871. *Polyfluoroalkyl Compounds of Silicon. Part V.* The Reaction of Trichlorosilane with Chlorotrifluoroethylene, and Halogen-abstraction by Silyl Radicals.*†

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Photochemical reaction of trichlorosilane with chlorotrifluoroethylene yields the compound $\mathrm{CHFCl{\cdot}CF_2{\cdot}SiCl_3}$ and not $\mathrm{CHF_2{\cdot}CFCl{\cdot}SiCl_3}$. A new type of radical chain reaction, involving alternate formation of silyl and alkyl radicals:

$$>\mathrm{SiHX} \xrightarrow{\text{u.v.}} >\mathrm{SiX}\cdot$$
$$>\mathrm{SiX}\cdot + >\mathrm{CHY} \longrightarrow >\mathrm{SiXY} + >\mathrm{CH}\cdot$$
$$>\mathrm{CH}\cdot + >\mathrm{SiHX} \longrightarrow >\mathrm{CH_2} + >\mathrm{SiX}\cdot \longrightarrow \text{etc.}$$
$$\text{where X and Y} = \text{halogen}$$

is proposed to account for the formation of the by-product $\mathrm{CH_2F{\cdot}CF_2{\cdot}SiCl_3}$. Silyl radicals thus abstract halogen rather than hydrogen, whereas alkyl or aryl radicals abstract hydrogen rather than halogen. The reaction of trichlorosilane with trifluoroethylene gives mainly the compound $\mathrm{CHF_2{\cdot}CHF{\cdot}SiCl_3}$. Hydrolysis of the compounds $\overset{\beta}{\mathrm{C}}\mathrm{HFX{\cdot}}\overset{\alpha}{\mathrm{C}}\mathrm{FY{\cdot}SiCl_3}$ shows that, although the main product is the alkane CHFX·CHFY, simultaneous loss of β-chlorine (X = Cl) occurs even when Y = F, and loss of β-fluorine (X = F) occurs when Y = H but not when Y = F.

Reaction of trichlorosilane with tetrafluoroethylene, initiated by ultraviolet light, smoothly gives the compounds $\mathrm{H{\cdot}[CF_2{\cdot}CF_2]_{\mathit{n}}{\cdot}SiCl_3}$; the 1 : 1-adduct, where $n = 1$, can be obtained in good yield.[1] The related olefin chlorotrifluoroethylene is known to be sensitive to attack by free radicals such as $\mathrm{CF_3}\cdot$, $\mathrm{CCl_3}\cdot$, or Br·, and the $\mathrm{CF_2}$ group of the olefin is attacked preferentially.[2] Thus, if the $\mathrm{SiCl_3}$ radical (as distinct from the hydrogen atom), formed when trichlorosilane is irradiated, attacks an olefin in an addition reaction, it can

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* Part IV, Geyer, Haszeldine, Leedham, and Marklow, *J.*, 1957, 4472.
† Cf. *Proc. Chem. Soc.*, 1959, 394.

[1] Haszeldine and Marklow, *J.*, 1956, 962.
[2] Haszeldine and Steele, *J.*, 1953, 1592.

be expected that photochemical reaction of trichlorosilane with chlorotrifluoroethylene would yield 2-chloro-1,1,2-trifluoroethyltrichlorosilane (I) rather than its isomer (II):

$$\underset{\text{(I)}}{CHFCl{\cdot}CF_2{\cdot}SiCl_3} \qquad \underset{\text{(II)}}{CHF_2{\cdot}CFCl{\cdot}SiCl_3} \qquad \underset{\text{(III)}}{CFCl_2{\cdot}CF_2{\cdot}SiCl_3}$$

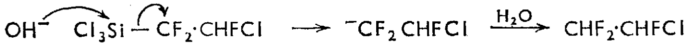
$$SiHCl_3 \xrightarrow{h\nu} SiCl_3{\cdot} + H{\cdot}$$
$$H{\cdot} + SiHCl_3 \longrightarrow H_2 + SiCl_3{\cdot}$$
$$SiCl_3{\cdot} + CF_2{:}CFCl \longrightarrow {\cdot}CFCl{\cdot}CF_2{\cdot}SiCl_3 \xrightarrow{SiHCl_3} CHFCl{\cdot}CF_2{\cdot}SiCl_3 + SiCl_3{\cdot} \longrightarrow \text{etc.}$$

