Carbene Chemistry. Part VII.[1] The Preparation and Pyrolysis of 2-Chloro-1,1-difluoroethyl-, 1-Chloro-1,2,2-trifluoroethyl-, and 1,2-Dichloro-1,2-difluoroethyl-trichlorosilanes [2,3]

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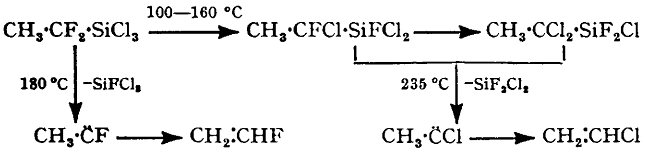
Pyrolysis of 2-chloro-1,1-difluoroethyltrichlorosilane at 225 °C mainly involves α-elimination and halogen-exchange followed by α-elimination to give a mixture of fluorochlorosilanes, 1-chloro-1-fluoroethylene, and 1,1-dichloroethylene as major products. At 140 °C only halogen-exchange takes place and 1,1,2-trichloroethylchlorodifluorosilane is formed exclusively; the half-life of the rearrangement reaction is *ca.* 50 min. Pyrolysis of the rearranged silane at 225 °C gives 1,1-dichloroethylene and a mixture of chlorofluorosilanes. Photochemical reaction of 1,2-dichloro-1,2-difluoroethylene with trichlorosilane gives a mixture of 1,2-dichloro-1,2-difluoroethyltrichlorosilane and 2-chloro-1,2-difluoroethyltrichlorosilane. 1,2-Dichloro-1,2-difluoroethyltrichlorosilane decomposes readily at 225 °C into a mixture of chlorofluorosilanes, 1,1-dichloro-2-fluoroethylene, and trichloroethylene. Photochemical reaction of chlorine with 1,2,2-trifluoroethyltrichlorosilane gives mainly 1-chloro-1,2,2-trifluoroethyltrichlorosilane, which on pyrolysis at 225 °C affords a mixture of chlorofluorosilanes, 1-chloro-2,2-difluoroethylene, and 1,1-dichloro-2-fluoroethylene; at 160 °C 1,1-dichloro-2,2-difluoroethyldichlorofluorosilane is formed exclusively.

THE products obtained when αα-difluoroalkyltrichlorosilanes are pyrolysed depend on the temperature employed.[1] Thus the pyrolysis of 1,1-difluoroethyltrichlorosilane at 100—150 °C gives only 1,1-dichloroethylchlorodifluorosilane, formed by two successive chlorine–fluorine exchange reactions, while at *ca.* 180 °C α-elimination of fluorine competes with halogen exchange, and at *ca.* 235 °C or above α-elimination from the rearranged compounds also occurs, *i.e.*



Attempts to detect the monohalogen-exchange compound $CH_3{\cdot}CFCl{\cdot}SiFCl_2$ were unsuccessful; replacement of chlorine by fluorine on silicon renders the silicon more susceptible to nucleophilic attack so that the second halogen-exchange is more rapid than the first.

The low-temperature pyrolysis of 2-chloro-1,1-difluoroethyltrichlorosilane (I) was investigated in the present work because in this compound the size of the CH_2Cl group could sterically hinder the halogen-exchange and thus allow the monohalogen-exchange compound $CH_2Cl{\cdot}CFCl{\cdot}SiFCl_2$ (II) to be detected.

The silane (I), prepared by the reduction of 2,2-dichloro-1,1-difluoroethyltrichlorosilane with trimethylsilane, was pyrolysed at temperatures from 140 to 225 °C. At 225 °C (16 h) the products were 1-chloro-1-fluoro-

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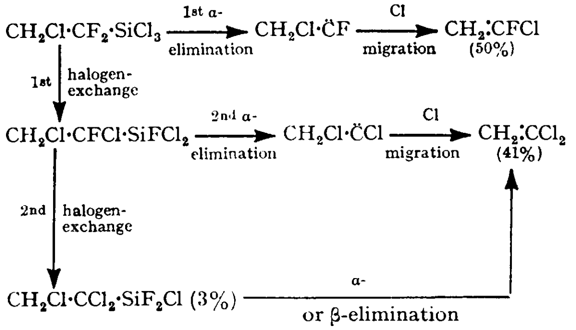
[1] Part VI, W. I. Bevan, R. N. Haszeldine, J. Middleton, and A. E. Tipping, *J.C.S. Dalton*, 1975, 252.

