tetrafluoroethylene will also occur about this stage as the concentration of the former becomes comparable with that of dimethylsilane and (I; R = Me). The final yields of the products indicate that in the *primary* reaction the chain propagation initially gives (II; R = Me, $n = 2$) in 20—30% yield and (I; R = Me) in 50—60% yield; these yields are then reduced by the occurrence of the secondary reactions. The fact that the compounds (III; R = Me, $x = y = 1$) and (III; R = Me, $x = 1$, $y = 2$) are formed in approximately equal yields (8%) suggests that in each of the secondary reactions the main product is that resulting from addition of one C_2F_4 unit in *ca.* 50% yield and of two C_2F_4 units in *ca.* 25% yield just as in the primary reaction.

That compounds of type (II; R = Me, $n = 1, 2, 3$ . . . .) can react further with tetrafluoroethylene was shown by the reaction of dimethyl-(1 : 1 : 2 : 2-tetrafluoroethyl)silane with tetrafluoroethylene to give dimethyldi-(1 : 1 : 2 : 2-tetrafluoroethyl)silane in 90% yield:



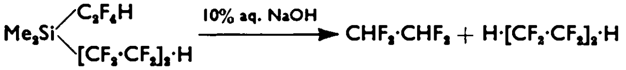
A stepwise procedure of this type enables compounds free from isomers to be obtained, and also enables a different alkyl group to be attached to silicon if required :



$$R_2SiH_2 \xrightarrow{R_2'C:CR_2'} R_2SiH{\cdot}[CR_2'{\cdot}CR_2']{\cdot}H \xrightarrow{R_2''C:CR_2''} R_2Si\begin{cases}[CR_2''{\cdot}CR_2'']{\cdot}H\\ [CR_2'{\cdot}CR_2']{\cdot}H\end{cases}$$

When the ratio dialkylsilane : tetrafluoroethylene is very small, the silane acts merely as an initiator for the long-chain polymerisation of tetrafluoroethylene to give a solid product with the typical waxy appearance of polytetrafluoroethylene.

The Si–H bond in the compounds mentioned above is not hydrolysed on contact with water, but even 1% aqueous alkali is sufficient to cleave it with formation of hydrogen. The polyfluoroalkyl groups present are liberated rapidly and quantitatively as αω-di-H-polyfluoroalkanes, *e.g.*,



$$Me_2Si\begin{cases}C_2F_4H\\ [CF_2{\cdot}CF_2]_2{\cdot}H\end{cases} \xrightarrow{10\%\ aq.\ NaOH} CHF_2{\cdot}CHF_2 + H{\cdot}[CF_2{\cdot}CF_2]_2{\cdot}H$$

and the pseudo-halogen nature of the polyfluoroalkyl group in such compounds is again apparent.[1] This provides a convenient method for the analysis of mixture of isomers as illustrated in the Experimental part.

The reaction of a dialkylsilane with a fluoro-olefin thus provides a very convenient method for the formation of compounds containing one or more CF_2–Si bonds, with the polyfluoroalkyl group of a controlled chain length.

The boiling points of the tetrafluoroethyl silicon compounds are slightly higher than those of the corresponding unsubstituted compounds; *e.g.*, cf. Me_2SiHEt 43°, $Me_2SiH(CF_2{\cdot}CF_2H)$ 62°; Me_2SiEt_2 96°, $Me_2Si(CF_2{\cdot}CF_2H)_2$ 119°.

The Si–H stretching band in the infrared is characteristic and proved of particular value in the present work for ascertaining that the compounds of type (III) are free from compounds of type (II). The pseudo-halogen nature of the polyfluoroalkyl group when attached to silicon causes a shift of the Si–H absorption to shorter wavelength similar to that produced by chlorine as shown in the annexed Table.

Si–H *Stretching frequencies.*

$—CH_2—\overset{\vert}{\underset{\vert}{Si}}—H$		$Cl—\overset{\vert}{\underset{\vert}{Si}}—H$		$—CF_2—\overset{\vert}{\underset{\vert}{Si}}—H$	
Me_2SiH_2	2150	$MeSiHCl_2$	2220	$Me_2SiH{\cdot}[CF_2{\cdot}CF_2]{\cdot}H$	2190
$MeSiH_3$	2180 2160	$SiHCl_3$	2250	$Me_2SiH[CF_2{\cdot}CF_2]_2{\cdot}H$	2190
SiH_4	2242 2178 2128			$Me_2SiH[CF_2{\cdot}CF_2]_3{\cdot}H$	2185

The $-CH_2$–Si–H, Cl–Si–H, and $-CF_2$–Si–H systems are thus characterised by Si–H absorption at 2150—2180, 2220—2250, and 2185—2200 respectively. Detailed discussion of the spectra of polyfluoroalkyl silicon compounds is deferred to a later paper.