Apart from polymeric material $H{\cdot}[CFCl{\cdot}CF_2]_n{\cdot}SiCl_3$ formed by reactions

$${\cdot}CFCl{\cdot}CF_2{\cdot}SiCl_3 + CF_2{:}CFCl \longrightarrow {\cdot}CFCl{\cdot}CF_2{\cdot}CFCl{\cdot}CF_2{\cdot}SiCl_3 \xrightarrow{SiHCl_3} H{\cdot}[CFCl{\cdot}CF_2]_2{\cdot}SiCl_3 + SiCl_3{\cdot} \longrightarrow \text{etc.}$$

two compounds, b. p. 120° and 97°, respectively, were isolated from the reaction of trichlorosilane with chlorotrifluoroethylene. The first has structure (I), as shown by the following reactions. Aqueous alkaline hydrolysis gave 91% of 1-chloro-1,2,2-trifluoroethane and 9% of trifluoroethylene; the chlorofluoroalkane is not dehydrochlorinated by aqueous base under the conditions used for the hydrolysis, so a concerted elimination reaction:

or chloride-ion elimination from the carbanion $^-CF_2{\cdot}CHFCl$, must accompany the main displacement reaction:



$$OH^- \; Cl_3Si{-}CF_2{\cdot}CHFCl \longrightarrow {}^-CF_2CHFCl \xrightarrow{H_2O} CHF_2{\cdot}CHFCl$$

Marked reactivity of halogen β to silicon thus appears even with chlorofluoroalkyl groups.

Photochemical chlorination of compound (I) yields 2,2-dichlorotrifluoroethyltrichlorosilane (III), hydrolysis of which gives 1,1-dichloro-1,2,2-trifluoroethane (87%) and chlorotrifluoroethylene (13%):

$$CFCl_2{\cdot}CF_2{\cdot}SiCl_3 \xrightarrow{OH^-} CFCl_2{\cdot}CHF_2 + CFCl{:}CF_2$$

Compound (II) would have given 1,2-dichloro-1,1,2-trifluoroethane as the main product, and the two isomeric dichlorotrifluoroethanes are readily distinguished by physical properties, particularly by infrared spectroscopy; the 1,2-dichloro-compound is also readily dechlorinated to give trifluoroethylene.

1,1-Dichloro-1,2,2-trifluoroethane had not been fully characterised previously, and it was therefore synthesised from 1,1,2,2-tetrachloroethane by standard procedures: [3]

$$CHCl_2{\cdot}CHCl_2 \xrightarrow{SbF_3,\ Sb^V} CHF_2{\cdot}CHCl_2 \xrightarrow{Cl_2,h\nu} CHF_2{\cdot}CCl_3 \xrightarrow{SbF_3,Sb^V} CHF_2{\cdot}CFCl_2$$

The product so obtained was identical with that obtained by hydrolysis of compound (III). The structures (I) and (III) are thus established.

The compound of b. p. 97° obtained by reaction of trichlorosilane with chlorotrifluoroethylene is 1,1,2-trifluoroethyltrichlorosilane (IV). Aqueous alkaline hydrolysis of this compound (IV) gave 1,1,2-trifluoroethane, and a very small amount of vinylidene fluoride:

$$\underset{\text{(IV)}}{CH_2F{\cdot}CF_2{\cdot}SiCl_3} \xrightarrow{OH^-} CH_2F{\cdot}CHF_2(+\ CF_2{:}CH_2)$$

Photochemical chlorination of the trifluoro-compound (IV) gave its dichloro-derivative (III), thus establishing the structure of the former.

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[3] Henne and Ladd, *J. Amer. Chem. Soc.*, 1936, **58**, 402; Bruesch, Huskins, Padbury, and Tarrant, *Ind. Eng. Chem.*, 1951, **43**, 1253.