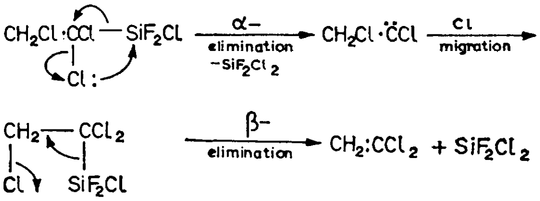
[2] Reported briefly in part by R. N. Haszeldine, ' Polyfluoroalkyl Silicon Compounds,' in ' New Pathways in Inorganic Chemistry,' eds. E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Cambridge University Press, Cambridge, 1968, p. 115.

[3] Reported in part as a preliminary communication, W. I. Bevan, R. N. Haszeldine, J. Middleton, and A. E. Tipping, *J. Organometallic Chem.*, 1970, **23**, C17.

ethylene (50%), 1,1-dichloroethylene (41%), the rearranged product 1,1,2-trichloroethylchlorodifluorosilane (III) (3%), and a mixture of tetrahalosilanes. At this temperature halogen-exchange thus accounts for *ca.* 50% of the products while pyrolysis of the silane $CH_3\cdot CF_2\cdot SiCl_3$ at 235 °C gave >60% of products arising *via* halogen-exchange.[1] This indicates that the increase in size, accompanying the introduction of a β-chlorine atom, makes the α-halogen-exchange more difficult and thus increases the contribution of the first α-elimination reaction:



As previously observed[4-6] for the pyrolyses of other chlorofluoroalkyltrihalosilanes, migration of chlorine rather than hydrogen in the intermediate carbenes took place. The exchange-product $CH_2Cl\cdot CCl_2\cdot SiF_2Cl$ (III) was found to be unstable under the reaction conditions (225 °C) and was 60% decomposed to 1,1-dichloroethylene and dichlorodifluorosilane after 16 h. It was not possible to determine whether this decomposition involved α- or β-elimination.



Since the rate of rearrangement of 2-chloro-1,1-difluoroethyltrichlorosilane appeared to be relatively slow an attempt was made to detect the monohalogen-exchange product (II) by n.m.r. spectroscopy. A sample of silane (I) was pyrolysed for increasing lengths of time at 140 °C in an n.m.r. sample tube with successive recording of the ^{19}F spectrum; the results are summarised in Table 1. The triplet signal for the α-CF_2 group of (I) (35·5 p.p.m. upfield of $CF_3\cdot CO_2H$) steadily decreased in intensity while the intensity of the singlet for the SiF_2Cl group of (III) (56·0 p.p.m.) correspondingly increased. Resonances ascribable to silane (II) were not observed which indicated that the concentration of silane (II) at any one time was low (<5%, the sensitivity limit of the spectrometer). Thus the second halogen-exchange is fast and the first halogen-exchange is the rate-determining step ($k_2 \gg k_1$).

$$CH_2Cl\cdot CF_2\cdot SiCl_3 \xrightarrow{k_1} CH_2Cl\cdot CFCl\cdot SiFCl_2 \xrightarrow{k_2} CH_2Cl\cdot CCl_2\cdot SiF_2Cl$$

A plot of $\log_{10}(a - x)$ against t gave a straight line from which a first-order rate constant k_1 of 0·014 min^{-1} at 140 °C in neat solution and a half-life $t_{1/2}$ of *ca.* 50 min at 140 °C were obtained. The steric effect of the chlorine on the β-carbon to silicon in hindering the halogen-exchange is well demonstrated by this result, since for the rearrangement of the silane $CH_3\cdot CF_2\cdot SiCl_3$ to $CH_3\cdot CCl_2\cdot SiF_2Cl$ in neat solution at 100 °C the half-life $t_{1/2}$ is *ca.* 21 min.[1]

Since the monohalogen-exchange intermediate (II) was not detected in this reaction it was considered that the preparation and pyrolysis of compounds as closely related as possible to such intermediates of general formula $RCFCl\cdot SiFCl_2$ would prove informative. To this end two silanes of general formula $RCFCl\cdot SiCl_3$, *i.e.* 1,2-dichloro-1,2-difluoroethyltrichlorosilane (IV) and 1-chloro-1,2,2-trifluoroethyltrichlorosilane (V), were prepared and their pyrolyses investigated.

