Polyfluoroalkyl Compounds of Silicon. Part XII.[1] Reactions of Trichlorosilane with 2-Chloro- and 2-Bromo-1,1-difluoroethylene

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Photochemical reaction of an excess of trichlorosilane with 2-chloro-1,1-difluoroethylene gives trichloro-(2,2-difluoroethyl)silane as the major product, and smaller amounts of trichloro-(1,1-difluoroethyl)silane and trichloro-(2-chloro-2,2-difluoroethyl)silane, whereas reaction with an excess of olefin present gives mainly trichloro-(2-chloro-2,2-difluoroethyl)silane together with trichloro-(2-chloro-1,1-difluoroethyl)silane. Formation of these products is explained in terms of initial trichlorosilyl radical addition to 2-chloro-1,1-difluoroethylene at the CF_2 group and a competing reduction of the olefin to 1,1-difluoroethylene followed by trichlorosilyl radical addition at the CH_2 group. Photochemical reaction of trichlorosilane with 2-bromo-1,1-difluoroethylene gives the reduced olefin 1,1-difluoroethylene and 2,2-difluoroethyl- and 2-bromo-2,2-difluoroethyl-trichlorosilanes.

PHOTOCHEMICAL additions of silicon hydrides to carbon–carbon multiple bonds have been well studied[2] and are regarded as mercury-photosensitised free-radical reactions in which the silyl radical, initially formed, adds to the unsaturated system, *e.g.* reactions (i) and (ii).

$$HSiR_3 \xrightarrow[Hg]{u.v.} H\cdot + \cdot SiR_3 \qquad (i)$$

$$\cdot SiR_3 + CH_2{:}CHR' \longrightarrow R_3Si\cdot CH_2\cdot \dot{C}HR' \qquad (ii)$$

Silicon hydrides are efficient chain-transfer agents and, provided that an excess of silane is used, the 1 : 1 adduct is generally formed in high yield [reaction (iii)].

$$R_3Si\cdot CH_2\cdot \dot{C}HR' + HSiR_3 \longrightarrow R_3Si\cdot CH_2\cdot CH_2R' + \cdot SiR_3 \qquad (iii)$$

With a number of unsymmetrical olefins, *e.g.* hexafluoropropene,[3] bidirectional silane additions have been observed; these results have been interpreted in terms of stability of the intermediate radical, polar effects in the transition state, and the degree of electrophilicity of the attacking silyl radical.

In the present work the reaction of trichlorosilane with 2-chloro-1,1-difluoroethylene has been investigated under various conditions as a possible route to trichloro-(1,1-difluoroethyl)silane (II) *via* reduction of the 1 : 1 adduct, trichloro-(2-chloro-1,1-difluoroethyl)silane (I) [reaction (iv)]; the reaction of the silane with 2-bromo-1,1-difluoroethylene has also been examined.

$$\begin{tikzcd} CF_2{:}CHCl + HSiCl_3 \arrow[r, "u.v."] & \underset{(I)}{CH_2Cl\cdot CF_2\cdot SiCl_3} \arrow[d, "reduction"] \\ & \underset{(II)}{CH_3\cdot CF_2\cdot SiCl_3} \quad (iv) \end{tikzcd}$$

The results obtained with 2-chloro-1,1-difluoroethylene are shown in the Table.

The trichlorosilyl radical was expected to add mainly to the CF_2 group of the olefin to give, as the major product, the 1 : 1 adduct (I); *cf.* the photochemical addition of trifluoroiodomethane to this olefin (90% $CF_3\cdot$ radical attack on the CF_2 group).[4] When an excess of silane was used (experiment A) it was expected that adduct (I) would be reduced in part to compound (II). Similarly if any of the adduct (V), resulting from trichlorosilyl radical attack on the CHCl group of the olefin, was formed in the reaction it too could be reduced in part to the known compound (IV).[5] However, the major product formed in experiment A was the reduced compound (IV), and it is doubtful whether this compound would have been formed in such high yield by initial trichlorosilyl radical attack on the CHCl group of the olefin followed by reduction of the resultant 1 : 1 adduct (V).

$$\text{(III)}\ CF_2Cl\cdot CH_2\cdot SiCl_3 \qquad \text{(IV)}\ CHF_2\cdot CH_2\cdot SiCl_3$$
$$\text{(V)}\ CHF_2\cdot ClCH\cdot SiCl_3$$

Photochemical reaction of trichlorosilane with 2-chloro-1,1-difluoroethylene

Expt.	Ratio of CF_2 : CHCl to $HSiCl_3$	Irradiation time (h)	Recovered olefin (%)	Products (%) (I)	(II)	(III)	(IV)
A	1 : 4	120	30		21	7	56
B	1 : 1	20	17	7		62	10
C *	4 : 1	8	75	9		43	
D *	10 : 1	8	90	9		35	

* A dark non-volatile oil was also formed.