The amount of the reduction product (IV) formed during the trichlorosilane–chlorotrifluoroethylene reaction depends upon the $\mathrm{CF_2{:}CFCl/SiHCl_3}$ ratio *in the liquid phase* (which is the phase exposed to ultraviolet light) in the reaction vessel. A high concentration of chlorotrifluoroethylene, obtained by carrying out the reaction at a pressure (*ca.* 6 atm.) sufficient to liquefy most of the olefin, gives the monochloro-product (I) with at most 10% of the reduction product (IV). Use of identical reactant ratios, but with a larger reaction vessel so that most of the chlorotrifluoroethylene is in the vapour phase, gives a much larger yield (45%) of the reduction product (IV). These observations suggested that the latter is formed by reaction of trichlorosilane with the monochloro-product (I) as its concentration in the liquid phase increases relatively to that of chlorotrifluoroethylene. This was confirmed by photochemical reaction of trichlorosilane with the pure compound (I): the reduced compound (IV) was obtained in 63% yield, together with silicon tetrachloride. The following radical chain reaction is suggested:

$$\mathrm{CHFCl{\cdot}CF_2{\cdot}SiCl_3 + SiCl_3{\cdot} \longrightarrow {\cdot}CHF{\cdot}CF_2{\cdot}SiCl_3 + SiCl_4}$$
$$\mathrm{{\cdot}CHF{\cdot}CF_2{\cdot}SiCl_3 + SiHCl_3 \longrightarrow CH_2F{\cdot}CF_2{\cdot}SiCl_3 + SiCl_3{\cdot}}$$

It will be noted that the trichlorosilyl radical abstracts chlorine from the β-carbon atom. Even after allowance for the fact that the β-chlorine atom in silicon compounds is often reactive, this free-radical abstraction is unusual, since (i) the chlorine of a $\mathrm{-CF_2{\cdot}CHFCl}$ group is normally very stable and (ii) alkyl (*e.g.*, $\mathrm{CH_3}$ or $\mathrm{CF_3}$) or aryl (*e.g.*, Ph) radical attack on a $\mathrm{CHX_2}$ group (*e.g.*, in $\mathrm{CHCl_3}$) abstracts hydrogen and not chlorine.[4] It is clear that silyl radicals can behave quite differently from alkyl radicals, probably because the Si–Cl bond dissociation energy (91 kcal. mole^{-1}) is considerably greater than the Si–H bond dissociation energy (76 kcal. mole^{-1}),[5] the reverse of the situation for C–Cl and C–H. The reaction $>\!\mathrm{Si{-}H} + >\!\mathrm{C{-}Cl} \longrightarrow >\!\mathrm{Si{-}Cl} + >\!\mathrm{C{-}H}$ thus results in an appreciable release of energy ~30 kcal. mole^{-1}).

Abstraction of chlorine from chlorobenzene by the triphenylsilyl radical has been observed recently,[6] but this does not involve a chain reaction of the type now suggested:

$$>\!\mathrm{SiHX} \xrightarrow[\text{peroxide}]{\text{u.v. or}} >\!\mathrm{SiX}{\cdot}$$
$$>\!\mathrm{SiX}{\cdot} + >\!\mathrm{CHY} \longrightarrow >\!\mathrm{SiXY} + >\!\mathrm{CH}{\cdot}$$
$$>\!\mathrm{CH}{\cdot} + >\!\mathrm{SiHX} \longrightarrow >\!\mathrm{CH_2} + >\!\mathrm{SiX}{\cdot} \longrightarrow \text{etc.}$$
$$\text{where X and Y} = \text{halogen}$$

The photochemical reaction of trichlorosilane with trifluoroethylene was also examined briefly, to eliminate the possibility that compound (IV) was formed as follows:

$$\mathrm{CHFCl{\cdot}CF_2{\cdot}SiCl_3 \longrightarrow CHF{:}CF_2 + SiCl_4}$$
$$\mathrm{CHF{:}CF_2 + SiCl_3{\cdot} \longrightarrow {\cdot}CHF{\cdot}CF_2{\cdot}SiCl_3 \xrightarrow{SiHCl_3} CH_2F{\cdot}CF_2{\cdot}SiCl_3 + SiCl_3{\cdot} \longrightarrow} \text{ etc.}$$