TABLE 1

Rearrangement of $CH_2Cl\cdot CF_2\cdot SiCl_3$ to $CH_2Cl\cdot CCl_2\cdot SiF_2Cl$ at 140 °C

Pyrolysis time (t/min)	% Rearrangement (x)	% Unrearranged ($a - x$)	$\log_{10}(a - x)$
15	14·3	85·7	1·9330
30	28·6	71·4	1·8537
45	43·0	57·0	1·7559
65	57·2	42·8	1·6314
95	71·5	28·5	1·4548
155	87·6	12·4	1·0934

The photochemical reaction of 1,2-dichloro-1,2-difluoroethylene with an excess of trichlorosilane gave (IV) (41%) and the reduced compound 2-chloro-1,2-difluoroethyltrichlorosilane (VI) (16%). These products are probably formed as shown in the following reaction scheme:

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

$$\cdot SiCl_3 + CFCl{:}CFCl \longrightarrow \dot{C}FCl\cdot CFCl\cdot SiCl_3 \xrightarrow{HSiCl_3} CHFCl\cdot CFCl\cdot SiCl_3 \quad (IV)$$

$$(IV) + \cdot SiCl_3 \longrightarrow SiCl_4 + CHFCl\cdot\dot{C}F\cdot SiCl_3$$

$$CHFCl\cdot\dot{C}F\cdot SiCl_3 \xrightarrow{HSiCl_3} CHFCl\cdot CHF\cdot SiCl_3 \quad (VI)$$

The reduction to give the reduced silane (VI) and not the isomer 1-chloro-1,2-difluoroethyltrichlorosilane is explained by the greater stability of the intermediate tertiary radical $CHFCl\cdot\dot{C}F\cdot SiCl_3$, in which the *d*-orbitals

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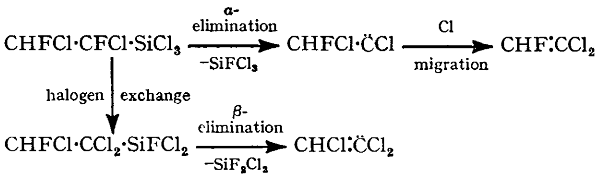
[4] R. N. Haszeldine and J. C. Young, *Proc. Chem. Soc.*, 1959, 394.

[5] W. I. Bevan, R. N. Haszeldine, and J. C. Young, *Chem. and Ind.*, 1961, 789.

[6] W. I. Bevan and R. N. Haszeldine, unpublished results.

of the adjacent silicon atom can delocalise the odd electron, as compared to the isomeric secondary radical $\dot{C}HF{\cdot}CFCl{\cdot}SiCl_3$. An examination of both the products of this reaction (IV) and (VI) by n.m.r. spectroscopy revealed that in each case the two diastereoisomeric forms (*erythro* and *threo*) were present.

The pyrolysis of silane (IV) at 225 °C (16 h) gave 1,1-dichloro-2-fluoroethylene (75%), trichloroethylene (17%), and a mixture of silicon tetrahalides.



$$\begin{tikzcd} CHFCl{\cdot}CFCl{\cdot}SiCl_3 \arrow[r, "\alpha\text{-elimination}", "-SiFCl_3"'] \arrow[d, "\text{halogen exchange}"] & CHFCl{\cdot}\ddot{C}Cl \arrow[r, "Cl", "\text{migration}"'] & CHF{:}CCl_2 \\ CHFCl{\cdot}CCl_2{\cdot}SiFCl_2 \arrow[r, "\beta\text{-elimination}", "-SiF_2Cl_2"'] & CHCl{:}CCl_2 & \end{tikzcd}$$

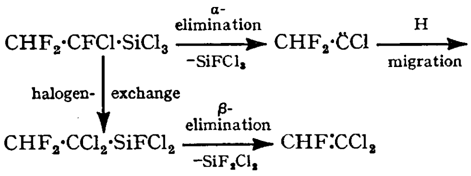
The observation that chlorine migration in the intermediate carbene occurs to the exclusion of hydrogen or fluorine migration is in agreement with previous work.[5,6] It has also been observed that with similar carbenes hydrogen migration occurs in preference to fluorine [6,7] or pentafluoroethyl [8] migration and that pentafluoroethyl migration occurs in preference to fluorine migration.[9] The order of migratory aptitudes is therefore: $Cl > H > C_2F_5 > F$.