The 1 : 1 adduct (I) was not detected in the products from this experiment, but the reduced product (II) (21%) was isolated.

Compound (III) was the unexpected major product of experiments B—D and was also a minor product of experiment A. Its structure was determined on the basis of the following chemical and physical evidence.

(i) Reduction with trimethylsilane gave compound (IV) (72%) [reactions (v) and (vi)].

$$CF_2Cl\cdot CH_2SiCl_3 + \cdot SiMe_3 \longrightarrow \dot{C}F_2\cdot CH_2SiCl_3 + ClSiMe_3 \quad (v)$$

$$\dot{C}F_2\cdot CH_2\cdot SiCl_3 + HSiMe_3 \longrightarrow CHF_2\cdot CH_2\cdot SiCl_3 + \cdot SiMe_3 \quad (vi)$$

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[1] Part XI, C. R. Pool, R. N. Haszeldine, and A. E. Tipping, *J.C.S. Perkin I*, 1974, 2293.

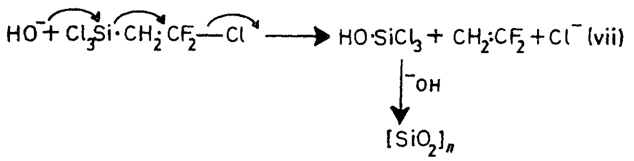
[2] M. G. Voronkov and E. Ya. Lukevits, ' Organic Insertion Reactions of Group IV Elements,' Consultants Bureau, New York, 1966.

[3] C. J. Attridge, G. W. Cross, R. N. Haszeldine, and M. J. Newlands, unpublished results.

[4] R. Gregory, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc. (C)*, 1968, 3020.

[5] T. N. Bell, R. N. Haszeldine, M. J. Newlands, and J. B. Plumb, *J. Chem. Soc.*, 1965, 2107.

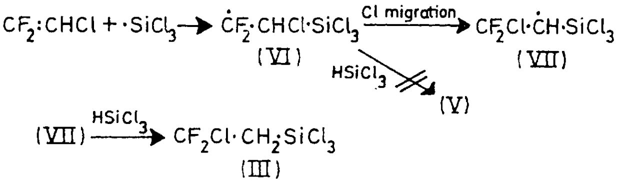
(ii) Hydrolysis with dilute aqueous sodium hydroxide, dilute aqueous pyridine, or water gave 1,1-difluoroethylene (>70%) as the only volatile product, *e.g.* reaction (vii). It has previously been shown[6] that hydrolysis of the silane $CH_2Cl{\cdot}CH_2{\cdot}SiCl_3$ similarly affords an olefin ($CH_2{:}CH_2$) and chloride ion.



(iii) The ^{19}F n.m.r. spectrum consisted of a triplet absorption (J 14·5 Hz) at $-39{\cdot}0$ p.p.m. from trifluoroacetic acid; the chemical shift is in the region expected for a CF_2Cl group[7,8] and the coupling is as expected for the grouping $CF_2Cl{\cdot}CH_2$. The triplet absorption at τ 7·2 in the ^1H spectrum is also consistent with the presence of the $CF_2Cl{\cdot}CH_2$ group.

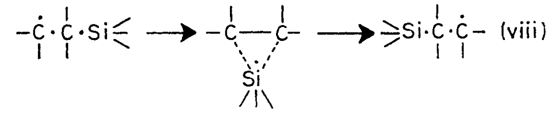
Three possible mechanisms which can account for the formation of compound (III) are now discussed.