EXPERIMENTAL

Photochemical reactions were carried out in sealed silica tubes or in the apparatus incorporating a 20 l. flask described and used earlier for the reaction of trifluoroiodomethane with nitric oxide.[4] There was no need to shake the 20 l. flask or to use mercury. Reaction times are undoubtedly excessive, and the greater part of the reaction is complete within 4—5 hr.

Dimethylsilane.—This was prepared in 67% yield from dimethyldichlorosilane (55 g., 0·425 mole) and excess of lithium aluminium hydride (10 g., 0·26 mole) in diethyl or di-*n*-butyl ether solution (100 ml.).[7] The product was condensed in traps cooled by liquid nitrogen and

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[7] Finholt, Bond, Wilzbach, and Schlesinger, *J. Amer. Chem. Soc.*, 1947, **69**, 2692; Peake, Nebergall, and Yun-ti-chen, *ibid.*, 1952, **74**, 1526.

freed from ether by distillation *in vacuo* (Found : *M*, 60. Calc. for C_2H_8Si : *M*, 60). Its purity was checked by infrared spectroscopy.

Dark Reaction of Dimethylsilane and Tetrafluoroethylene.—Dimethylsilane (4 mmoles) and tetrafluoroethylene (2 mmoles) failed to react when kept in a sealed 50 ml. Pyrex tube in the dark for 4 months.

Photochemical Reaction of Dimethylsilane with Tetrafluoroethylene.—(a) *In a silica tube under pressure.* Dimethylsilane (1·20 g., 20 mmoles) and tetrafluoroethylene (1·18 g., 11·80 mmoles) (mole-ratio $Me_2SiH_2 : C_2F_4 = 1{\cdot}695 : 1$) were sealed in a 200 ml. silica tube and exposed to ultraviolet radiation from a Hanovia S 250 U type arc used without the filter. Rapid reaction ensued and liquid products were clearly detectable after 5 hr., but the irradiation was continued for a further 19 hr. Hydrogen was not detectable as a non-condensable gas by the sensitive vacuum techniques available, and all the tetrafluoroethylene had been used. The products were distilled *in vacuo* to give unchanged dimethylsilane (11·4 mmoles, 57%), dimethyl-(1 : 1 : 2 : 2-tetrafluoroethyl)silane (1·04 g., 6·35 mmoles, 54%), a mixture of the compounds $(CH_3)_2SiH{\cdot}[CF_2{\cdot}CF_2]_2{\cdot}H$ and $(CH_3)_2Si(CF_2{\cdot}CF_2H)_2$ (0·42 g., 1·61 mmoles, 27%), and a small residue. A small amount of an oil of higher b. p. remained in the reaction vessel. The polyfluoroalkyl silicon compounds were identified by comparison of their physical properties and infrared spectra with the analysed samples prepared as in (b) below. The analytical procedure used is described below.

In a second experiment, a large excess of dimethylsilane was used. Tetrafluoroethylene (1·40 g., 14 mmoles) and dimethylsilane (4·20 g., 70 mmoles) (mole-ratio $Me_2SiH_2 : C_2F_4 = 5 : 1$) were irradiated in a sealed 340 ml. silica tube for 24 hr. Distillation then gave unchanged dimethylsilane (80%) and liquid products (2·171 g.) which were fractionated to give (i) dimethyl-(1 : 1 : 2 : 2-tetrafluoroethyl)silane (1·852 g., 11·6 mmoles, 83%), b. p. 62—64°, and (ii) a residue (0·160 g., 9%) shown by analysis of the type outlined below to consist of dimethyl-(1 : 1 : 2 : 2 : 3 : 3 : 4 : 4-octafluorobutyl)silane (0·125 g., 78%) and dimethyldi-(1 : 1 : 2 : 2-tetrafluoroethyl)silane (0·035 g., 22%). The experiment has thus produced the compounds $Me_2SiH(C_2F_4H)$, $Me_2SiH{\cdot}[C_2F_4]_2{\cdot}H$, and $Me_2Si(C_2F_4H)_2$ in 83%, 7%, and 2% yield respectively.

