Polyfluoroalkyl Derivatives of Silicon. Part XIV.[1] Reaction of Trichlorosilane with 1,3,3,3-Tetrafluoropropene and 2-Chloro-1,3,3,3-tetrafluoropropene

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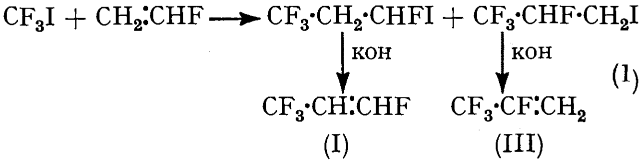
Photochemical reaction of trichlorosilane with 1,3,3,3-tetrafluoropropene gives trichloro(2-fluoro-1-trifluoromethyl)silane and trichloro(1,3,3,3-tetrafluoropropyl)silane (ratio 37 : 13), together with telomeric material. Similarly 2-chloro-1,3,3,3-tetrafluoropropene affords a mixture of trichloro(2-chloro-1,3,3,3-tetrafluoropropyl)silane and the reduced compound trichloro(1,3,3,3-tetrafluoropropyl)silane (ratio 7 : 3) in high yield. Treatment of trichloro(2-chloro-1,3,3,3-tetrafluoropropyl)silane with quinoline yields mainly *cis*- and *trans*-trichloro(1,3,3,3-tetrafluoropropenyl)silane and a lesser amount of *cis*- and *trans*-trichloro(2-chloro-3,3,3-trifluoropropenyl)silane. This olefin mixture when fluorinated with antimony trifluoride gives a mixture of the trifluorosilyl analogues which is stable to 350 °C *in vacuo*.

As part of a further study of photochemical reactions of silanes with fluoro-olefins [1-5] the addition reactions of trichlorosilane with 1,3,3,3-tetrafluoropropene, (I), and 2-chloro-1,3,3,3-tetrafluoropropene, (II), have been investigated.

RESULTS AND DISCUSSION

1,3,3,3-*Tetrafluoropropene*, (I).—The olefin, prepared by reaction of trifluoroiodomethane with vinyl fluoride and dehydroiodination of the resulting 1 : 1 adducts,[6] was obtained as a mixture of (I) and 2,3,3,3-tetrafluoropropene, (III), in the ratio 9 : 1 [equation (1)]. Photochemical reaction of this olefin mixture with excess of



$$\begin{tikzcd} CF_3I + CH_2{:}CHF \arrow[r] & CF_3{\cdot}CH_2{\cdot}CHFI \arrow[d, "KOH"] + & CF_3{\cdot}CHF{\cdot}CH_2I \arrow[d, "KOH"] & (1) \\ & \underset{(I)}{CF_3{\cdot}CH{:}CHF} & \underset{(III)}{CF_3{\cdot}CF{:}CH_2} & \end{tikzcd}$$

trichlorosilane gave unchanged olefin (63% recovered), a mixture of the 1 : 1 adducts trichloro(2-fluoro-1-trifluoromethylethyl)silane, (IV) (46%), and (trichloro-1,3,3,3-tetrafluoropropyl)silane, (V) (16%), formed from olefin (I) [equation (2)], trichloro(2,3,3,3-tetrafluoropropyl)silane, (VI) (7%), formed from olefin (III) [equation (3)], and telomeric material.

$$(I) \xrightarrow{HSiCl_3} \underset{(IV)}{CF_3{\cdot}CH(SiCl_3){\cdot}CH_2F} + \underset{(V)}{CF_3{\cdot}CH_2{\cdot}CHF{\cdot}SiCl_3} \quad (2)$$

$$(III) \xrightarrow{HSiCl_3} \underset{(VI)}{CF_3{\cdot}CHF{\cdot}CH_2{\cdot}SiCl_3} \quad (3)$$

The 1 : 1 adducts were not separated, but they were identified from a molecular-weight determination on the mixture, g.l.c., and n.m.r. spectroscopy. The ^{19}F n.m.r. spectrum of the major adduct (IV) showed the presence of a $CF_3{\cdot}CH$ grouping (d, J 10.3 Hz) and a CH_2F group (t, J 51.1 Hz). The spectra of adduct (V) showed the presence of a CHF group (J 54.1 Hz) which was not adjacent to the CF_3 group and those of adduct (VI) showed the presence of a CHF group adjacent to the CF_3 group [$J(CF_3{-}F)$ 12.7; $J(CF_3{-}H)$ 8.1 Hz]. Pure adduct (V) was also separated from the reaction of $HSiCl_3$ with olefin (II) (see later).