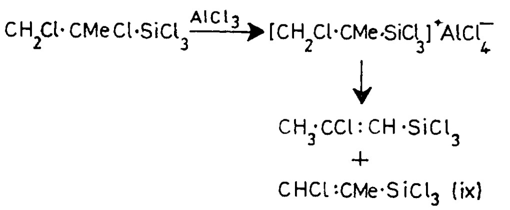
(a) *Intermediate radical rearrangement by chlorine migration.* Addition of the trichlorosilyl radical to the olefin $CF_2{:}CHCl$ at the CHCl group would afford the intermediate radical (VI). Rearrangement of this radical by a 1,2-chlorine atom shift would give the radical (VII), which on hydrogen abstraction from trichlorosilane would afford the observed product (III). Since the adduct (V) was not detected in the products, rearrangement of the intermediate radical (VI) to the radical (VII) would have to be rapid, which suggests that the intermediate (VII) is appreciably more stable than the intermediate (VI). However, the following evidence suggests that the reverse is true. The photochemical reaction of an equimolar mixture of compound (IV) and chlorine gave compounds (III) (69%) and (V) (9%), $CHF_2{\cdot}CCl_2{\cdot}SiCl_3$ (15%), and $CF_2Cl{\cdot}CHCl{\cdot}SiCl_3$ (7%). This implies that the tertiary radical $\dot{C}F_2{\cdot}CH_2{\cdot}SiCl_3$ is more stable than the isomeric secondary radical $CHF_2{\cdot}\dot{C}H{\cdot}SiCl_3$. Thus the tertiary radical (VI) is likely to be more stable than the secondary radical (VII) and hence the rearrangement of (VI) to (VII) is unlikely.

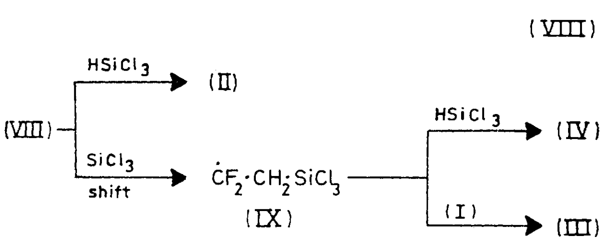


SCHEME 1

(b) *Intermediate radical rearrangement by trichlorosilyl migration.* The overlap of the silicon *d* orbitals with a lone electron on a neighbouring carbon atom could facilitate the migration of silicon from one carbon atom to another [reaction (viii)]. Such free-radical rearrangements have not been reported, but comparable carbonium ion rearrangements have been observed, *e.g.* the dehydrochlorination of 1,2-dichloro-2-trichlorosilylpropane with aluminium trichloride[9] [reaction (ix)]. If rearrangement of the radical (VIII) by trichlorosilyl migration does take place then the mechanism shown in Scheme 2 accounts for the formation of compound (III) and the other observed products. The primary radical (VIII) can either abstract a hydrogen atom from trichlorosilane or rearrange to the tertiary radical (IX), which can then react as shown. If abstraction of chlorine by trichlorosilyl radical from the 1 : 1 adduct (I) takes place, then irradiation of (I) with a trace of initiator ($HSiCl_3$) should promote the rearrangement of (I) to (III), and at higher trichlorosilane concentration the expected product is compound (IV) formed by reduction of rearranged (III). A quantity of compound (I) was prepared by the photochemical reaction between 1,1-dichloro-2,2-difluoroethylene and trichlorosilane followed by reduction of the resultant 1 : 1 adduct $CHCl_2{\cdot}CF_2{\cdot}SiCl_3$ with trimethylsilane. The photochemical reaction between (I) and trichlorosilane (2 mol %) gave unchanged (I) (92%) and the rearranged compound (III) was not detected. A second photochemical reaction using equimolar amounts of reactants gave (II) (78%) and compound (IV) was not detected. Thus rearrangement of the intermediate radical (VIII) by trichlorosilyl migration is considered not to occur.







SCHEME 2

(c) *The reduction–addition reaction.* It has been clearly established that trichlorosilane can effectively reduce alkyl chlorides[10] or trichloro(chloroalkyl)silanes[11]

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[6] L. H. Sommer and F. G. Whitworth, *J. Amer. Chem. Soc.*, 1946, **68**, 485.

[7] E. G. Brame, *Analyt. Chem.*, 1962, **34**, 591.

[8] Unpublished data from this department.

[9] V. F. Mironov, *Chem. Z.*, 1961, 3973.

