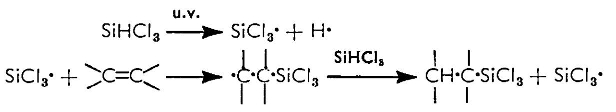
376. *Polyfluoroalkyl Compounds of Silicon. Part VII.*[1] *The Thermal and Hydrolytic Stabilities of α-, β-, and γ-Fluorine-substituted Alkylpolysiloxanes* *

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

Hydrolysis and pyrolysis studies on the compounds $[CHF_2\cdot CF_2\cdot Si\cdot O_{1.5}]_n$, $[CHF_2\cdot CH_2\cdot Si\cdot O_{1.5}]_n$, $[CF_3\cdot CH_2\cdot CH_2\cdot Si\cdot O_{1.5}]_n$, and $[CF_3\cdot CH_2\cdot CH_2]_4Si$ show that the α- and β-fluoro-substituted compounds are relatively unstable to pyrolysis and to aqueous alkaline hydrolysis, whereas the γ-substituted compounds are unaffected by aqueous alkali, and decompose appreciably *in vacuo* only at temperatures in excess of 350—400°.

The results are reported of an investigation carried out some years ago on the effect of fluorine substitution on the thermal and hydrolytic stabilities of polyfluoroalkyl polysiloxanes containing fluorine in the α-, β-, or γ-position relative to silicon.

The photochemical reaction of trichlorosilane with the appropriate fluoro-olefin:



$$SiHCl_3 \xrightarrow{u.v.} SiCl_3\cdot + H\cdot$$

$$SiCl_3\cdot + {>}C{=}C{<} \longrightarrow \cdot\overset{|}{\underset{|}{C}}\cdot\overset{|}{\underset{|}{C}}\cdot SiCl_3 \xrightarrow{SiHCl_3} CH\cdot\overset{|}{\underset{|}{C}}\cdot SiCl_3 + SiCl_3\cdot$$

gave the α-, β-, and γ-substituted compounds $CHF_2\cdot CF_2\cdot SiCl_3$ (from C_2F_4)[2], $CHF_2\cdot CH_2\cdot SiCl_3$ (from $CH_2{:}CF_2$), and $CF_3\cdot CH_2\cdot CH_2\cdot SiCl_3$ (from $CF_3\cdot CH{:}CH_2$)[2].

2,2-Difluoroethyltrichlorosilane was converted into the trimethoxy-compound $CHF_2\cdot CH_2\cdot Si(OMe)_3$ by reaction with methanol, and nuclear magnetic resonance (n.m.r.) investigation of the methoxy-compound showed that fluorine was β to silicon. The ^{19}F n.m.r. spectrum showed a doublet of triplets centred at +27·2 p.p.m. from trifluoroacetic acid, as expected for first-order coupling between ^{19}F and ^{1}H in the grouping $CHF_2\cdot CH_2$; the group $CH_3\cdot CF_2$ would have shown a simple quadruplet. The ^{1}H n.m.r. spectrum showed a triplet of triplets centred at τ 3·99 (β-hydrogen split by α-CH_2 and β-CF_2), a singlet at τ 6·40 (methoxy-groups), and a triplet of doublets centred at τ 8·64 (α-hydrogen split by β-CH and β-CF_2). The ^{1}H spectrum expected for $CH_3\cdot CF_2$ is a simple triplet (β-CH_3 split by α-CF_2).

Hydrolysis. The fluoroalkyltrichlorosilanes were converted into the polysiloxanes in the normal way by addition of water to their ethereal solutions, followed by completion of the condensation by heating where necessary. The polysiloxanes $[CHF_2\cdot CF_2\cdot Si\cdot O_{1.5}]_n$ and $[CHF_2\cdot CH_2\cdot Si\cdot O_{1.5}]_n$ underwent Si–C bond fission when treated with cold 5% aqueous

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* Preliminary publication, *Proc. Chem. Soc.*, 1960, 147.

[1] Part VI, R. N. Haszeldine, M. J. Newlands, and J. B. Plumb, preceding Paper.