(b) *In a 20 l. bulb at sub-atmospheric pressure.* Dimethylsilane (19·5 g., 0·325 mole) and tetrafluoroethylene (21·5 g., 0·215 mole) (mole-ratio $Me_2SiH_2 : C_2F_4 = 1{\cdot}51 : 1$, total pressure 493 mm. at 20°) were transferred to the evacuated 20 l. bulb of the photochemical apparatus.[4] The ultraviolet lamp was inserted into the silica inner tube and as soon as it was switched on an immediate rapid reaction was apparent and a mist of fine globules of product formed in the bulb. After 4 hr. the liquid products had collected at the bottom of the bulb and reaction was essentially complete; irradiation was continued for a further 20 hr. without apparent change. Hydrogen was not detected as a reaction product. The more volatile products were pumped from the bulb and distilled to give (i) unchanged dimethylsilane (0·166 mole, 51%) (Found: *M*, 60), (ii) *dimethyl-*(1 : 1 : 2 : 2-*tetrafluoroethyl*)*silane* (16·13 g., 47%), b. p. 62·3° (Found : C, 29·7; H, 4·8%; *M*, 160. $C_4H_8F_4Si$ requires C, 30·0; H, 5·0%; *M*, 160), (iii) a mixture (7·52 g., 27%), b. p. 119° (Found: C, 27·4; H, 3·2. Calc. for $C_6H_8F_8Si$: C, 27·7; H, 3·1%), of dimethyldi-(1 : 1 : 2 : 2-tetrafluoroethyl)silane (1·88 g., 7·2 mmoles, 7%) and dimethyl-(1 : 1 : 2 : 2 : 3 : 3 : 4 : 4-octafluorobutyl)-silane (5·64 g., 21·6 mmoles, 20%), (iv) a mixture (2·17 g., 8%), b. p. 98°/70 mm. (Found : C, 26·4; H, 2·2. Calc. for $C_8H_8F_{12}Si$: C, 26·7; H, 2·2%), of dimethyl-(1 : 1 : 2 : 2 : 3 : 3 : 4 : 4-octafluorobutyl)-(1 : 1 : 2 : 2-tetrafluoroethyl)-silane (2·01 g., 5·60 mmoles, 8%) and (1 : 1 : 2 : 2 : 3 : 3 : 4 : 4 : 5 : 5 : 6 : 6-dodecafluorohexyl)dimethylsilane (0·16 g., 0·45 mmole, 0·5%), and (v) a viscous residue (18%) of higher b. p. (*i.e.*, more than $3C_2F_4$ units per dimethylsilane unit) obtained by draining the less-volatile products from the reaction flask and as a residue from the distillation.

Yields are based on tetrafluoroethylene, and the method of analysis of the mixtures is described below.

Reaction of Dimethyl-(1 : 1 : 2 : 2-*tetrafluoroethyl*)*silane with Tetrafluoroethylene.*—The polyfluoroalkylsilane (5·222 g., 32·6 mmoles) and tetrafluoroethylene (1·75 g., 17·5 mmoles) (mole-ratio 1·87 : 1), irradiated for 40 hr. in a sealed 200 ml. silica tube with the liquid phase shielded, gave unchanged dimethyl-(1 : 1 : 2 : 2-tetrafluoroethyl)silane (2·44 g., 15·3 mmoles, 47%), and *dimethyldi-*(1 : 1 : 2 : 2-*tetrafluoroethyl*)*silane* (4·05 g., 15·6 mmoles, 90% based on tetrafluoroethylene used), b. p. 120° (Found : C, 27·7; H, 2·9. $C_6H_8F_8Si$ requires C, 27·7; H, 3·1%). Infrared spectroscopic examination showed that Si–H bonds were absent. The small residue from the distillation (0·1 g.) was not examined.

Stability of Dimethyl-(1 : 1 : 2 : 2-*tetrafluoroethyl*)*silane to Water.*—The compound (0·234 g., 1·46 mmoles) was shaken in a 500-ml. bulb with water (10 ml.) for 1 hr. at 20°. Under such conditions the silicon compound is in the vapour phase. The bulb was connected to an apparatus for the manipulation of volatile compounds and opened; a non-condensable gas had not been produced. The volatile products were distilled to give only unchanged starting material (1·45 mmoles, 99%).

Alkaline Hydrolysis of Dimethyl-(1 : 1 : 2 : 2-*tetrafluoroethyl*)*silane.*—The compound (0·308 g., 1·925 mmoles) was shaken with 15% aqueous sodium hydroxide (10 ml.) at 20° for 10 min. The total volatile products were measured manometrically and the condensable fraction was then collected in a trap cooled by liquid oxygen. The non-condensable gas was hydrogen (1·90 mmoles, 99%) and the condensable gas was 1 : 1 : 2 : 2-tetrafluoroethane (1·90 mmoles, 99%) (Found: *M*, 102. Calc. for $C_2H_2F_4$: *M*, 102), identified spectroscopically.[1] A second experiment gave essentially the same results.

Alkaline Hydrolysis of Dimethyldi-(1 : 1 : 2 : 2-*tetrafluoroethyl*)*silane.*—The silane (0·1875 g., 0·72 mmole), shaken in a sealed tube with 10% aqueous sodium hydroxide (10 ml.) for 10 min., liberated 1 : 1 : 2 : 2-tetrafluoroethane (identified spectroscopically) essentially quantitatively, but no hydrogen.