[10] J. A. Kerr, B. J. A. Smith, A. F. Trotman-Dickenson, and J. C. Young, *Chem. Comm.*, 1966, **6**, 157.

[11] W. I. Bevan and R. N. Haszeldine, in preparation.

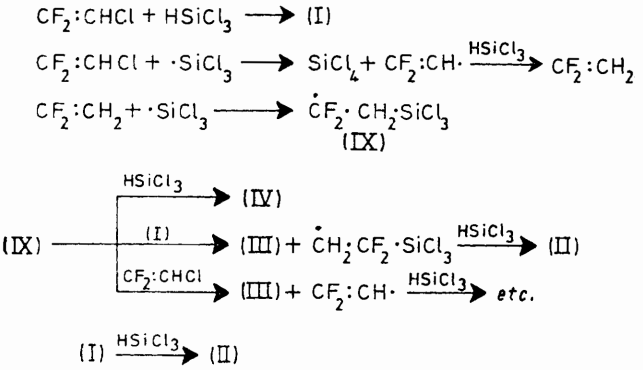
under photochemical conditions; such reductions are energetically favourable, *i.e.*[12] reaction (x) (35 kcal

$$\mathrm{C-Cl + Si-H \longrightarrow C-H + Si-Cl} + ca.\,35\ \mathrm{kcal\ mol^{-1}} \qquad (\mathrm{x})$$

mol^{-1} $\simeq$ 147 kJ mol^{-1}). It is thus possible that irradiation of a mixture of a chloro-olefin and trichlorosilane would result to some extent in reduction of the olefin. Addition of the silane to the reduced olefin can then take place. Such a reaction is proposed to account for the formation of the alkylsilane (III). Some of the olefin $CF_2{:}CHCl$ is reduced to 1,1-difluoroethylene and attack by trichlorosilyl radical on this olefin gives the intermediate radical (IX), which can (*a*) abstract a hydrogen atom from trichlorosilane to give (IV), or (*b*) abstract a chlorine atom from the adduct (I) to give (III), or (*c*) abstract a chlorine atom from unchanged $CF_2{:}CHCl$ to give (III).

It has been reported previously [5] that irradiation of a mixture of 1,1-difluoroethylene and trichlorosilane affords the 1 : 1 adduct (IV) in high yield.

Scheme 3, which accounts for all the observed products, is thus considered to be the most satisfactory.



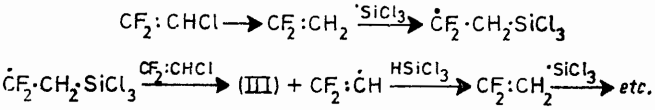
SCHEME 3

The reduced olefin $CF_2{:}CH_2$ was not detected in the products, which suggests that its steady state concentration is low and that it is more reactive towards trichlorosilyl radical attack than the reactant olefin.

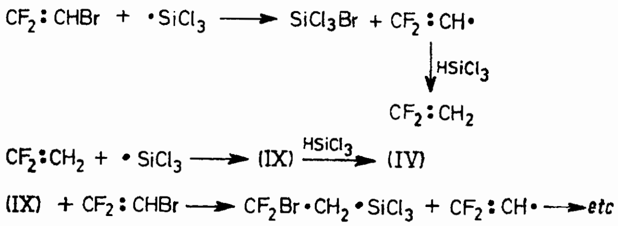
In the presence of an excess of trichlorosilane (experiment A) reduction of the 1 : 1 adduct (I) to compound (II) and formation of the reduced olefin $CF_2{:}CH_2$–Cl_3SiH 1 : 1 adduct (IV) are favoured. With equimolar concentrations of reactants (experiment B), reduction of the adduct (I) apparently does not take place and the adduct was isolated in low yield. Also although the 1 : 1 adduct (IV) was isolated in low yield, the major product is the trichloro(chloroalkyl)silane (III), which probably arises mainly by the chain reaction shown (Scheme 4).

At higher olefin : silane ratios (experiments C and D) compounds (I) and (III) are the only identified products (*ca.* 50%). Under such conditions telomerisation reactions are favoured, as shown by the high-boiling oils obtained.

