Carbene Chemistry. Part VI.[1] Preparation and Pyrolysis of (1,1-Difluoroethyl)silanes [2,3]

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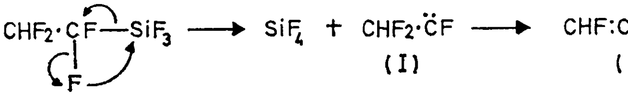
Photochemical reduction of trichloro(2-chloro-1,1-difluoroethyl)- or trichloro(2,2-dichloro-1,1-difluoroethyl)-silane with tri-n-butyltin hydride gives trichloro(1,1-difluoroethyl)silane, which on reaction with methanol or antimony trifluoride is converted into the trimethoxo- and trifluoro-analogues, respectively. Pyrolysis of trichloro-(1,1-difluoroethyl)silane in the range 100—150 °C gives chloro(1,1-dichloroethyl)difluorosilane exclusively by interchange of chlorine on silicon by fluorine on the α-carbon atom. At higher temperature (>235 °C) a mixture of vinyl fluoride, vinyl chloride, and chlorofluorosilanes is formed *via* α elimination to give intermediate carbenes. Thermal decomposition of (1,1-difluoroethyl)trifluorosilane at 120 °C affords quantitative yields of vinyl fluoride and silicon tetrafluoride; in the presence of added isobutene the intermediate fluoro(methyl)carbene is trapped to give the corresponding cyclopropane. The corresponding trimethoxo-compound decomposes at 150 °C to give a mixture of fluoromethoxosilanes and a polymeric oil, but at 240 °C vinyl fluoride is also formed *via* α elimination. Chloro(1,1-dichloroethyl)difluorosilane is stable at 205 °C, but at temperatures >235 °C it decomposes by α elimination to yield dichlorodifluorosilane and chloro(methyl)carbene, which rearranges to vinyl chloride.

THERMAL decomposition of trifluoro(polyfluoroethyl)-silanes at *ca.* 140 °C affords a carbene which, if not trapped, rearranges to an olefin, *e.g.* as in equation (1).[2-5] Carbene (I) reacts with olefins to give cyclopropanes [4] and inserts into C–H,[6] Si–H,[7] and Si–halogen [7] bonds. The interpretation of these pyrolyses was based on earlier work on the thermal decompositions of trichloro(polyfluoroalkyl)silanes [8,9] which require higher temperatures (*ca.* 225 °C) and are often complicated by concurrent formation of chlorine-containing olefins *via* halogen exchange between fluorine on the α-carbon atom and chlorine on silicon,[9] *e.g.* as in Scheme 1. That thermal decomposition of the compounds $CHFCl{\cdot}CF_2{\cdot}SiCl_3$[8] and $CFCl_2{\cdot}CF_2{\cdot}SiCl_3$[8] did not give products formed *via* halogen exchange suggested that such exchange was favoured by small substituents on the β-carbon atom. The thermal decomposition of a silane with only hydrogen as β substituent, trichloro(1,1-difluoroethyl)silane (II), was thus investigated.



$$CHF_2{\cdot}CF{-}SiF_3 \longrightarrow SiF_4 + \underset{(I)}{CHF_2{\cdot}\ddot{C}F} \longrightarrow CHF{:}CF_2 \qquad (1)$$

$$\begin{tikzcd}
CHF_2{\cdot}CF_2{\cdot}SiCl_3 \arrow[r, "(i)"] \arrow[d, "(ii)"'] & (I) \arrow[r] & CF_2{:}CHF\ (29\%) \\
CHF_2{\cdot}CFCl{\cdot}SiCl_2F \arrow[r, "(ii)"] \arrow[d, "(ii)"'] & CHF_2{\cdot}\ddot{C}Cl \arrow[r] & CF_2{:}CHCl\ (21\%) \\
CHF_2{\cdot}CCl_2{\cdot}SiClF_2 \arrow[r, "(iii)"] & CHF{:}CCl_2\ (22\%) &
\end{tikzcd}$$