Free-radical attack on trifluoroethylene occurs mainly on the CHF group,[7] so that trichlorosilane would be expected to give the compound $\mathrm{CHF_2{\cdot}CHF{\cdot}SiCl_3}$ (V) rather than (IV). That the 1 : 1 adduct is mainly (V) and not (IV) is shown by its b. p. (104°), by its infrared spectrum which differs appreciably from that of (IV), and by its aqueous alkaline hydrolysis:

$$\underset{\text{(V)}}{\mathrm{CHF_2{\cdot}CHF{\cdot}SiCl_3}} \xrightarrow{\mathrm{OH^-}} \underset{90\%}{\mathrm{CHF_2{\cdot}CH_2F}} + \underset{9\%}{\mathrm{CHF{:}CHF}} + \underset{1\%}{\mathrm{CF_2{:}CH_2}}$$

Formation of vinylidene fluoride suggests that a small amount of compound (IV) was

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[4] Kharasch, Jensen, and Urry, *J. Amer. Chem. Soc.*, 1947, **69**, 1100.

[5] Cottrell, " The Strengths of Chemical Bonds," Butterworths, London, 1958, 2nd edn.

[6] Curtice, Gilman, and Hammond, *J. Amer. Chem. Soc.*, 1957, **79**, 4754.

[7] Haszeldine and Steele, *J.*, 1957, 2800.

probably also produced by the trichlorosilane–trifluoroethylene reaction, but it was certainly not the main product. Nuclear magnetic resonance studies of compounds (I), (IV), and (V) are in agreement with the proposed structures.

The olefin formed when polychlorofluoro- or polyfluoro-ethyl derivatives of silicon are hydrolysed gives a guide to the structure of the silicon compound, if ejection of halide ion from the β-position is assumed. Failure to obtain olefin also gives a guide to structure. Thus, the chlorine in the compound $CF_2Cl{\cdot}CF_2{\cdot}SiCl_3$ is attached to a CF_2 group and hence particularly stable; hydrolysis of this compound gives only the chlorofluoroethane $CF_2Cl{\cdot}CHF_2$. By contrast, the compound $CH_2Cl{\cdot}CH_2{\cdot}SiCl_3$ yields only ethylene.[8] The compounds $CHFCl{\cdot}CF_2{\cdot}SiCl_3$, $CH_2F{\cdot}CF_2{\cdot}SiCl_3$, and $CHF_2{\cdot}CHF{\cdot}SiCl_3$ lie between these extremes of reactivity and give mainly the fluoroalkane, but with some loss of β-halogen to give an olefin. Loss of β-fluorine occurred when the β-group was CH_2F, and also when it was CHF_2 with CHF as the α-group, but not when the β-group was CHF_2 with CF_2 as the α-group (*i.e.*, in hydrolysis of $CHF_2{\cdot}CF_2{\cdot}SiCl_3$ [1]).

While this work was in progress, several other reports [9] appeared on the reaction of trichlorosilane with chlorotrifluoroethylene, under various methods of catalysis, and both possible products (I) and (II) have been claimed by different authors. In no case was an unequivocal proof of structure given. Conditions most nearly approaching those used in the present work were used by McBee *et al.*, who report a somewhat unstable 1 : 1 adduct of b. p. 117°; compound (I), obtained under the experimental conditions described below, showed no signs of instability or of decomposition during distillation.

EXPERIMENTAL

Photochemical reactions were carried out in sealed silica tubes which were filled by use of apparatus for manipulation of volatile compounds. Moisture, air, etc., were excluded. Molecular weights were determined by Regnault's method. A Perkin–Elmer model 21 spectrophotometer was used to determine infrared spectra. The ultraviolet light was a Hanovia 500 watt. The gas–liquid chromatography column was constructed from 2 metres of 5 mm. tubing containing 40% by weight of dinonyl phthalate supported on 80-mesh Celite.