Photochemical reaction of the olefin $CF_2{:}CHBr$ with trichlorosilane (1 : 1 molar ratio) gave 1,1-difluoroethylene (17%), bromotrichlorosilane (50% based on $SiHCl_3$), 2-bromo-2,2-difluoroethyltrichlorosilane (X), (17%) and compound (IV) (47%), the latter two formed *via* radical addition to 1,1-difluoroethylene (Scheme 5).



SCHEME 4



SCHEME 5

The isolation of the olefin $CH_2{:}CF_2$ from this reaction and not from the corresponding $CF_2{:}CHCl$ reaction, and the absence of products resulting from trichlorosilyl radical addition to the reactant olefin $CF_2{:}CHBr$, can be explained by a weaker carbon–halogen bond in the bromo-olefin which makes halogen abstraction easier and results in a fast build-up in the concentration of the reduced olefin.

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 vacuo* in 360 ml silica tubes which were shaken and irradiated with a Hanovia S500 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 spectrophotometer model 21 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 ^{1}H and with external trifluoroacetic acid and internal tetramethylsilane as the respective references), and g.l.c. (Perkin-Elmer 116, 154B, or 451 Fraktometer).

2-Chloro-1,1-difluoroethylene was prepared in 36% overall yield by fluorination of pentachloroethane with antimony trifluoride–antimony pentachloride followed by dechlorination of the resultant 1,2,2-trichloro-1,1-difluoroethane, with zinc in ethanol.[13]

Trichloro-(2,2-difluoroethyl)silane and trichloro-(2-chloro-1,1-difluoroethyl)silane were prepared by photochemical addition of trichlorosilane to 1,1-difluoroethylene (75%) [5] and 1,1-dichloro-2,2-difluoroethylene (43%),[11] respectively.

Reaction of Trichlorosilane with 2-*Chloro*-1,1-*difluoroethylene*.—(a) 4 : 1 *Molar ratio*. A mixture of the olefin

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[12] T. L. Cottrell, 'The Strengths of Chemical Bonds,' Butterworths, London, 2nd edn., 1958.

[13] A. L. Henne and E. C. Ladd, *J. Amer. Chem. Soc.*, 1936, **58**, 402; A. L. Henne and R. P. Ruh, *ibid.*, 1948, **70**, 1025.

(20·0 g, 0·203 mol) and trichlorosilane (110 g, 0·815 mol) on irradiation (120 h) gave (i) unchanged olefin (6·0 g, 61 mmol, 30% recovered), (ii) unchanged trichlorosilane (75 g, 0·55 mol, 67·5% recovered), (iii) a mixture (23 g) of trichlorosilane and silicon tetrachloride, (iv) a mixture of trichloro-(2,2-difluoroethyl)silane (IV) (16·0 g, 80·1 mmol, 56%) and trichloro-(2-chloro-2,2-difluoroethyl)-silane (III) (2·3 g, 9·8 mmol, 7%) as estimated by n.m.r., and (v) trichloro-(1,1-difluoroethyl)silane (II) (6·0 g, 30·0 mmol, 21%) (Found: C, 11·8; H, 1·5; Cl, 53·4%; *M*, 198. $C_2H_3Cl_3F_2Si$ requires C, 12·0; H, 1·5; Cl, 53·2%; *M*, 199·5), b.p. 80—82 °C; τ 8·2 (t, CH_3, J_{FH} 22·5 Hz); ^{19}F n.m.r. δ 27·0 p.p.m. (q, CF_2).

(b) 1 : 1 *Molar ratio.* A mixture of the olefin (9·85 g, 0·10 mol) and trichlorosilane (13·5 g, 0·10 mol), on irradiation (20 h), gave (i) unchanged olefin (1·71 g, 17·2 mmol, 17% recovered), (ii) unchanged trichlorosilane (2·00 g, 14·8 mmol, 15% recovered), (iii) a mixture (3·25 g), b.p. 40—125 °C, of trichloro-(2,2-difluoroethyl)silane (IV) (1·65 g, 8·3 mmol, 10%), trichlorosilane, and silicon tetrachloride as estimated by g.l.c., and (iv) a major fraction (13·3 g, 57·0 mmol) (Found: C, 10·5; H, 0·9; Cl, 61·3. Calc. for $C_2H_2Cl_4Si$: C, 10·3; H, 0·9; Cl, 61·0%), which was shown by n.m.r. to consist of trichloro-(2-chloro-1,1-difluoroethyl)silane (I) (1·35 g, 5·8 mmol, 7%) and trichloro-(2-chloro-2,2-difluoroethyl)silane (III) (11·95 g, 51·2 mmol, 62%).