SCHEME 1 (*i*), α Elimination; (*ii*), halogen exchange; and (*iii*), β elimination

RESULTS AND DISCUSSION

Silane (II) had previously been obtained in low yield (21%) from the photochemical reaction of trichlorosilane with 1-chloro-2,2-difluoroethylene (4 : 1 molar ratio),[10] but in the present work higher yields were obtained by photochemical reduction of trichloro(2,2-dichloro-1,1-

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difluoroethyl)silane, (III), with trimethylsilane (1 : 1 molar ratio) to give trichloro(2-chloro-1,1-difluoroethyl)silane, (IV) (60%),[10] which on further reaction with an excess of trimethylsilane gave silane (II) (82%). Difficulty was found in isolating silane (II) in a pure state and

$$\underset{\text{(II)}}{CH_3{\cdot}CF_2{\cdot}SiCl_3} \quad \underset{\text{(III)}}{CHCl_2{\cdot}CF_2{\cdot}SiCl_3} \quad \underset{\text{(IV)}}{CH_2Cl{\cdot}CF_2{\cdot}SiCl_3}$$

the use of tri-n-butyltin hydride was thus investigated. Photochemical reaction with silane (IV) (1 : 1 molar ratio) gave (II) (64%), tri-n-butyltin chloride (83%), and n-butane (*ca.* 15%), while silane (III) (2 : 1 molar ratio) gave (II) (50%) and tri-n-butyltin chloride (83%).

The results from the thermal decomposition of silane (II) at various temperatures are shown in Table 1.

TABLE 1

The pyrolysis of trichloro(1,1-difluoroethyl)silane

		Product (%)		
θ_c/°C	t/h	$CH_3{\cdot}CCl_2{\cdot}SiClF_2$ (V)	$CH_2{:}CHF$	$CH_2{:}CHCl$
100	2	99		
150	12	98		
180	8	91	8	
205	12	63	29	3
235	16	12	34	53
310	7		31	61
400	1·5		54	35

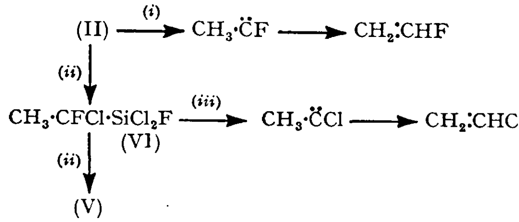
The only product at 100 and 150 °C was chloro(1,1-dichloroethyl)difluorosilane, (V), which was subsequently found to be stable up to *ca.* 200 °C. The formation of this compound is powerful evidence in favour of a halogen-exchange mechanism because the conditions used (100 °C for 2 h) were much milder than the known minimum conditions (*ca.* 225 °C for 16 h)[8,9] required for decomposition of compounds of the type $R{\cdot}CF_2{\cdot}SiCl_3$ *via* α elimination to give a carbene. The observation that thermal decomposition of silane (II) in the presence of an excess of isobutene at 100 °C gave only rearranged (V) and no cyclopropane derivatives shows that carbenes are not intermediates in the exchange process. The rearranged silane (V) is considered to arise by two halogen-exchange reactions each involving a four-centred transition state of the type suggested earlier [equation (2)].[9]

$$\text{(II)} \underset{\text{slow}}{\xrightarrow{k_1}} \underset{\text{(VI)}}{CH_3{\cdot}CFCl{\cdot}SiCl_2F} \underset{\text{fast}}{\xrightarrow{k_2}} \underset{\text{(V)}}{CH_3{\cdot}CCl_2{\cdot}SiClF_2} \quad (2)$$