[2] A. M. Geyer and R. N. Haszeldine, *J.*, 1957, 1038; A. M. Geyer, R. N. Haszeldine, K. Leedham, and R. J. Marklow, *J.*, 1957, 4472; R. N. Haszeldine and R. J. Marklow, *J.*, 1956, 962.

sodium hydroxide, whereas $[CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}Si{\cdot}O_{1\cdot5}]_n$ was unaffected by cold 40% aqueous sodium hydroxide or by 5% aqueous sodium hydroxide at 80°; when it was refluxed with 10% aqueous sodium hydroxide it dissolved completely, presumably to give the sodium salt of trifluoropropylsilanetriol. Acidification reprecipitated a silanetriol–polysiloxane mixture. It is clear that Si–C bond fission does not occur; indeed the Si–C bond in the 3,3,3-trifluoropropyl compounds was so resistant to alkaline hydrolysis that the compound $(CF_3{\cdot}CH_2{\cdot}CH_2)_2SiH_2$ could be converted into the corresponding silicone by refluxing with 20% aqueous sodium hydroxide,[1] and the compound $(CF_3{\cdot}CH_2{\cdot}CH_2)_4Si$ was unaffected by boiling 20% aqueous sodium hydroxide.

1,1,2,2,-Tetrafluoroethane resulted from the alkaline hydrolysis of 1,1,2,2-tetrafluoroethylpolysiloxane:

$$CHF_2{\cdot}CF_2{\cdot}Si{\cdot}O_{1\cdot5} + OH^- \longrightarrow HO{\cdot}Si{\cdot}O_{1\cdot5} + CHF_2{\cdot}CF_2^- \xrightarrow{H_2O} CHF_2{\cdot}CHF_2$$

In contrast, treatment of 2,2-difluoroethylpolysiloxane with aqueous alkali gave only vinyl fluoride, probably by a concerted β-elimination:

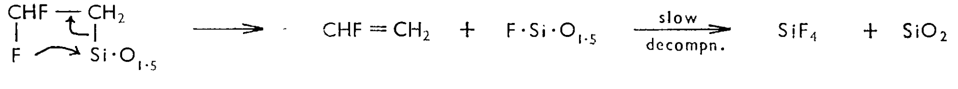
The compound $CHF_2{\cdot}CH_3$ was stable under the conditions used for this hydrolysis, and hence was not an intermediate in the hydrolysis.

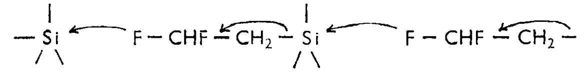
Pyrolyses. Samples of 2,2-difluoroethylpolysiloxane were heated *in vacuo* at a constant temperature in the range 158—320° for 6 hr. The only gaseous products were vinyl fluoride and silicon tetrafluoride, and the former was evolved more rapidly than the latter. Although 95% of the theoretical amount of vinyl fluoride was evolved at temperatures above 200°, Si–F bonds remained in the solid residue even from a pyrolysis at 320°, when only 58% of the theoretical amount of silicon tetrafluoride had been liberated. When the white residue was heated to 503°, a further 12% of silicon tetrafluoride was evolved:

$$4\,CHF_2{\cdot}CH_2{\cdot}Si{\cdot}O_{1\cdot5} \xrightarrow{320^\circ} 4\,CH_2{:}CHF + 4F{\cdot}Si{\cdot}O_{1\cdot5} \xrightarrow{503^\circ} SiF_4 + 3SiO_2$$

Experiments where the volatile products were removed continuously also showed that vinyl fluoride was liberated more rapidly then silicon tetrafluoride and that the divergence between the rates increased with increasing temperature. Plots of the molar ratio $CH_2{:}CHF/SiF_4$ against time showed that the ratio passed through a maximum, but the 4 : 1 ratio expected by the above equation was never attained, probably because the heating period was too short.

A 4-centre transition state involving β-elimination of fluorine by nucleophilic attack on silicon is in accord with these results and with gas-kinetic studies on 2,2-difluoroethyltrifluorosilane.[3] The silicon attacked need not be the one to which the polyfluoroalkyl group is attached, and could be in an adjacent site in the solid:





Pyrolysis of 1,1,2,2-tetrafluoroethylpolysiloxane is more complex. Charring occurs in the 150—220° range studied, so that a satisfactory weight balance could not be obtained.

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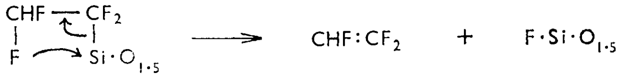
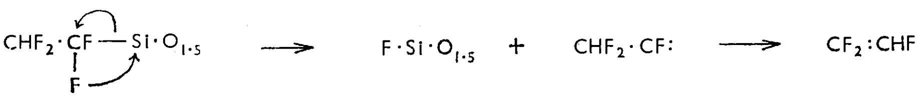
[3] R. N. Haszeldine, R. F. Simmons, and P. J. Robinson, *J.*, 1964, 1890.