(c) 1 : 4 *Molar ratio.* A mixture of the olefin (30·0 g, 0·305 mol) and trichlorosilane (10·0 g, 74·0 mmol), on irradiation (8 h), gave (i) unchanged olefin (22·95 g, 0·233 mol, 75% recovered), (ii) a mixture (8·77 g) shown by n.m.r. spectroscopy to consist of trichloro-(2-chloro-1,1-difluoroethyl)silane (I) (1·57 g, 6·75 mmol, 9%) and trichloro-(2-chloro-2,2-difluoroethyl)silane (III) (7·20 g, 30·75 mmol, 43%), and (iii) a dark, non-volatile oil (*ca.* 8 g) which was not examined further.

(d) 1 : 10 *Molar ratio.* A mixture of the olefin (48·1 g, 0·488 mol) and trichlorosilane (5·99 g, 44·5 mmol), on irradiation (8 h), gave (i) unchanged olefin (43·0 g, 0·437 mol, 90% recovered), (ii) a mixture of trichloro-(2-chloro-1,1-difluoroethyl)silane (I) (0·84 g, 3·6 mmol, 9%) and trichloro-(2-chloro-2,2-difluoroethyl)silane (III) (3·36 g, 14·4 mmol, 35%), and (iii) a dark, non-volatile oil (*ca.* 7·5 g) which was not examined further.

Hydrolysis of Trichloro-(2-chloro-2,2-difluoroethyl)silane (III).—Samples of the silane which contained 2—3% of trichloro-(2-chloro-1,1-difluoroethyl)silane (I) were hydrolysed *in vacuo* in a hydrolysis bulb with (i) aqueous 0·02M-sodium hydroxide, (ii) 1% (v/v) aqueous pyridine, and (iii) water to give 1,1-difluoroethylene (Found: *M*, 64. Calc. for $C_2H_2F_2$: *M*, 64) in yields of (i) 72%, (ii) 75%, and (iii) 75%, respectively.

Reduction of Trichloro-(2-chloro-2,2-difluoroethyl)silane (III).—A mixture of trimethylsilane[14] (1·48 g, 20·0 mmol) and the silane (III) (2·33 g, 10·0 mmol), on irradiation (100 h), gave (i) unchanged trimethylsilane (0·82 g, 11·0 mmol, 55% recovered), (ii) chlorotrimethylsilane (0·91 g, 8·4 mmol, 93%) identified by its i.r. spectrum and g.l.c. retention time, and (iii) trichloro-(2,2-difluoroethyl)silane (IV) (1·44 g, 7·2 mmol, 72%).

Chlorination of Trichloro-(2,2-difluoroethyl)silane (IV).—A mixture of the silane (20·0 g, 0·10 mol) and anhydrous chlorine (3·55 g, 0·10 mol), on irradiation (3 h), gave a mixture of unchanged chlorine and hydrogen chloride, and higher-boiling material (22·81 g) which consisted of the following products, as estimated by n.m.r., (i) unchanged silane (IV) (6·38 g, 32·0 mmol, 32% recovered), (ii) trichloro-(2-chloro-2,2-difluoroethyl)silane (III) (11·0 g, 47·0 mmol, 69%), (iii) trichloro-(1-chloro-2,2-difluoroethyl)-silane (V) (1·40 g, 6·0 mmol, 9%); ^{19}F n.m.r. δ 36·0 p.p.m. (ABdd, CHF_2, *J* 52 and 12 Hz), (iv) trichloro-(1,1-dichloro-2,2-difluoroethyl)silane (2·69 g, 10·0 mmol, 15%); ^{19}F n.m.r. δ 42·0 p.p.m. (d, CHF_2, J_{HF} 55 Hz); and (v) trichloro-(1,2-dichloro-2,2-difluoroethyl)silane (1·34 g, 5·0 mmol, 7%); ^{19}F n.m.r. δ −41 p.p.m. (d, CF_2Cl, J_{HF} 12 Hz). The mixture (22·5 g) was distilled through a column packed with glass helices (125 cm) to give an almost pure sample (n.m.r.) of trichloro-(2-chloro-2,2-difluoroethyl)-silane (III) (*ca.* 2 g), b.p. 128—130 °C, which on hydrolysis with aqueous 0·02M-sodium hydroxide gave 1,1-difluoroethylene (70%) as the only volatile product.