The yield of the rearranged product (V) remained at >90% for pyrolysis temperatures up to 180 °C, but between 180 and 205 °C α elimination began to compete (Scheme 2). At temperatures >205 °C the halogen-exchange product (V) was found to undergo α-chlorine elimination to give vinyl chloride, the yield of which at 265 °C was almost quantitative (Table 3). Thus at these higher temperatures a concurrent second route [equation (3)] to vinyl chloride is added to the scheme. Pyrolyses

$$\text{(V)} \xrightarrow[-SiF_2Cl_2]{\alpha\text{ elimination}} CH_3{\cdot}\ddot{C}Cl \longrightarrow CH_2{:}CHCl \quad (3)$$

at 235 and 310 °C both gave vinyl chloride as the major olefinic product, showing that at these temperatures halogen exchange was the preferred initial major reaction rather than the first α elimination. However, at 400 °C the first α elimination to give vinyl fluoride (54%) predominated over the halogen-exchange reaction to give vinyl chloride (35%).



SCHEME 2 (*i*), First α elimination ($-SiFCl_3$); (*ii*), halogen exchange; and (*iii*), second α elimination ($-SiF_2Cl_2$)

The expected monohalogen-exchange product, (VI), was not detected in the products of the low-temperature pyrolyses and so an experiment was designed to detect it. A sample of silane (II) was sealed in a thick-walled n.m.r. tube and heated for various lengths of time at 100 °C, the ^{19}F n.m.r. spectrum being recorded after each period of heating. All the spectra showed an absorption band (q) at 27·0 p.p.m., due to reactant silane, and a band (s) at 60·0 p.p.m., due to rearranged silane (V); absorption bands expected for the intermediate (VI) were not observed.

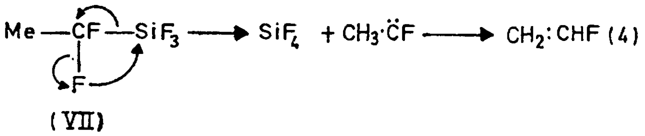
These results suggested that the second halogen exchange to give silane (V) was rapid compared with the first halogen exchange to give (VI) and that the concentration of (VI) at any given time was low (<5%, limiting sensitivity of instrument). That the reaction may indeed be treated as a first-order reaction (2) (where $k_2 \gg k_1$), rather than as a pair of consecutive reactions, was shown by the straight line obtained by plotting $\log_{10}$ [unchanged reactant] against time (Table 2). From this plot the rate constant $k_1 = 0{\cdot}033$ min^{-1}, in neat liquid at 100 °C, and half-life of the reaction, $t_{\frac{1}{2}}$ = *ca.* 21 min at 100 °C, were obtained; it is emphasised that these values are only approximate since a full kinetic investigation was not carried out.

TABLE 2

Rearrangement of silane (II) at 100 °C

Pyrolysis time/min	% Rearranged (x)	% Unchanged ($100 - x$)	$\log_{10}(100 - x)$
5	3	97	1·9868
15	30	70	1·8451
30	53	47	1·6721
45	75	25	1·3979
60	84	16	1·2041
75	92	8	0·9031

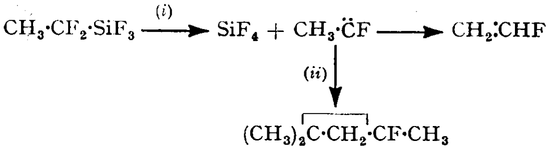
The halogen-exchange process is probably initiated by internal nucleophilic attack by fluorine on silicon and the effect of replacement of chlorine on silicon by fluorine would be to render the silicon atom more susceptible to internal nucleophilic attack. This would make the rate (k_2) of the second halogen exchange much faster than that (k_1) of the first. Support for this explanation is given by the observation that the α-elimination process to give a carbene, which is also considered to involve initial internal nucleophilic attack by fluorine on silicon, occurs at a much lower temperature with trifluoro- than trichlorosilyl compounds. Thus reaction of silane (II) with antimony trifluoride gave (1,1-difluoroethyl)trifluorosilane, (VII) (80%), which decomposed readily at 120 °C (3 h) to afford quantitative yields of vinyl fluoride and silicon tetrafluoride [equation (4)]. In contrast the trichlorosilyl analogue (II) on pyrolysis at 180 °C (8 h) gave only a low yield (8%) of the α-elimination product vinyl fluoride.