Trichlorosilane, chlorotrifluoroethylene, and trifluoroethylene were distilled *in vacuo* to analytical and spectroscopic purity. Yields are based on the reactant not in excess.

Reaction of Trichlorosilane with Chlorotrifluoroethylene.—(a) *To give mainly* 2-*chloro*-1,1,2-*trifluoroethyltrichlorosilane.* Trichlorosilane (160 g., 1·18 moles) and chlorotrifluoroethylene (44·5 g., 0·38 mole) in a 280-ml. tube (olefin mainly in the liquid phase) were shaken and irradiated for 46 hr., to give (i) unchanged trichlorosilane (120 g.), (ii) a major fraction (55·4 g.), boiling from 35°/760 mm. to 55°/55 mm., and (iii) a residue of polymeric material (25·6 g.). Redistillation of the middle fraction (ii) gave a forerun containing crude product (IV) (*ca.* 10 g., max. yield 10%), b. p. 70—120°/760 mm., and 2-*chloro*-1,1,2-*trifluoroethyltrichlorosilane* (42·7 g., 45%), b. p. 120—121° (Found: C, 9·6; H, 0·4; Cl, 56·1%; *M*, 255. $C_2HCl_4F_3Si$ requires C, 9·5; H, 0·4; Cl, 56·3%; *M*, 252).

Use of an excess of trichlorosilane in the reactants minimises polymer formation. The irradiation time is probably excessive, since all the olefin had been consumed.

(b) *To produce mainly* $CH_2F{\cdot}CF_2{\cdot}SiCl_3$. Trichlorosilane (31·3 g., 0·23 mole) and chlorotrifluoroethylene (8·2 g., 0·07 mole) were sealed in a 280-ml. silica tube; the olefin was thus largely in the vapour phase. All the olefin had been consumed after 48 hours' irradiation with shaking. The liquid products were distilled to give unchanged trichlorosilane (14·3 g.), silicon tetrachloride (6·4 g., 53%), an intermediate fraction (4·0 g.), b. p. 70—90°, and 1,1,2-*trifluoroethyltrichlorosilane* (6·9 g., 45%, b. p. 96·4—96·8°) on redistillation (Found: C, 10·8; H, 1·1%; *M*, 218. $C_2H_2Cl_3F_3Si$ requires C, 11·0; H, 0·9%; *M*, 217·5).

Hydrolysis of the Compounds $CHFCl{\cdot}CF_2{\cdot}SiCl_3$ *and* $CH_2F{\cdot}CF_2{\cdot}SiCl_3$.—Compound (I) (0·593 g., 2·35 mmoles) reacted immediately when shaken in a 330-ml. sealed tube with air-free 10%

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[8] Sommer, Goldberg, Dorfman, and Whitmore, *J. Amer. Chem. Soc.*, 1946, **68**, 1083.

[9] Ponomarenko, Sokolov, and Petrov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1956, 628; McBee, Roberts, and Puerckhauer, *J. Amer. Chem. Soc.*, 1957, **79**, 2329; Tarrant, Dyckes, Dunmire, and Butler, *ibid.*, p. 6536; B.P. 764,288 (*Chem. Abs.*, 1957, **51**, 14,786); Haluska, U.S.P. 2,800,494 (*Chem. Abs.*, 1957, **51**, 17,982).

aqueous sodium hydroxide (5 ml.). After 30 min., distillation gave 1-chloro-1,2,2-trifluoroethane (90%) (Found: C, 20·4; H, 1·8%; *M*, 118. Calc. for $C_2H_2ClF_3$: C, 20·2; H, 1·7%; *M*, 118·5), b. p. (isoteniscope) 17·2°, and trifluoroethylene (9%) identified spectroscopically. Swarts [10] reports b. p. 17° for $CHF_2{\cdot}CHFCl$. Strong bands in its infrared spectrum at 3·35, 8·87, and 11·19 μ distinguish $CHF_2{\cdot}CHFCl$ (b. p. 17·2°) from $CF_3{\cdot}CH_2Cl$ (b. p. 6·1°) with main bands at 3·33, 3·47 (doublet), 7·86, 8·65, and 11·70 μ, and from $CF_2Cl{\cdot}CH_2F$ (b. p. 12°) with main bands at 3·38, 3·47 (doublet), 8·10, 10·25, and 11·90 μ.