Analytical Procedure for Mixtures of Products containing more than 1 C_2F_4 *Unit per Silicon Atom.*—(a) *A mixture containing* $Me_2SiH\cdot[C_2F_4]_2\cdot H$ *and* $Me_2Si(CF_2\cdot CHF_2)_2$. Preliminary qualitative experiments revealed that the mixture was decomposed by 1% aqueous sodium hydroxide at room temperature to give a mixture of hydrogen, $CHF_2\cdot CHF_2$, and $H\cdot[CF_2\cdot CF_2]_2\cdot H$. The last two compounds were identified by means of their vapour pressures, molecular weights, and infrared spectra.[1] In a typical analysis, the mixture (295·5 mg., 1·137 mmoles), shaken with 10% aqueous sodium hydroxide (10 ml.) at 20° for 10 min., gave hydrogen (0·845 mmole) as a non-condensable gas. The amount of the compound $Me_2SiH\cdot[C_2F_4]_2\cdot H$ present in the mixture (74%) is thus obtained directly, since only this compound can liberate hydrogen. The amount of $Me_2Si(CF_2\cdot CHF_2)_2$ is thus 26%. No attempt was made to separate the mixture of the compounds $H\cdot[CF_2\cdot CF_2]\cdot H$ and $H\cdot[CF_2\cdot CF_2]_2\cdot H$ obtained as a condensable gas (1·335 mmoles, 93%), but its average molecular weight was determined (Found: *M*, 153·6), and used to calculate the percentage of the gases present in the mixture and hence the composition of the original mixture: $Me_2SiH\cdot[C_2F_4]_2\cdot H$ 68%, $Me_2Si(CF_2\cdot CHF_2)_2$ 32%. The agreement between the two methods of analysis is considered adequate for this purpose, and the first analysis is probably more nearly correct. The accuracy could be improved considerably by use of more suitable gas-measuring equipment, and by heating the aqueous solution to help to expel the gases.

(b) *A mixture containing* $Me_2SiH\cdot[C_2F_4]_3\cdot H$ *and* $Me_2Si(CF_2\cdot CHF_2)(CF_2\cdot CF_2\cdot CF_2\cdot CHF_2)$, *with smaller amounts of* $Me_2SiH\cdot[C_2F_4]_2\cdot H$ *and* $Me_2Si(CF_2\cdot CHF_2)_2$. The mixture (959 mg.), shaken with 10% aqueous sodium hydroxide (20 ml.) at 20° for 10 min., gave hydrogen (0·65 mmole), $H\cdot[CF_2\cdot CF_2]\cdot H$ (2·32 mmoles), $H\cdot[CF_2\cdot CF_2]_2\cdot H$ (2·64 mmoles), and $H\cdot[CF_2\cdot CF_2]_3\cdot H$ (0·18 mmole). The condensable gases were fractionated *in vacuo* and the analysis of various fractions was carried out spectroscopically. The amount of $H\cdot[CF_2\cdot CF_2]_3\cdot H$ gives immediately the amount of $Me_2SiH\cdot[C_2F_4]_3\cdot H$ in the mixture (0·18 mmole, 65 mg.). The hydrogen produced arises from both $Me_2SiH\cdot[C_2F_4]_3\cdot H$ and $Me_2SiH\cdot[C_2F_4]_2\cdot H$, and since 0·18 mmole of the former is present, 0·47 mmole of the latter (122 mg.) must be present also. The $H\cdot[CF_2\cdot CF_2]_2\cdot H$ arises from both $Me_2SiH\cdot[C_2F_4]_2\cdot H$ and $Me_2Si(CF_2\cdot CHF_2)(CF_2\cdot CF_2\cdot CF_2\cdot CHF_2)$, and since 0·47 mmole of the former is present, there must be 2·17 mmoles of the latter (780 mg.). The $H\cdot[CF_2\cdot CF_2]\cdot H$ arises from both $Me_2Si(CF_2\cdot CHF_2)(CF_2\cdot CF_2\cdot CF_2\cdot CHF_2)$ and $Me_2Si(CF_2\cdot CHF_2)_2$, and since 2·17 mmoles of the former are present, there must be 0·15 mmole of $H\cdot[CF_2\cdot CF_2]\cdot H$ arising from 0·075 mmole of the latter (18 mg.), each molecule of which yields two of $H\cdot[CF_2\cdot CF_2]\cdot H$ on hydrolysis. The analytical figures lead to an apparent total weight for the original mixture of 985 mg.; *i.e.*, the error is approx. 3%.

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