The products $CHF{:}CF_2$ and SiF_4 increased in yield with increase in temperature, and can arise either by β-elimination:



or by α-elimination to give a carbene, followed by rearrangement:[4]



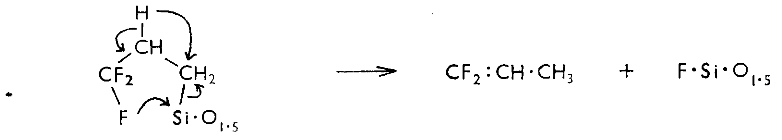
The α-elimination mechanism is more probable in the light of gas-kinetic studies on trifluoro-1,1,2,2-tetrafluoroethylsilane.[5]

3,3,3-Trifluoropropylpolysiloxane is much more stable, and decomposition sets in only at temperatures in excess of 400°. Even at *ca.* 450°, only 5—10% decomposition occurs during 6 hr., to give the compounds $CF_2{:}CH{\cdot}CH_3$, $CF_3{\cdot}CH_2{\cdot}CH_3$, $CF_3{\cdot}CH_3$, CHF_3, and SiF_4, and at 500° 1,1,1-trifluoropropane is the major product. The main reaction is thus homolytic C–Si fission accompanied to a lesser extent by homolytic C–C fission:

$$CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}Si{\cdot}O_{1{\cdot}5} \longrightarrow CF_3{\cdot}CH_2{\cdot}CH_2{\cdot} + Si{\cdot}O_{1{\cdot}5}$$

$$CF_3{\cdot}CH_2{\cdot}CH_2{\cdot} \longrightarrow CF_3{\cdot}CH_2{\cdot} \longrightarrow CF_3{\cdot}$$

followed by abstraction of hydrogen by the radicals to give 1,1,1-trifluoropropane, 1,1,1-trifluoroethane, and trifluoromethane. 1,1-Difluoropropene arises by dehydrofluorination of 1,1,1-trifluoropropane, by dehydrofluorination of the $CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}Si$ group followed by homolytic cleavage of the allylic radical $CF_2{:}CH{\cdot}CH_2{\cdot}$ from silicon, or possibly by attack of γ-fluorine on silicon with simultaneous proton migration and C–Si cleavage:



The silicon again need not be the one to which the trifluoropropyl group donating the fluorine is attached.

Pyrolysis of the silicone $[(CF_3{\cdot}CH_2{\cdot}CH_2)_2Si{\cdot}O]_n$ and of the silane $(CF_3{\cdot}CH_2{\cdot}CH_2)_4Si$ gave results similar to those obtained with 3,3,3-trifluoropropylpolysiloxane.

To obtain good thermal stability in a fluoroalkyl-silicone or -polysiloxane with maximum retention of other desirable features such as (i) chemical resistance, (ii) insolubility in organic solvents and resistance to swelling by organic solvents, and (iii) oxidation resistance, it is evident that the fluorine must be in the γ-position relative to silicon and also that there should be as many fluorine atoms there as possible.

EXPERIMENTAL

Gases and volatile materials were manipulated in a conventional vacuum system to ensure minimum contact with air or moisture. The ultraviolet radiation was from a Hanovia 500w

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[4] R. N. Haszeldine and J. C. Young, *Proc. Chem. Soc.*, **1959**, 394; W. I. Bevan, R. N. Haszeldine, and J. C. Young, *Chem. and Ind.*, **1961**, 789.

[5] G. Fishwick, R. N. Haszeldine, P. J. Robinson, and R. F. Simmons, unpublished results.

lamp. N.m.r. spectra were recorded on a Perkin-Elmer R10 spectrometer at frequencies of 60 Mc/sec.(^{1}H) and 56·46 Mc./sec.(^{19}F).

Reaction of 3,3,3-*Trifluoropropene with Trichlorosilane.*—3,3,3-Trifluoropropene (17·0 g., 0·18 mole) and freshly distilled trichlorosilane (72·0 g., 0·53 mole), sealed *in vacuo* in a 300 ml. silica tube and shaken and irradiated for 100 hr., gave trichlorosilane (47·0 g., 0·35 mole, 65%), 3,3,3-trifluoropropyltrichlorosilane (27·3 g., 0·12 mole, 66%) b. p. 112—114°, and *trichloro*-5,5,5-*trifluoro*-2-*trifluoromethylpentylsilane* (3·52 g., 0·012 mole, 13%) (Found: C, 22·3; H, 2·1. $C_6H_7Cl_3F_6Si$ requires C, 22·0; H, 2·1%), b. p. 171—172°. Traces of trichlorosilane, detected by infrared spectroscopy, in the 3,3,3-trifluoropropyltrichlorosilane were removed by re-irradiation with a further quantity of trifluoropropene. Fractionation then gave 3,3,3-trifluoropropyltrichlorosilane (Found: C, 15·8; H, 1·5. Calc. for $C_3H_4Cl_3F_3Si$: C, 15·5; H, 1·7%), b. p. 113—114° (lit.,[1] 113°).