Compound (IV) (0·809 g., 3·72 mmoles) similarly reacted with 10% aqueous sodium hydroxide (8 ml.) to give 1,1,2-trifluoroethane (99%) (Found: C, 28·3; H, 3·8%; *M*, 84. Calc. for $C_2H_3F_3$: C, 28·6; H, 3·6%; *M*, 84), b. p. (isoteniscope) 3·0°, and vinylidene fluoride (*ca.* 1%). 1,1,2-Trifluoroethane has b. p. 5° or 3°.[11] The absence of 1,1,1-trifluoroethane (b. p. −47°) shows that no rearrangement of fluorine in the alkane has occurred.

No reaction was detected when the compounds $CHF_2{\cdot}CHFCl$ and $CHF_2{\cdot}CH_2F$ were treated with 10% aqueous sodium hydroxide under the conditions used above, or even when the solution was heated to 70°.

Reaction of Trichlorosilane with 2-*Chloro*-1,1,2-*trifluoroethyltrichlorosilane.*—Trichlorosilane (24·7 g., 183 mmoles) and 2-chloro-1,1,2-trifluoroethyltrichlorosilane (5·0 g., 19·8 mmoles), shaken and irradiated for 110 hr., gave unchanged trichlorosilane, silicon tetrachloride (2·0 g., 11·8 mmoles) (Found: *M*, 165. Calc. for $SiCl_4$: *M*, 170), b. p. 57—58°, identified spectroscopically (characteristic band 15·2 μ), and 1,1,2-trifluoroethyltrichlorosilane (2·7 g., 12·4 mmoles, 63%) (Found: *M*, 218. Calc. for $C_2H_2Cl_3F_3Si$: *M*, 217·5), b. p. 97°, spectroscopically identical with the compound obtained earlier. 2-Chloro-1,1,2-trifluoroethyltrichlorosilane itself is stable photochemically under these conditions. Mixtures of it with trichlorosilane remain unchanged when kept in the dark.

Chlorination of the Compounds $CHFCl{\cdot}CF_2{\cdot}SiCl_3$ *and* $CH_2F{\cdot}CF_2{\cdot}SiCl_3$.—Compound (I) (10·4 g., 41 mmoles) and anhydrous chlorine (5·0 g., 71 mmoles), shaken and irradiated in a 280-ml. tube for 87 hr., gave residual chlorine, removed by reaction with mercury, hydrogen chloride (42 mmoles) (Found: *M*, 36·5. Calc. for HCl: *M*, 36·5), and 2,2-*dichloro*-1,1,2-*trifluoroethyltrichlorosilane* (11·1 g., 95%) (Found: C, 8·7; H, 0·1; Cl, 61·8. $C_2Cl_5F_3Si$ requires C, 8·4; Cl, 61·9%), b. p. 138°.

Compound (IV) (4·1 g., 19 mmoles) and chlorine (3·8 g., 53 mmoles), similarly treated for 168 hr., gave hydrogen chloride (39 mmoles) and 2,2-dichloro-1,1,2-trifluoroethyltrichlorosilane (94%), redistilled to give the pure compound (5·0 g., 89%), b. p. 137—139°, spectroscopically identical with the compound obtained above.

When 2,2-dichloro-1,1,2-trifluoroethyltrichlorosilane (1·62 g., 5·65 mmoles) had been shaken in a 330-ml. tube with 10% aqueous sodium hydroxide (10 ml.) for 30 min., 1,1-dichloro-1,2,2-trifluoroethane (87%), and chlorotrifluoroethylene (13%) were obtained. 1,1-Dichloro-1,2,2-trifluoroethane is stable to aqueous alkali under these conditions.