The ratio (37 : 13) of 1 : 1 adducts, (IV) and (V), cannot be regarded as quantitative because the adduct yield was only 62% and telomeric material of unknown composition was formed. However, on a qualitative basis, this ratio can be compared with that obtained previously for photochemical reaction of $HSiCl_3$ with hexafluoropropene which gave the 1 : 1 adducts $CF_3{\cdot}CF(SiCl_3){\cdot}CHF_2$ and $CF_3{\cdot}CHF{\cdot}CF_2{\cdot}SiCl_3$ in the ratio 65 : 35.[5] Thus in both reactions predominant attack by the highly electrophilic trichlorosilyl radical takes place at the most sterically hindered internal vinylic carbon atoms. The adduct (VI) obtained *via* trichlorosilyl radical attack on the terminal CH_2 group of olefin (III) was the expected exclusive product since addition to the olefin $CF_3{\cdot}CH{:}CH_2$ is reported [3] to take place *via* exclusive attack on the terminal CH_2 group.

2-*Chloro*-1,3,3,3-*tetrafluoropropene*, (II).—Photochemical reaction of $HSiCl_3$ with olefin (II) (4 : 1 molar ratio) gave silicon tetrachloride (29%), (V) (29%), and the 1 : 1 adduct trichloro(2-chloro-1,3,3,3-tetrafluoropropyl)silane, (VII) (66%). The n.m.r. spectra of adduct

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[1] Part XIII, R. N. Haszeldine, C. R. Pool, and A. E. Tipping, *J.C.S. Dalton*, 1975, 2177.

[2] R. N. Haszeldine and R. J. Marklow, *J. Chem. Soc.*, 1956, 962; A. M. Geyer and R. N. Haszeldine, *ibid.*, 1957 1038, 1925; R. N. Haszeldine and J. C. Young, *ibid.*, 1960, 4503; D. Cooper, R. N. Haszeldine, and M. J. Newlands, *J. Chem. Soc.* (*A*), 1967, 2098.

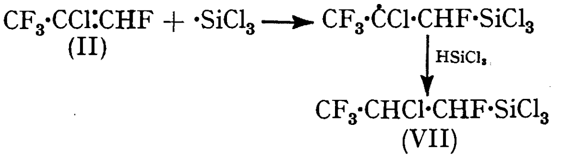
[3] A. M. Geyer, R. N. Haszeldine, K. Leedham, and R. J. Marklow, *J. Chem. Soc.*, 1957, 4472.

[4] W. I. Bevan and R. N. Haszeldine, unpublished work; W. I. Bevan, R. N. Haszeldine, J. Middleton, and A. E. Tipping, *J.C.S. Dalton*, 1974, 2305.

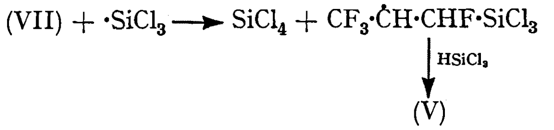
[5] C. J. Attridge, C. J. Bridge, D. Cooper, G. Cross, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, unpublished work.

[6] R. Gregory, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc.* (*C*), 1970, 1750.

(VII), although in agreement with the proposed structure, were complex, which indicates that adduct (VII) was formed [equation (4)] as a mixture of the two possible diastereoisomers. The reduced silane (V) is considered to have been formed by reduction of adduct (VII) (equation (5)]. The possibility that (V) was formed by reduction of olefin (II) to (I), followed by addition of $HSiCl_3$ to the reduced olefin [equation (6)], was ruled out because $HSiCl_3$ reacts with (I) to afford a mixture of adducts (IV) and (V) with the former predominating (see earlier).