The ratio of the yields of 1,1-dichloro-2-fluoroethylene and trichloroethylene is 4·4 : 1·0 which compares favourably with the ratio of 5·7 : 1·0 found in the pyrolysis of the silane $CHFCl{\cdot}CF_2{\cdot}SiCl_3$ under similar conditions,[6] a reaction which was considered to involve the intermediate silane $CHFCl{\cdot}CFCl{\cdot}SiFCl_2$.

$$CHFCl{\cdot}CF_2{\cdot}SiCl_3 \xrightarrow{225^{\circ}} \underset{(59\%)}{CHF{:}CFCl} + \underset{(17\%)}{CHF{:}CCl_2} + \underset{(3\%)}{CHCl{:}CCl_2}$$

Photochemical chlorination of the trifluoroethylene–trichlorosilane adduct, $CHF_2{\cdot}CHF{\cdot}SiCl_3$, with chlorine gave a mixture of high-boiling products which was shown, by n.m.r. spectroscopy, to contain unchanged starting material (13% recovered), (V) (70%), 2-chloro-1,2,2-trifluoroethyltrichlorosilane (7%), and 1,2-dichloro-1,2,2-trifluoroethyltrichlorosilane (10%). Careful fractional distillation of this mixture gave a pure sample of the required silane (V) (44%). The large excess of α-chlorination over β-chlorination demonstrates that the intermediate tertiary radical, $CHF_2{\cdot}\dot{C}F{\cdot}SiCl_3$, stabilised by the adjacent vacant *d*-orbitals on silicon, is more stable than the isomeric tertiary radical $\dot{C}F_2{\cdot}CHF{\cdot}SiCl_3$ in which such delocalisation by silicon is not possible.

The pyrolysis of silane (V) at 225 °C (16 h) gave 1-chloro-2,2-difluoroethylene (37%), 1,1-dichloro-2-fluoroethylene (45%), and a mixture of tetrahalosilanes.



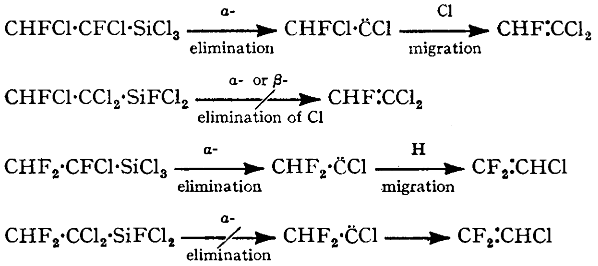
$$\begin{tikzcd} CHF_2{\cdot}CFCl{\cdot}SiCl_3 \arrow[r, "\alpha\text{-elimination}", "-SiFCl_3"'] \arrow[d, "\text{halogen-exchange}"] & CHF_2{\cdot}\ddot{C}Cl \arrow[r, "H", "\text{migration}"'] & CF_2{:}CHCl \\ CHF_2{\cdot}CCl_2{\cdot}SiFCl_2 \arrow[r, "\beta\text{-elimination}", "-SiF_2Cl_2"'] & CHF{:}CCl_2 & \end{tikzcd}$$

The ratio of the yields of 1-chloro-2,2-difluoroethylene and 1,1-dichloro-2-fluoroethylene is 1·0 : 1·2. This is in close agreement with the ratio of the same olefins obtained from the pyrolysis of the silane $CHF_2{\cdot}CF_2{\cdot}SiCl_3$ at 225 °C (1·0 : 1·05).[6]

$$CHF_2{\cdot}CF_2{\cdot}SiCl_3 \longrightarrow \underset{(29\%)}{CHF{:}CF_2} + \underset{(21\%)}{CHCl{:}CF_2} + \underset{(22\%)}{CHF{:}CCl_2}$$

The similar ratios of olefins found in the decompositions of the silanes $RCF_2{\cdot}SiCl_3$ and $RCFCl{\cdot}SiCl_3$ is good evidence in favour of the formation and subsequent decomposition of the monohalogen-exchange intermediate $RCFCl{\cdot}SiFCl_2$.