Reaction of 1,1-*Difluoroethylene with Trichlorosilane.*—Three 360 ml. silica tubes, each containing 1,1-difluoroethylene (4·25 g., 66 mmoles) and trichlorosilane (17·8 g., 132 mmoles) and sealed *in vacuo*, were shaken and irradiated for 24 hr. to give unchanged trichlorosilane, 2,2-difluoroethyltrichlorosilane (22·8 g., 114 mmoles, 59%), b. p. 100—111°, and higher telomers which were not studied further. Traces of contaminant trichlorosilane were removed from the 2,2-difluoroethyltrichlorosilane by further irradiation with difluoroethylene. Fractionation then gave pure 2,2-*difluoroethyltrichlorosilane* (Found: C, 12·1; H, 1·5. $C_2H_3Cl_3F_2Si$ requires C, 12·1; H, 1·5%), b. p. 110—111°.

Preparation of the Polysiloxanes, Silicones, and Disiloxanes.—The general procedure followed was to dissolve the appropriate chlorosilane (10—20 g.) in diethyl ether (20—50 ml.) and then to hydrolyse it by dropwise addition of an excess of ice–water (20—30 ml.) to the stirred solution (30 min.). The ethereal layer was separated, combined with 4 further ethereal extracts of the aqueous layer, and the whole was washed once with water to remove hydrogen chloride. The ethereal solution was dried (K_2CO_3) and the solvent evaporated. Complete condensation of the silanol–polysiloxane mixtures was achieved by heating them *in vacuo* at 70—80° for 1 hr.; the solid was ground and heated at 100° *in vacuo* for 30 min. The *polysiloxane* $[CHF_2{\cdot}CH_2{\cdot}Si{\cdot}O_{1{\cdot}5}]_n$ was thus obtained in 97% yield (Found: C, 20·5; H, 2·8. $C_2H_3F_2O_{1{\cdot}5}Si$ requires C, 20·5; H, 2·6%), the polysiloxane $[CHF_2{\cdot}CF_2{\cdot}Si{\cdot}O_{1{\cdot}5}]_n$ in 96% yield,[2] and the polysiloxane $[CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}Si{\cdot}O_{1{\cdot}5}]_n$ (Found: C, 24·1; H, 2·7. Calc. for $C_3H_4F_3O_{1{\cdot}5}Si$: C, 24·2; H, 2·7%) in 75% yield.[2] Complete cross-linking of trifluoropropylpolysiloxane was achieved by adding 2 drops of concentrated sulphuric acid to the viscous liquid from the hydrolysis and then heating to 200° *in vacuo* for 2 hr. The cooled solid was stored *in vacuo* over phosphorus pentoxide (2 weeks) then ground, washed with 2% aqueous sodium hydroxide then water, and dried and stored *in vacuo* over phosphorus pentoxide. Infrared-spectroscopic examination showed that Si–OH bands were then absent.

The product $[(CF_3{\cdot}CH_2{\cdot}CH_2)_2Si{\cdot}O]_n$, prepared by aqueous alkaline hydrolysis of $(CF_3{\cdot}CH_2{\cdot}CH_2)_2SiH_2$ [1] was identical with the silicone obtained by aqueous alkaline hydrolysis of $(CF_3{\cdot}CH_2{\cdot}CH_2)_2SiCl_2$.[2]

Reaction of the Polysiloxanes with Aqueous Sodium Hydroxide.—To a sample of the polysiloxane (0·2—0·6 g.) in an evacuated 300 ml. hydrolysis bulb was added 5% aqueous sodium hydroxide (15—25 ml.) which had been boiled and allowed to cool *in vacuo*; air was not allowed to enter the hydrolysis bulb. The mixture was shaken for 20 min. then kept at room temperature for 2 hr. 2,2-Difluoroethylpolysiloxane gave only vinyl fluoride (90% yield) (Found: *M*, 45·6. Calc. for C_2H_3F: *M*, 46·0), and 1,1,2,2-tetrafluoroethylpolysiloxane gave only 1,1,2,2-tetrafluoroethane (98% yield) (Found: *M*, 101. Calc. for $C_2H_2F_4$: *M*, 102), identified by their infrared spectra.