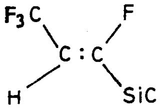
$$\begin{array}{lcl} \underset{\mathrm{(II)}}{\mathrm{CF_3{\cdot}CCl{:}CHF}} + {\cdot}\mathrm{SiCl_3} & \longrightarrow & \mathrm{CF_3{\cdot}\dot{C}Cl{\cdot}CHF{\cdot}SiCl_3} \\ & & \big\downarrow{\scriptstyle \mathrm{HSiCl_3}} \\ & & \underset{\mathrm{(VII)}}{\mathrm{CF_3{\cdot}CHCl{\cdot}CHF{\cdot}SiCl_3}} \end{array} \qquad (4)$$

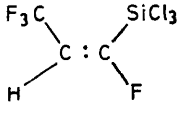


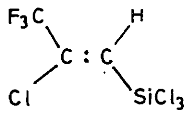
$$\begin{array}{lcl} \mathrm{(VII)} + {\cdot}\mathrm{SiCl_3} & \longrightarrow & \mathrm{SiCl_4} + \mathrm{CF_3{\cdot}\dot{C}H{\cdot}CHF{\cdot}SiCl_3} \\ & & \big\downarrow{\scriptstyle \mathrm{HSiCl_3}} \\ & & \mathrm{(V)} \end{array} \qquad (5)$$

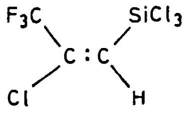
$$\mathrm{CF_3{\cdot}CCl{:}CHF} \xrightarrow{{\cdot}\mathrm{SiCl_3}} \mathrm{CF_3{\cdot}\dot{C}{:}CHF} \xrightarrow{\mathrm{HSiCl_3}} \mathrm{(I)} \qquad (6)$$

Reaction of adduct (VII) with quinoline gave olefin (I) (trace), unchanged (VII) (26%), trichloro(*cis*-1,3,3,3-tetrafluoropropenyl)silane, (VIIIa) (29%), trichloro(*trans*-1,3,3,3-tetrafluoropropenyl)silane, (VIIIb) (6%), trichloro(*cis*-2-chloro-3,3,3-trifluoropropenyl)silane, (IXa) (7%), and trichloro(*trans*-2-chloro-3,3,3-trifluoropropenyl)silane, (IXb) (2%). Olefins (VIIIa) and (VIIIb) were identified by comparison of their n.m.r. spectra with those of the olefins prepared by reaction of $HSiCl_3$ with tetrafluoropropyne.[7] The major olefin (IX) isomer was assigned structure (IXa) on the basis of the observation in the n.m.r. spectra of coupling (1.6 Hz) between the CF_3 group and the proton; the other isomer showed no such coupling.

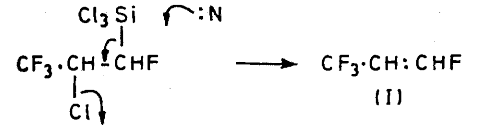

(VIIIa)


(VIIIb)

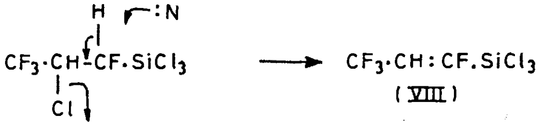

(IXa)


(IXb)

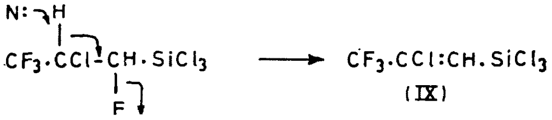
The products are considered to be formed by the elimination reactions (7)—(9). This result is in contrast to the previous observation[1] that reaction of the silanes $CH_2Cl{\cdot}CHF{\cdot}SiCl_3$ and $CH_2F{\cdot}CHF{\cdot}SiCl_3$ with quinoline gave vinyl fluoride from exclusive nucleophilic attack by quinoline at silicon.



(7)



(8)

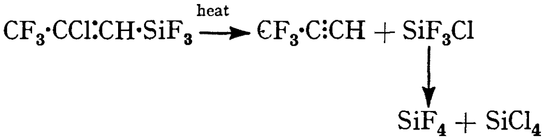


(9)

The formation of the trichlorosilyl-substituted olefins (VIII) and (IX) in the present reaction is probably due to a combination of the bulk and strong electron-withdrawing effect of the trifluoromethyl group. The size of the CF_3 group could sterically hinder attack at silicon relative to attack at hydrogen and its $-I$ effect renders the hydrogen atoms in the CHCl and CHF groups acidic and thus susceptible to attack by base. Dehydrochlorination of adduct (VII) to give (VIII) is, as expected on the basis of the relative C–Cl and C–F bond strengths, more favoured than dehydrofluorination to give (IX).