(4)

(VII)

Pyrolysis of compound (VII) at 140 °C in the presence of an excess of isobutene gave vinyl fluoride (46%), 1-fluoro-1,2,2-trimethylcyclopropane (VIII) (48%), and silicon tetrafluoride (99%) (Scheme 3). This demonstrates the intermediacy of the carbene $CH_3{\cdot}\ddot{C}F$ in thermal decomposition of silane (VII) and also shows that the rate of intramolecular rearrangement of the carbene at 140 °C is approximately the same as that of intermolecular reaction between the carbene and isobutene. However, when the silanes (II) and (V) were pyrolysed at 265 and 280 °C, respectively, in the presence of an excess of cyclohexene, the expected norcaranes were not detected. This suggests that, at the higher pyrolysis temperatures, the rates of intramolecular rearrangement of the carbenes $CH_3{\cdot}\ddot{C}F$ and $CH_3{\cdot}\ddot{C}Cl$ to vinyl fluoride and vinyl chloride, respectively, are fast compared with the rates of intermolecular reaction of the carbenes with cyclohexene.

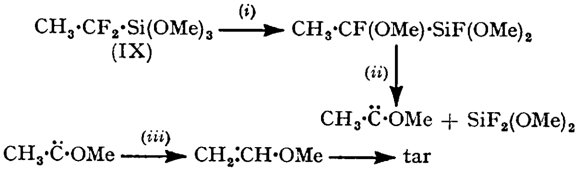


(VIII)

SCHEME 3 (*i*), Heat; (*ii*), $(CH_3)_2C{:}CH_2$

In order to determine whether interchange could take place between a methoxo-group on silicon and fluorine on the α-carbon atom, (1,1-difluoroethyl)trimethoxosilane (IX), was prepared (82%) by the reaction between (II) and methanol. At 150 °C complete decomposition of (IX) occurred to give a mixture of fluoromethoxosilanes, intractable material, and small amounts of methanol and tetramethoxosilane. Pyrolysis at this temperature for shorter periods gave unchanged silane (IX) and a similar mixture; olefins and exchange products were not detected by n.m.r. At a lower temperature (100 °C) the silane (IX) slowly decomposed (33%) with similar results.

The absence in the pyrolysis mixtures of vinyl fluoride, the α-elimination product, suggests that α exchange was the preferred initial reaction followed by rapid decomposition of the exchange product, *i.e.* as in Scheme 4. At 240 °C the products were vinyl fluoride (27%), a mixture of fluoromethoxosilanes (37%), and tar, so α elimination then successfully competes with the exchange reaction.



SCHEME 4 (*i*), Exchange, (*ii*), α elimination, and (*iii*), H migration

$$\text{(IX)} \longrightarrow SiF(OMe)_3 + CH_3{\cdot}\ddot{C}F \longrightarrow CH_2{:}CHF \quad (5)$$

EXPERIMENTAL

Reactants and products were manipulated, where possible, in a conventional vacuum system to avoid contamination with air or moisture. Photochemical reactions were carried out in silica tubes (*ca.* 10 cm^3) which were shaken and irradiated with a Hanovia S.500 u.v. lamp at a distance of *ca.* 15 cm. Products were separated either by repeated fractional condensation *in vacuo* or by fractional distillation through a column. The identities of products were established by molecular-weight determination (Regnault's method), elemental analysis, i.r. spectroscopy (Perkin-Elmer model 21 spectrophotometer with sodium-chloride optics), n.m.r. spectroscopy (Perkin-Elmer R10 spectrometer operating at 56·46 MHz for ^{19}F and 60·0 MHz for ^1H with external trifluoroacetic acid and internal tetramethylsilane as the respective references), and g.l.c. [Perkin-Elmer 116, 154B, or 451 Fraktometers fitted with columns (4 m) packed with Silicone SE 30 oil (30%) on Celite].