The olefins $CHF{:}CCl_2$ and $CHCl{:}CF_2$ could arise either by α-elimination from the starting materials or by α-elimination from the rearranged silanes $CHFCl{\cdot}CCl_2{\cdot}SiFCl_2$ and $CHF_2{\cdot}CCl_2{\cdot}SiFCl_2$; the former mechanism is preferred because elimination of chlorine rather than fluorine from the rearranged silanes is unlikely.



$$CHFCl{\cdot}CFCl{\cdot}SiCl_3 \xrightarrow[\text{elimination}]{\alpha\text{-}} CHFCl{\cdot}\ddot{C}Cl \xrightarrow[\text{migration}]{Cl} CHF{:}CCl_2$$

$$CHFCl{\cdot}CCl_2{\cdot}SiFCl_2 \;\overset{\alpha\text{- or }\beta\text{-}}{\underset{\text{elimination of Cl}}{\nrightarrow}}\; CHF{:}CCl_2$$

$$CHF_2{\cdot}CFCl{\cdot}SiCl_3 \xrightarrow[\text{elimination}]{\alpha\text{-}} CHF_2{\cdot}\ddot{C}Cl \xrightarrow[\text{migration}]{H} CF_2{:}CHCl$$

$$CHF_2{\cdot}CCl_2{\cdot}SiFCl_2 \;\overset{\alpha\text{-}}{\underset{\text{elimination}}{\nrightarrow}}\; CHF_2{\cdot}\ddot{C}Cl \longrightarrow CF_2{:}CHCl$$

Three fluorine atoms on silicon render the latter electron poor and therefore more susceptible to nucleophilic attack than the silicon atom in the corresponding trichlorosilyl compounds. As a result fluoroethyltrifluorosilanes decompose rapidly at moderate temperature (*ca.* 140 °C/3 h),[1,6] and the stepwise replacement of fluorine in the $-SiF_3$ group by chlorine causes an increase in the decomposition temperature up to that observed for the decomposition of fluoroethyltrichlorosilanes (*ca.* 225 °C/16 h).[1,5,6] Thus fluoroethylchlorodifluorosilanes will probably be completely decomposed at *ca.* 170 °C (5 h) and fluoroethyldichlorofluorosilanes will probably be completely decomposed at *ca.* 200 °C (10 h). The elimination of dichlorodifluorosilane from the silanes $CH_3{\cdot}CCl_2{\cdot}SiF_2Cl$ [1] and $CH_2Cl{\cdot}CCl_2{\cdot}SiF_2Cl$ is relatively slow at *ca.* 225 °C (77 and 60% decomposition, respectively, after 16 h) and it is therefore probable that elimination of trichlorofluorosilane from compounds of the type $RCCl_2{\cdot}SiFCl_2$ will be even more difficult. Hence if the ethyl group contains both chlorine and fluorine the fluorine is eliminated in preference to chlorine.

The ease with which the monohalogen-exchange compounds can undergo the second halogen-exchange was

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[7] W. I. Bevan and R. N. Haszeldine, *J.C.S. Dalton*, 1974, 2509.

[8] J. H. Atherton, R. Fields, and R. N. Haszeldine, *J. Chem. Soc. (C)*, 1971, 366.

[9] R. Fields and R. N. Haszeldine, *J. Chem. Soc.*, 1964, 1881.

demonstrated by an n.m.r. study of the low-temperature pyrolysis of the silane (V). At 160 °C (20 h) the silane had rearranged to the compound $\mathrm{CHF_2{\cdot}CCl_2{\cdot}SiFCl_2}$ to the extent of 85%. The temperature of the pyrolysis was well below that necessary to promote β-fluorine elimination from the rearranged product (probably *ca.* 200 °C) hence further reaction was not observed.

It is clear that the products formed during the thermal decomposition of alkylsilicon compounds $\mathrm{RCF_2{\cdot}SiCl_3}$ and $\mathrm{RCFCl{\cdot}SiCl_3}$ depend on the size of the group R and the pyrolysis temperatures used. Exclusive halogen exchange occurs at low temperatures and is particularly rapid when R is small ($\mathrm{CH_3}$ or $\mathrm{CH_2Cl}$). When steric crowding around the α-carbon atom is increased by increasing the size of the group R (CHFCl, $\mathrm{CHF_2}$, *etc.*) the rate of halogen-exchange is slower and longer pyrolysis times are required for complete reaction. In compounds of type $\mathrm{RCF_2{\cdot}SiCl_3}$ when the first halogen-exchange has taken place the second halogen-exchange is, in all cases, rapid. In compounds where group R is bulky (R = $\mathrm{CF_2Cl}$ or $\mathrm{CFCl_2}$) halogen-exchange is found not to occur.[5,6]

At higher temperatures and as the size of group R increases, α-elimination becomes the major reaction.