Reduction of Trichloro-(2,2-dichloro-1,1-difluoroethyl)silane.—A mixture of trichloro-(2,2-dichloro-1,1-difluoroethyl)silane (8·30 g, 30·8 mmol) and trimethylsilane (2·28 g, 30·8 mmol), on irradiation (100 h), gave a product (10·45 g), which on distillation through a packed column (15 cm) afforded (i) chlorotrimethylsilane (2·80 g, 26·0 mmol, 87%), b.p. 56—58 °C, (ii) *trichloro-(2-chloro-1,1-difluoroethyl)silane* (I) (4·28 g, 18·4 mmol, 60%) (Found: C, 10·5; H, 0·8; Cl, 61·1. $C_2H_2Cl_4F_2Si$ requires C, 10·3; H, 0·8; Cl, 60·7%), b.p. 132 °C; τ 6·1 (t, CH_2Cl, J_{FH} 16·0 Hz); ^{19}F n.m.r. δ 35·5 p.p.m. (t, CF_2), and (iii) a residue (3·0 g), b.p. >132 °C.

Reaction of Trichloro-(2-chloro-1,1-difluoroethyl)silane (I) *with Trichlorosilane.*—(a) *Catalytic amount of trichlorosilane.* A mixture of the silane (I) (2·34 g, 10·0 mmol) and trichlorosilane (0·027 g, 0·2 mmol), on irradiation (120 h) *in vacuo* in a silica tube (*ca.* 100 ml), gave (i) unchanged (I) (2·15 g, 9·2 mmol, 92%) and (ii) a fraction (0·20 g) consisting of silicon tetrachloride, trichloro-(1,1-difluoroethyl)silane (II), and trichloro-(2-chloro-1,1-difluoroethyl)-silane (g.l.c., i.r., and n.m.r.).

(b) *Equimolar ratio of reactants.* A mixture of the silane (I) (2·70 g, 11·6 mmol) and trichlorosilane (1·56 g, 11·6 mmol), on irradiation as in the previous experiment (100 h), gave (i) a mixture (0·2 g) of trichlorosilane and silicon tetrachloride, (ii) silicon tetrachloride (1·63 g, 9·6 mmol, 83%), and (iii) a fraction (2·2 g) consisting of silicon tetrachloride and trichloro-(1,1-difluoroethyl)silane (II); this fraction on repeated fractional condensation *in vacuo* gave the pure silane (II) (1·8 g, 9·0 mmol, 78%).

Preparation of 2-Bromo-1,1-difluoroethylene.—1,2-Dibromo-1,1-difluoroethane[15] (26·5 g, 118 mmol) was condensed *in vacuo* onto dry powdered potassium hydroxide (*ca.* 30 g) contained in a 100 ml flask and the flask and contents heated at 80 °C (30 min) gave 2-bromo-1,1-difluoroethylene (12·8 g, 90·0 mmol, 76%) (Found: *M*, 142. Calc. for C_2HBrF_2: *M*, 143), the i.r. spectrum of which was identical with that reported.[16]

Reaction of Trichlorosilane with 2-Bromo-1,1-difluoroethylene.—A mixture of the silane (12·1 g, 90·0 mmol) and the olefin (12·8 g, 90·0 mmol), on irradiation (100 h), gave (i) unchanged olefin (2·85 g, 20·0 mmol, 22% recovered), (ii) 1,1-difluoroethylene (0·77 g, 12·0 mmol, 17%) (Found: *M*, 64. Calc. for $C_2H_2F_2$: *M*, 64), (iii) bromotrichloro-

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silane (9·6 g, 44·8 mmol, 50%), and (iv) a mixture (9·95 g), shown by n.m.r. spectroscopy to consist of trichloro-(2,2-difluoroethyl)silane (IV) (6·60 g, 33·0 mmol, 47%) and 2-bromo-2,2-difluoroethyltrichlorosilane (3·35 g, 12·0 mmol, 17%); τ 6·1 (t, CH_2, J_{FH} 13·0 Hz); ^{19}F n.m.r. δ −29·0 p.p.m. (t, CF_2Br).

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