Trichloro(2,2-dichloro-1,1-difluoroethyl)silane, (III), was prepared by photochemical reaction of 1,1-dichlorodifluoroethylene with trichlorosilane,[11] and trichloro(2-chloro-1,1-difluoroethyl)silane, (IV), was prepared by reduction of (III) with an equimolar amount of trimethylsilane.[10]

Preparation of Trichloro(1,1-*difluoroethyl*)*silane*, (II).—(a) *By reduction of silane* (IV) *with trimethylsilane.* A mixture of silane (IV) (3·00 g, 12·8 mmol) and trimethylsilane (1·85 g, 25·0 mmol) on irradiation (100 h) gave (*i*) unchanged trimethylsilane (0·83 g, 11·0 mmol, 44% recovered), (*ii*) chlorotrimethylsilane (1·09 g, 10·0 mmol, 80%), (*iii*) a mixture (0·5 g) of chlorotrimethylsilane and (II), and (*iv*) (II) (2·10 g, 10·5 mmol, 82%) (Found: *M*, 198. Calc. for $C_2H_3Cl_3F_2Si$: *M*, 199·5), the i.r. and n.m.r. spectra of which were identical with those reported.[10]

(b) *By reduction of silane* (IV) *with tri-n-butyltin hydride.* A mixture of the silane (2·01 g, 8·6 mmol) and the hydride (2·50 g, 8·6 mmol) on irradiation (50 h), gave (*i*) n-butane (0·24 g, 4·1 mmol) (Found: *M*, 58. Calc. for C_4H_{10}: *M*, 58), (*ii*) (II) (1·10 g, 5·5 mmol, 64%), (*iii*) tri-n-butyltin chloride (2·31 g, 7·1 mmol, 83%), and (*iv*) a black residue (0·5 g).

(c) *By reduction of silane* (III) *with tri-n-butyltin hydride.* A mixture of the silane (2·61 g, 9·7 mmol) and the hydride (5·46 g, 18·8 mmol) on irradiation (50 h) gave (*i*) n-butane (0·27 g, 4·65 mmol), (*ii*) (II) (0·96 g, 4·8 mmol, 50%), (*iii*) tri-n-butyltin chloride (5·04 g, 15·5 mmol, 83%), and (*iv*) a black residue (*ca.* 1·5 g).

Fluorination of Silane (II).—The silane (1·53 g, 7·65

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[11] W. I. Bevan and R. N. Haszeldine, unpublished work.

mmol), repeatedly passed in the vapour state *in vacuo* over an excess of powdered antimony trifluoride containing a small amount of antimony pentachloride, gave (1,1-*difluoroethyl*)*trifluorosilane* (0·94 g, 6·15 mmol, 80%) (Found: C, 16·0; H, 2·1%; *M*, 151. $C_2H_3F_5Si$ requires C, 16·0; H, 2·0%; *M*, 150).

Reaction of Silane (II) *with Methanol*.—The silane (1·40 g, 7·0 mmol) and methyl alcohol (0·68 g, 21·3 mmol) were mixed *in vacuo* at −196 °C and the mixture allowed to warm slowly to room temperature to give (*i*) hydrogen chloride (0·72 g, 19·8 mmol, 93%), which was removed as it was formed, (*ii*) a mixture (0·2 g) of unchanged methanol and (1,1-*difluoroethyl*)*trimethoxosilane*, (IX), and (*iii*) (IX) (1·06 g, 5·72 mmol, 82%) (Found: C, 32·5; H, 6·7. $C_5H_{12}F_2O_3Si$ requires C, 32·3; H, 6·5%); (^1H n.m.r. spectrum) τ 6·35 (9H, s, OMe) and 8·46 [3H, t, CH_3, *J*(FH) 24·1 Hz]; (^{19}F n.m.r. spectrum) δ 27·0 p.p.m. (q, CF_2).