Attempts to prepare trichloro(trifluoromethyl)silane and (trifluoromethyl)trimethylsilane, as precursors to difluorocarbene, by the photochemical reaction of trifluoroiodomethane with hexachlorodisilane and hexamethyldisilane, respectively, were unsuccessful.

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.* 360 ml) which were shaken and irradiated with a Hanovia S.500 u.v. lamp at a distance of 15 cm. Products were separated either by repeated fractional distillation *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 spectrophotometer model 21 with sodium chloride optics), n.m.r. spectroscopy (Perkin-Elmer R 10 spectrometer operating at 56·46 MHz for ^{19}F and 60·0 MHz for ^{1}H with external trifluoroacetic and internal tetramethylsilane as the respective references), and g.l.c. [Perkin-Elmer 116, 154B, or 451 Fraktometers using 4 m columns of Silicone SE 30 oil (30%) on Celite].

2-Chloro-1,1-difluoroethyltrichlorosilane[10] was prepared by the reduction of 2,2-dichloro-1,1-difluoroethyltrichlorosilane with trimethylsilane,[1] and 1,2,2-trifluoroethyltrichlorosilane was prepared by the photochemical reaction of trichlorosilane with trifluoroethylene.[11]

Pyrolysis of 2-*Chloro*-1,1-*difluoroethyltrichlorosilane*, (I).—(a) *At* 225 °C. The silicon compound (2·37 g, 10·1 mmol), sealed in a Dreadnought tube (*ca.* 360 ml) and heated at 225 °C (16 h), gave (i) a mixture (14·87 mmol, 73%) of 1-chloro-1-fluoroethylene and chlorofluorosilanes which, on hydrolysis (10% aqueous sodium hydroxide), gave 1-chloro-1-fluoroethylene (0·41 g, 5·1 mmol, 50%) (Found: *M*, 82. Calc. for $\mathrm{C_2H_2ClF}$: *M*, 80·5), (ii) 1,1-dichloroethylene (0·41 g, 4·16 mmol, 41%), and (iii) 1,1,2-trichloroethylchlorodifluorosilane (III) (0·06 g, 0·25 mmol, 3%); ^{1}H n.m.r. τ 5·9 (s, $\mathrm{CH_2Cl}$); ^{19}F δ 56·0 p.p.m. (s, $\mathrm{SiF_2Cl}$).

(b) *At* 140 °C. A sample of the silane was sealed in a thick-walled n.m.r. tube and pyrolysed for increasing times at 140 °C. After each pyrolysis the ^{19}F n.m.r. spectrum was recorded and the percentage rearrangement of silane (I) to silane (III) determined from the peak integration curves.

Pyrolysis of 1,1,2-*Trichloroethylchlorodifluorosilane* (III).—The silane obtained by carrying the previous reaction to completion was heated in a thick-walled n.m.r. tube at 225 °C (16 h). The ^{19}F n.m.r. spectrum showed the presence of unchanged silane and two fluorochlorosilanes (bands at 40 and 71 p.p.m.) while the ^{1}H spectrum showed singlet absorptions at τ 5·9 [unchanged (III), 40%] and 3·65 ($\mathrm{CH_2{:}CCl_2}$, 60%). When the tube was opened and the products treated with water *in vacuo* 1,1-dichloroethylene (Found: *M*, 96. Calc. for $\mathrm{C_2H_2Cl_2}$: *M*, 97), was obtained as the only volatile product.