Fluorination of the mixture of olefins (VIII) and (IX) with antimony trifluoride gave a mixture (70%) of the corresponding trifluorosilyl compounds, $CF_3{\cdot}CH{:}CF{\cdot}SiF_3$ and $CF_3{\cdot}CCl{:}CH{\cdot}SiF_3$, which resisted pyrolysis at 350 °C (48 h) *in vacuo* and was almost quantitatively recovered (97%) unchanged. Traces of silicon tetrafluoride and 3,3,3-trifluoropropyne were detected in the pyrolysis product which could have arisen by reaction (10) or (11). Since $SiCl_4$ was not detected the former mechanism is more likely.

$$\mathrm{CF_3{\cdot}CH{:}CF{\cdot}SiF_3} \xrightarrow{\text{heat}} \mathrm{SiF_4} + \mathrm{CF_3{\cdot}CH{:}C{:}} \longrightarrow \mathrm{CF_3{\cdot}C{:}CH} \qquad (10)$$



$$\begin{array}{lcl} \mathrm{CF_3{\cdot}CCl{:}CH{\cdot}SiF_3} & \xrightarrow{\text{heat}} & \mathrm{CF_3{\cdot}C{:}CH} + \mathrm{SiF_3Cl} \\ & & \qquad\qquad\big\downarrow \\ & & \qquad\qquad \mathrm{SiF_4} + \mathrm{SiCl_4} \end{array} \qquad (11)$$

Thus the α-fluoro-olefin $CF_3{\cdot}CH{:}CF{\cdot}SiF_3$ is thermally more stable than the α-chloro- and α-bromo-olefins $CH_2{:}CCl{\cdot}SiF_3$ and $CH_2{:}CBr{\cdot}SiF_3$ which decompose at *ca.* 280 °C. In contrast, (1-chloro-1-fluoroalkyl)trifluorosilanes, $RCFCl{\cdot}SiF_3$,[8] decompose at *ca.* 150 °C *via* nucleophilic attack of the α fluorine on silicon.

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

[8] W. I. Bevan, R. N. Haszeldine, J. Middleton, and A. E. Tipping, *J. Organometallic Chem.*, 1970, **23**, C17; *J.C.S. Dalton*, 1975, 620.

EXPERIMENTAL

Techniques used were as described previously.[4] ^{19}F n.m.r. chemical shifts are relative to external trifluoroacetic acid. 2-Chloro-1,3,3,3-tetrafluoropropene, (II), was prepared by photochemical chlorination of 1,3,3,3-tetrafluoropropene, (I) (98%), followed by dehydrochlorination of the resulting dichloride with potassium hydroxide *in vacuo* (69%). Spectral details of compounds marked with an asterisk are in Supplementary Publication No. SUP 21471 (5 pp.).*

Photochemical Reaction of Trichlorosilane with a Mixture of (I) *and* 2,3,3,3-*Tetrafluoropropene* (III).—A mixture of (I) (12.0 g, 0.105 mol), (III) (1.19 g, 10.35 mmol), and $HSiCl_3$ (49.2 g, 0.36 mol), sealed in a silica ampoule (*ca.* 250 cm^3) and irradiated at a distance of 15 cm from a Hanovia S500 u.v. lamp (15 d), gave (*i*) a mixture of unchanged olefin (8.3 g, 72.5 mmol, 63% recovered), (*ii*) unchanged $HSiCl_3$ (*ca.* 45 g, *ca.* 90% recovered), (*iii*) a mixture (7.35 g, 29.2 mmol, 69%) (Found: *M* 245. Calc. for $C_3H_3Cl_3F_4Si$: *M* 250.5), b.p. 64 °C, shown by g.l.c. (4 m Silicone at 75 °C) to contain three components (ratio 64 : 25 : 11) identified by n.m.r. spectroscopy as trichloro(2-fluoro-1-trifluoromethylethyl)silane, (IV) * (4.92 g, 19.6 mmol, 46%), trichloro(1,3,3,3-tetrafluoropropyl)silane, (V) * (1.69 g, 6.62 mmol, 16%), and trichloro(2,3,3,3-tetrafluoropropyl)silane, (VI) * (0.74 g, 2.9 mmol, 7%), and (*iv*) a teleomeric residue (*ca.* 1.5 g) which was not examined further.