Pyrolyses.—*Silane* (II). (a) *At* 150 °C. The silane (1·46 g, 7·3 mmol), sealed in a Dreadnought tube (*ca*. 50 cm³) and heated at 150 °C (12 h), gave *chloro*(1,1-*dichloroethyl*)*difluorosilane*, (V) (1·43 g, 7·15 mmol, 98%) (Found: C, 12·3; H, 1·5; Cl, 53·3. $C_2H_3Cl_3F_2Si$ requires C, 12·0; H, 1·5; Cl, 53·2%), b.p. 84—86 °C; τ 7·90 (s, CH_3); δ 60·0 p.p.m. (s, $SiClF_2$).

(b) *At other temperatures*. The pyrolyses were carried out in Dreadnought tubes (*ca*. 360 cm³) and the products were separated into high-boiling [(V)] and low-boiling fractions (mixture of the olefins $CH_2{:}CHF$ and $CH_2{:}CHCl$, and silicon tetrahalides). The low-boiling fraction was hydrolysed with 10% aqueous sodium hydroxide, dried (P_2O_5), and the olefin composition estimated by g.l.c. The results of these pyrolyses are shown in Table 1.

(c) ^{19}F *N.m.r. studies*. The silane was sealed in a thick-walled n.m.r. tube and pyrolysed for various lengths of time at 100 °C. After each pyrolysis the ^{19}F n.m.r. spectrum was recorded and the percentage rearrangement to silane (V) was determined by repeated peak integration. The results are shown in Table 2. A plot of $\log_{10}(100 - x)$ against time gave a straight line.

(1,1-*Difluoroethyl*)*trifluorosilane*. The silicon compound (0·82 g, 5·47 mmol), sealed in a Dreadnought tube (*ca*. 360 cm³) and heated at 120 °C (3 h), gave a mixture (0·82 g, 10·9 mmol, 100%) of vinyl fluoride and silicon tetrafluoride which, when hydrolysed with 10% aqueous sodium hydroxide, afforded vinyl fluoride (0·25 g, 5·40 mmol, 99%) (Found: *M*, 46. Calc. for C_2H_3F: *M*, 46).

Silane (V). Samples of the silicon compound were pyrolysed in Dreadnought tubes (*ca*. 360 cm³) at various temperatures and the products were separated into high-boiling (unchanged silane) and low-boiling fractions (vinyl chloride and silicon tetrahalides). Hydrolysis of the low-boiling fraction with 10% aqueous sodium hydroxide gave pure vinyl chloride. The results of the pyrolyses are shown in Table 3.

TABLE 3

Pyrolysis of silane (V)

θ_c/°C	*t*/h	Unchanged (V)/%	$CH_2{:}CHCl$ (%)
205	12	97	
235	16	16	77
265	8		92
300	7		95
400	5		95

Silane (IX). Samples of the silane were sealed in thick-walled n.m.r. tubes and then pyrolysed. After each pyrolysis the ^1H and ^{19}F n.m.r. spectra were determined.

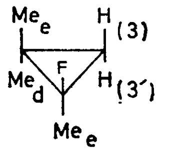
(a) *At* 150 °C. During the pyrolysis the sample blackened and, as the triplet (assigned to the Me group) and the singlet (assigned to the MeO groups) decreased in intensity in the ^1H n.m.r. spectra, there was a parallel increase in intensity of singlets at τ 6·30 [$FSi(OMe)_3$], 6·40 [$F_2Si(OMe)_2$], 6·75 ($F_3Si{\cdot}OMe$), and 6·45 [$Si(OMe)_4$]; a weak absorption was also observed at τ 8·8 (d, *J ca*. 6 Hz) but this could not be assigned. Two strong singlet absorptions gradually appeared in the ^{19}F spectra at δ 84 [$FSi(OMe)_3$] and 85 p.p.m. [$F_2Si(OMe)_2$]; two weaker singlet absorptions at 87 ($F_3Si{\cdot}OMe$) and 79 p.p.m. (unknown) were also observed. When the tube was opened after 10·5 h at 150 °C a dark non-volatile oil remained after the volatile products had been removed.