Preparation of 1,2-*Dichloro*-1,2-*difluoroethyltrichlorosilane*.—A mixture of 1,2-dichloro-1,2-difluoroethylene (9·98 g, 75·0 mmol) and trichlorosilane (33·5 g, 0·25 mol), on irradiation (60 h), gave (i) unchanged trichlorosilane (24·7 g, 0·184 mol, 74% recovered), b.p. 32—38 °C, (ii) a mixture (*ca.* 3 g), b.p. 38—65 °C, of unchanged trichlorosilane contaminated with silicon tetrachloride, (iii) an intermediate fraction (*ca.* 1 g), b.p. <90 °C at 130 mmHg, (iv) a major fraction (11·5 g), b.p. 90—92 °C at 130 mmHg, and (v) a residue (*ca.* 3 g), b.p. >92 °C at 130 mmHg. The major fraction (iv) was shown by g.l.c. (column at 70 °C) to contain two components in the ratio 28 : 72 which were separated and identified as 2-chloro-1,2-difluoroethyltrichlorosilane (VI) (2·8 g, 12·0 mmol, 16%) and 1,2-*dichloro*-1,2-*difluoroethyltrichlorosilane* (IV) (8·3 g, 31·0 mmol, 41%) (Found: C, 9·1; H, 0·7; Cl, 66·3. $\mathrm{C_2HCl_5F_2Si}$ requires C, 8·9; H, 0·4; Cl, 66·1%).

The n.m.r. spectra of $\mathrm{C\overset{a}{H}\overset{c}{F}Cl{\cdot}C\overset{b}{H}\overset{d}{F}{\cdot}SiCl_3}$ (VI) revealed the presence of two diastereoisomers (A and B) (relative abundance 60 : 40); the ^{19}F spectrum consisted of four bands (all dd) at 62·0, 64·0, 78·0, and 78·6 p.p.m. to high field of reference and the ^{1}H spectrum consisted also of four bands (all dd) at τ 3·55, 3·60, 5·20, and 5·27. The ^{19}F n.m.r. bands at 62·0 and 78·6 p.p.m. were assigned to the CHFCl and CHF group fluorines, respectively, in isomer (B) and those at 64·0 and 78·0 p.p.m. to the same fluorines in the major isomer (A). The ^{1}H bands at τ 3·55 and 5·20 were assigned to the CHFCl and CHF protons, respectively, in isomer (A) and those at τ 3·60 and 5·27 to the same protons in isomer (B). The coupling constants were almost identical in the two isomers: $J_{\mathrm{ac}} \bumpeq J_{\mathrm{bd}}$ *ca.* 51 Hz; J_{cd} *ca.* 24 Hz; J_{cb} *ca.* 14 Hz; J_{ab} *ca.* 5 Hz.

The n.m.r. spectra of $\mathrm{C\overset{a}{H}\overset{b}{F}Cl{\cdot}C\overset{c}{F}Cl{\cdot}SiCl_3}$ showed the presence of two diastereoisomers (C and D) in equal abundance; the ^{19}F spectrum showed three regions of absorption at 53·1 p.p.m. (dd, CHFCl group in isomer C), 67·0 p.p.m. (dd, CFCl group in isomer C), and 63·0 p.p.m. (two overlapping dd, CHFCl and CFCl groups in isomer D) and the ^{1}H spectrum consisted of two absorption regions, one for each

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[10] W. I. Bevan, R. N. Haszeldine, J. Middleton, and A. E. Tipping, *J.C.S. Dalton*, 1975, in the press.

[11] C. J. Attridge, D. Cooper, R. N. Haszeldine, and M. J. Newlands, unpublished results.

isomer centred on τ 3·51 (dd) and 3·60 (dd). The coupling constants were almost identical in the two isomers: J_{ab} 49 Hz; J_{ac} 3·8 Hz; J_{bc} 31·5 Hz.

Pyrolysis of 1,2-*Dichloro*-1,2-*difluoroethyltrichlorosilane*.—The silicon compound (1·21 g, 4·5 mmol), sealed *in vacuo* in a Dreadnought tube (*ca.* 360 ml) and heated at 225 °C (16 h), gave (i) 1,1-dichlorofluoroethylene (0·39 g, 3·38 mmol, 75%) (Found: *M*, 114. Calc. for C_2HCl_2F: *M*, 115), (ii) trichloroethylene (0·10 g, 0·77 mmol, 17%) (Found: *M*, 144. Calc. for C_2HCl_3: *M*, 145·5), and (iii) a mixture (4·15 mmol, 92%) of tetrahalosilanes which was completely hydrolysed by dilute aqueous sodium hydroxide.