A control experiment showed that 1,1-difluoroethane, a possible primary product from the hydrolysis of $[CHF_2{\cdot}CH_2{\cdot}Si{\cdot}O_{1{\cdot}5}]_n$, was recovered unchanged (98%) under the conditions used for the hydrolysis of the polysiloxane.

Trifluoropropylpolysiloxane (0·20 g.) gave no gaseous product when heated with 5% aqueous sodium hydroxide (15 ml.) at 80° for 0·5 hr. It dissolved immediately in refluxing 10% aqueous sodium hydroxide, and acidification (aq. HCl) of the cold solution precipitated a silanetriol–polysiloxane mixture (Found: C, 24·2; H, 2·8%).

The hydrolytic stability of the compound $[(CF_3{\cdot}CH_2{\cdot}CH_2)_3Si]_2O$ is demonstrated by its preparation from the corresponding silane by reaction with 20% aqueous base at reflux temperature.[1]

Thermal Stabilities of the Polysiloxanes.—Sealed Dreadnought tubes (130—140 ml. capacity) containing 0·5—1·0 g. samples and sealed *in vacuo* were introduced rapidly into a preheated furnace. The required temperature (±2°) was reached in *ca.* 30 min. and maintained for 6 hr. Volatile products were fractionated and identified by molecular weight, infrared spectroscopy, analysis, and gas–liquid chromatography. Silicon tetrafluoride was destroyed when necessary by 10% aqueous sodium hydroxide at room temperature.

(*a*) 2,2-*Difluoroethylpolysiloxane.* The results are shown in the annexed Table.

Temp.	158°	170°	178°	185°	203°	220°	251°	320°
Polysiloxane (g.)	0·637	0·635	0·634	0·642	0·573	0·562	0·600	0·495
Vinyl fluoride (%)	4·2	20·1	45·7	80·4	94·6	95·3	94·6	94·6
Silicon tetrafluoride (%)	0·0	2·7	7·9	12·7	30·9	38·4	46·6	57·8

A sample (0·230 g.) of the residue from the 251° pyrolysis was heated *in vacuo* at 503° (6 hr.) to give silicon tetrafluoride (4·8 ml.), thus making the total yield of silicon tetrafluoride 70%.

(*b*) 1,1,2,2-*Tetrafluoroethylpolysiloxane.* Evolution of silicon tetrafluoride and trifluoroethylene began at 160—170° and was rapid at 180—200°.

(*c*) 3,3,3-*Trifluoropropylpolysiloxane.* The results are shown in the Table.

Temp.	Polysiloxane (g.)	Volatile products (mole %)	Yield (%)					Recovered polysiloxane (%)
			$CF_2{:}CH{\cdot}CH_3$	CF_3Et	CF_3Me	CHF_3	SiF_4	
285°	5·940	0·94	0·74	0	0	0	0	96
403	0·100	4·86	4·86	0	0	0	0	79
450	0·722	7·5	2·1	2·1	0	3·3	0	75
500	1·000	55·6	0	26	3·1	11	12·2	—*

Charring occurred at temps. >450°.

* Recovery not attempted.

Pyrolysis of the Silicone $[(CF_3{\cdot}CH_2{\cdot}CH_2)_2Si{\cdot}O]_n$.—The liquid silicone (0·636 g.) was stable at 400° under the conditions used for the pyrolysis of the polysiloxane $[CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}Si{\cdot}O_{1{\cdot}5}]_n$. Charring was extensive after 6 hr. at 500°, and the volatile products (77 mole %) contained 1,1,1-trifluoropropane (41% yield), 1,1,1-trifluoroethane (16% yield), and trifluoromethane, together with traces of 3,3,3-trifluoropropene.

*Pyrolysis of Tetrakis-*3,3,3,*-trifluoropropylsilane.*—Pyrolysis of 0·3—0·6 g. samples under the conditions used for the polysiloxanes gave the results shown in the annexed Table.

Temp.	350°	400°	450°	500°
Recovered silane (%)	97	67	29	1
Gaseous products (%)	2	19	41	54
Carbonaceous material (%)	1	14	30	45

At 350° the gaseous products were traces of 1,1,1-trifluoroethane and 1,1-difluoropropene. At all other temperatures the gaseous products were, in order of decreasing mole proportions, $CF_3{\cdot}CH_2{\cdot}CH_3$, $CF_3{\cdot}CH_3$, SiF_4, $CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}SiF_3$, CHF_3, and CH_4. 1,1-Difluoropropene was not detected at pyrolysis temperatures above 400°.

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