(b) *At* 100 °C. A sample of the silane heated at 100 °C (32 h) slowly darkened and the n.m.r. spectra showed that 33% of the silane had decomposed to a similar mixture of products as in the previous experiment.

(c) *At* 240 °C. The silane (0·29 g, 1·57 mmol) heated at 240 °C (5 h) gave (*i*) vinyl fluoride (0·02 g, 0·42 mmol, 27%), (*ii*) a mixture of fluoromethoxosilanes (0·58 mmol, 37%), and (*iii*) a dark non-volatile oil (*ca*. 0·2 g).

Silane (II) *in the presence of cyclohexene*. A mixture of the silane (1·37 g, 6·9 mmol) and cyclohexene (5·90 g, 72·0 mmol), sealed in a Dreadnought tube (*ca*. 360 cm³) and heated at 265 °C (5 h), gave (*i*) a mixture (10·6 mmol, 77%) of vinyl fluoride and silicon tetrahalides which after hydrolysis (10% aqueous sodium hydroxide) yielded vinyl fluoride (0·16 g, 3·6 mmol, 52%), (*ii*) unchanged cyclohexene (5·32 g, 64·9 mmol, 90% recovered), and (*iii*) a black tar (*ca*. 0·8 g).

(1,1-*Difluoroethyl*)*trifluorosilane in the presence of isobutene*. A mixture of the silane (4·40 g, 29·3 mmol) and isobutene (4·36 g, 78·0 mmol), sealed in a Dreadnought tube (*ca*. 360 cm³) and heated at 140 °C (2·5 h), gave (*i*) a mixture (42·5 mmol, 73%) of silicon tetrafluoride and vinyl fluoride shown by hydrolysis to contain vinyl fluoride (0·62 g, 13·4 mmol, 46%), (*ii*) unchanged isobutene (3·38 g, 59·8 mmol, 76% recovered), and (*iii*) 1-*fluoro*-1,2,2-*trimethylcyclopropane*, (VIII) (1·42 g, 13·9 mmol, 48%) (Found: C, 70·5; H, 11·1%; *M*, 103. $C_6H_{11}F$ requires C, 70·5; H, 10·8%; *M*, 102); τ 8·42 [d, 1H, $H_{(3)}$, *J*($FH_{(3)}$) 2·8 Hz], 8·55 [d, 3H, Me_c, *J*(FMe) 22·5 Hz], 8·80 [d, 1H, $H_{(3')}$, *J*($FH_{(3')}$) 11·5 Hz], 8·83 [d, 3H, Me_a, *J*(FMe) 2·4 Hz], and 9·00 [d, 3H, Me_d, *J*(FMe) 3·0 Hz]; δ 23·1 p.p.m. (qd mult).



Silane (V) *in the presence of cyclohexene*. A mixture of the silane (1·44 g, 7·2 mmol) and cyclohexene (6·10 g, 74·2 mmol), sealed in a Dreadnought tube (*ca*. 360 cm³) and heated at 285 °C (5 h), gave (*i*) a mixture (11·8 mmol, 82%) of vinyl chloride and silicon tetrahalides, which on hydrolysis (10% aqueous sodium hydroxide) afforded vinyl chloride (0·30 g, 4·8 mmol, 67%), (*ii*) unchanged cyclohexene (5·90 g, 72·0 mmol, 97% recovered), and (*iii*) a black tar (*ca*. 0·3 g).

Silane (II) *in the presence of isobutene*. An equimolar mixture of the silane and isobutene was sealed in a thick-walled n.m.r. tube and the ^{19}F and ^{1}H n.m.r. spectra recorded. The tube and contents were then heated at 100 °C (1·5 h) and the spectra again recorded; only absorption bands due to isobutene and silane (V) were observed.

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