Preparation of 1-*Chloro*-1,2,2-*trifluoroethyltrichlorosilane* (V).—A mixture of 1,2,2-trifluoroethyltrichlorosilane (20·0 g, 92·0 mmol) and chlorine (6·55 g, 92·0 mmol), on irradiation (16 h), gave a mixture of hydrogen chloride and unchanged chlorine, and a higher-boiling mixture (23·0 g) which was shown by n.m.r. spectroscopy to contain 1-chloro-1,2,2-trifluoroethyltrichlorosilane (70%), 2-chloro-1,2,2-trifluoroethyltrichlorosilane (7%), 1,2-dichloro-1,2,2-trifluoroethyltrichlorosilane (10%), and unchanged starting silane (13%). Fractionation of this mixture gave 1-chloro-1,2,2-trifluoroethyltrichlorosilane (10·2 g, 40·5 mmol, 44%) (Found: C, 9·9; H, 0·5; Cl, 56·1. Calc. for $C_2HCl_4F_3Si$: C, 9·5; H, 0·4; Cl, 56·3%), b.p. 120—121 °C (lit.,[12] 116—118 °C); ^1H n.m.r. band at τ 4·0 (td, CHF_2, J_{HF_a} 54·9, J_{HF_b} 5·0 Hz); ^{19}F n.m.r. δ 47·5 (ABdd, 2F, CHF_2, J_{AB} 295, $J_{F_aF_b}$ 14·0 Hz) and 73·6 p.p.m. (td, 1F, CFCl).

Pyrolysis of 1-*Chloro*-1,2,2-*trifluoroethyltrichlorosilane*.—(a) *At* 265 °C. The silane (1·70 g, 6·75 mmol), sealed in a Dreadnought tube (*ca.* 360 ml) and heated at 225 °C (16 h), gave (i) a mixture of tetrahalosilanes (5·55 mmol, 82%), (ii) 1-chloro-2,2-difluoroethylene (0·246 g, 2·50 mmol, 37%) (Found: *M*, 98. Calc. for C_2HClF_2: *M*, 98·5), and (iii) 1,1-dichlorofluoroethylene (0·35 g, 3·0 mmol, 45%) (Found: *M*, 115. Calc. for C_2HCl_2F: *M*, 115).

(b) *At* 160 °C. The silane, sealed in a heavy-walled n.m.r. tube and heated at 160 °C (20 h), was shown by n.m.r. to have rearranged to 1,1-dichloro-2,2-difluoroethyldichlorofluorosilane to the extent of 85%; ^{19}F n.m.r. δ 41·0 (dd, 2F, CHF_2, J_{HF} 55·0, J_{FF} 4·5 Hz) and 42·0 p.p.m. (td, 1F, $SiFCl_2$, J_{HF} *ca.* 1 Hz).

Reaction of Trifluoroiodomethane with Hexamethyldisilane.—A mixture of trifluoroiodomethane (5·90 g, 30·0 mmol) and hexamethyldisilane (2·19 g, 15·0 mmol), on irradiation in a silica tube (*ca.* 50 ml) (100 h), gave (i) trifluoromethane (0·69 g, 10·0 mmol, 88%), (ii) unchanged trifluoroiodomethane (3·65 g, 18·6 mmol, 62% recovered), (iii) a mixture (2·00 g, 9·2 mmol) shown by g.l.c. (4 m column at 20 °C) and i.r. spectroscopy to contain unchanged hexamethyldisilane (0·79 g, 5·4 mmol, 36% recovered), iodotrimethylsilane (1·12 g, 3·75 mmol, 20%), and hexamethyldisiloxane (0·08 g, 0·5 mmol, 5%), and (iv) a dark non-volatile oil (*ca.* 1·5 g).

Reaction of Trifluoroiodomethane with Hexachlorodisilane.—A mixture of trifluoroiodomethane (8·42 g, 43·0 mmol) and hexachlorodisilane (4·23 g, 15·7 mmol), on irradiation (12 days), gave (i) unchanged trifluoroiodomethane (8·40 g, 42·8 mmol, 99% recovered), (ii) a mixture (0·3 g) of hexachlorodisilane and two minor unknown components (g.l.c., 4 m, column at 20 °C), and (iii) unchanged hexachlorodisilane (3·43 g, 12·8 mmol, 82% recovered).

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