Synthesis of 1,1-*Dichloro*-1,2,2-*trifluoroethane.*—1,1,2,2-Tetrachloroethane (240 g., 1·43 moles), anhydrous antimony trifluoride (190 g., 1·06 moles), and antimony pentachloride (50 g., 0·17 mole), in a 1-l. flask under a reflux condenser maintained at 60° and connected to a trap cooled to −78°, were heated under reflux so that steady evolution of product occurred. This was washed with 10% aqueous sodium hydroxide, then water, dried (P_2O_5), and distilled to give 1,1-*dichloro*-2,2-*difluoroethane* (70·0 g., 36%) (Found: C, 17·8; H, 1·5%; *M*, 135. $C_2H_2Cl_2F_2$ requires C, 17·8; H, 1·5%; *M*, 135), b. p. 59—61° (mainly 60°). Gas–liquid chromatography showed that only one compound was present. The more volatile reaction products were discarded.

The dichlorodifluoroethane (23·6 g., 0·175 mole) and chlorine (12·0 g., 0·169 mole), sealed in two evacuated 280-ml. silica tubes, were exposed to ultraviolet radiation from a 250 w mercury lamp for 13 hr., to give a mixture (24·0 g., 84%) (Found: C, 14·2; H, 0·7%; *M*, 167. Calc. for $C_2HCl_3F_2$: C, 14·4; H, 0·6%; *M*, 169·5), b. p. 71—74°, shown by infrared spectroscopy and gas–liquid chromatography to contain 95% of the compound $CHF_2{\cdot}CCl_3$ (b. p. 73·0°) and 5% of the compound $CF_2Cl{\cdot}CHCl_2$ (b. p. 71·9°).

The mixture (6·0 g., 35 mmoles) was heated to 130° in a 200-ml. autoclave with antimony trifluoride (2·1 g., 12 mmoles) and antimony pentachloride (1 g.) for 15 hr. The volatile

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[10] Swarts, *Mem. Couronne Acad. Belg.*, 1901, **61**, 1.

[11] Henne and Rennoll, *J. Amer. Chem. Soc.*, 1936, **58**, 889; Young, Fukuhara, and Bigelow, *ibid.*, 1940, **62**, 1171.

products were washed with 5% aqueous sodium hydroxide, then distilled to give 1,1-*dichloro*-1,2,2-*trifluoroethane* (2·8 g., 52%) (Found: C, 15·9; H, 0·8%; *M*, 152. $C_2HCl_2F_3$ requires C, 15·7; H, 0·65%; *M*, 153), b. p. (isoteniscope) 30·2°. Gas–liquid chromatography and infrared spectroscopy showed that only one compound of formula $C_2HCl_2F_3$ was obtained and in particular that the compounds $CF_3{\cdot}CHCl_2$ (b. p. 28·7°) and $CF_2Cl{\cdot}CHFCl$ (b. p. 28·2°) were absent. A $-CCl_3$ group undergoes halogen exchange more easily than a $-CF_2Cl$ or $-CHCl_2$ group.

Reaction of Trichlorosilane with Trifluoroethylene.—Trichlorosilane (50·0 g., 0·37 mole) and trifluoroethylene (8·8 g., 0·11 mole), divided equally between two 250-ml. silica tubes, were irradiated as for chlorotrifluoroethylene for 65 hr., to give the 1 : 1 adduct, mainly 1,2,2-*trifluoroethyltrichlorosilane* (12·0 g., 50%) (Found: C, 11·0; H, 0·9%; *M*, 219. $C_2H_2Cl_3F_3Si$ requires C, 11·0; H, 0·9%; *M*, 217·5), b. p. 104°.

A sample (0·890 g., 4·11 mmoles) of the adduct reacted immediately when shaken with air-free 10% aqueous sodium hydroxide (10 ml.) in a 330-ml. tube for 30 min., to give volatile products (4·12 mmoles, 100%) containing 1,1,2-trifluoroethane (90%), 1,2-difluoroethylene (9%), and vinylidene fluoride (1%). 1,1,2-Trifluoroethane is stable to aqueous alkali under the conditions used above.

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