Attempts to separate the components of the 1 : 1 adduct fraction by fractional distillation through a spinning-band column (50 cm) were unsuccessful.

Reaction of $HSiCl_3$ *with* (II).—A mixture of $HSiCl_3$ (40.0 g, 0.293 mol) and (II) (11.2 g, 75.5 mmol), treated as in the previous experiment (300 h) and the products distilled through a fractionating column (30 cm), gave (*i*) $HSiCl_3$ (*ca.* 30 g, *ca.* 75% recovered), b.p. 32—33 °C, (*ii*) $SiCl_4$ (3.7 g, 21.8 mmol, 29%), b.p. 65 °C, and (*iii*) a mixture (19.6 g, 72.0 mmol, 95%), b.p. 50—60 °C at 42 mmHg,† of (V) (5.41 g, 21.7 mmol, 29%) and trichloro(2-chloro-1,3,3,3-tetrafluoropropyl)silane, (VII) (14.2 g, 50.3 mmol, 66%). This mixture was redistilled through a spinning-band column (50 cm) at reduced pressure (44 mmHg) to afford *trichloro*(1,3,3,3-*tetrafluoropropyl*)*silane*, (V) * (5.25 g, 21.5 mmol, 29%) (Found: C, 14.1; H, 1.3. $C_3H_3Cl_3F_4Si$ requires C, 14.4; H, 1.2%), b.p. 52 °C at 44 mmHg, and *trichloro*(2-*chloro*-1,3,3,3-*tetrafluoropropyl*)*silane*, (VII) * (14.0 g, 49.4 mmol, 65%) (Found: C, 13.0; H, 0.7. $C_3H_2Cl_4F_4Si$ requires C, 12.7; H, 0.7%), b.p. 59 °C at 44 mmHg.

Reaction of (VII) *with Quinoline.*—Silane (VII) (4.2 g, 14.8 mmol) was added dropwise (30 min) to quinoline (4.0 g, 31.0 mmol) and the reaction mixture slowly warmed until an exothermic reaction started. The reaction was allowed to subside and the volatile products were separated to give (*i*) (I) (trace), (*ii*) unchanged silane (1.1 g, 3.9 mmol, 26% recovered), and (*iii*) a mixture (1.2 g, 4.8 mmol, 44%) (Found: *M* 250. Calc. for $C_3HCl_3F_4Si$: *M* 247.5), shown by g.l.c. (2 m dinonyl phthalate at 80 °C) and n.m.r. spectroscopy to contain four components (A)—(D) in the ratio 65 : 15 : 16 : 4. Components (A) and (B) were identified as trichloro(*cis*-1,3,3,3-tetrafluoropropenyl)silane (VIIIa) (0.78 g, 3.15 mmol, 29%) and trichloro(*trans*-1,3,3,3-tetrafluoropropenyl)silane, (VIIIb) (0.17 g, 0.67 mmol, 6%), respectively, by comparison of their ^1H and ^{19}F n.m.r. spectra with those of authentic samples prepared by reaction of $HSiCl_3$ with tetrafluoropropyne.[7] Components (C) and (D) were identified as the *cis*- and *trans*-isomers of trichloro(2-chloro-3,3,3-trifluoropropenyl)silane, (IXa) and (IXb) * (0.25 g, 0.95 mmol, 9%).

Fluorination of a Mixture of (VIII) *and* (IX).—A mixture (0.5 g) of the olefins as prepared in the previous experiment (ratio 79 : 21), treated with a large excess (*ca.* 25 g) of SbF_3 containing SbF_5 (5% by weight) *in vacuo* at room temperature, gave a mixture (0.28 g, 70%) (Found: *M* 202. Calc. for C_3HF_7Si: *M* 198) of the corresponding trifluorosilanes.* This mixture (0.25 g), sealed in a Pyrex ampoule (*ca.* 60 cm^3) and heated at 350 °C (48 h), gave (*i*) SiF_4 (trace), (*ii*) 3,3,3-trifluoropropyne (trace), and (*iii*) unchanged reactant (0.24 g, 97% recovered). Reaction at 240 °C (96 h) gave only unchanged reactant (100%).

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† 1 mmHg ≈ 13.6 × 9.8 Pa.