Carbene Chemistry. Part IV.[1] Carbene Intermediates in Pyrolyses of Trifluoro(polyfluoroethyl)silanes, Trichloro(polyfluoroethyl)silanes, and Trichloro(trichloromethyl)silane [2,3]

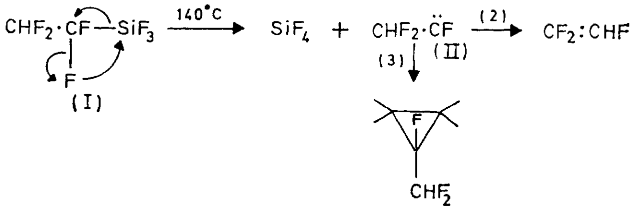
By **William I. Bevan** and **Robert N. Haszeldine,*** Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD

Thermal decomposition of the silanes $CH_2F\cdot CF_2\cdot SiF_3$ and $CFCl_2\cdot CF_2\cdot SiF_3$ at 140 °C occurs by α elimination of silicon tetrafluoride to give a carbene which rearranges to an olefin; in the former case the carbene has been trapped with isobutene. Similarly pyrolysis of a mixture of trichloro(trichloromethyl)silane and cyclohexene at 250—260 °C gives 7,7-dichloronorcarane *via* the intermediacy of dichlorocarbene. Thermal decomposition of the silanes $CH_2F\cdot CF_2\cdot SiCl_3$ and $CHF_2\cdot CF_2\cdot SiCl_3$ at 225 °C affords, in each case, a mixture of chlorofluorosilanes and three olefins, two of which contain chlorine. The chlorine-free olefins are formed *via* α elimination of trichlorofluorosilane and rearrangement of the resultant carbenes. Formation of the chlorine-containing olefins involves exchange of chlorine on silicon for fluorine on the α-carbon atom to give the rearranged silanes $R\cdot CFCl\cdot SiCl_2F$ and $R\cdot CCl_2\cdot SiClF_2$ ($R = CH_2F$ or CHF_2), which then decompose by α elimination of dichlorodifluorosilane and β elimination of chlorotrifluorosilane, respectively.

THE initial work on the pyrolysis of (polyhalogenoalkyl)silicon compounds [2,3] revealed that α elimination occurred

$$\succ\text{CX}\cdot\text{Si}\preceq\ \longrightarrow\ \succ\ddot{\text{C}} + \succeq\text{SiX} \qquad (1)$$

[equation (1)] to give a carbene (X = F or Cl). Subsequent kinetic [4,5] and other [6] studies showed that trifluoro(1,1,2,2-tetrafluoroethyl)silane (I) decomposes at *ca.* 140 °C by unimolecular α elimination of silicon tetrafluoride with a three-centre transition state to give (difluoromethyl)fluorocarbene, (II). This carbene rearranges by hydrogen migration [equation (2)] or reacts with added olefin [equation (3)].[4,6] More recently the carbene (II) has been reported to insert into C–H,[6]



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[1] Part III, R. N. Haszeldine, D. L. Scott, and A. E. Tipping, *J.C.S. Perkin I*, 1974, 1440.

[2] Reported in part as a preliminary communication, W. I. Bevan, R. N. Haszeldine, and J. C. Young, *Chem. and Ind.*, 1961, 789; see also R. N. Haszeldine and J. C. Young, *Proc. Chem. Soc.*, 1959, 394.

[3] 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.

[4] G. Fishwick, R. N. Haszeldine, C. Parkinson, P. J. Robinson, and R. F. Simmons, *Chem. Comm.*, 1965, 382.

[5] R. N. Haszeldine, P. J. Robinson, and W. J. Williams, *J.C.S. Perkin II*, 1973, 1013.

[6] R. N. Haszeldine and J. G. Speight, *Chem. Comm.*, 1967, 995.

Si–H,[7] and Si–halogen[7] bonds. Trimethyl(1,1,2,2-tetrafluoroethyl)silane has been shown to decompose analogously to give carbene (II), but a much higher temperature was required (290—300 °C).[8]

In the present work trifluoro(1,1,2-trifluoroethyl)silane, (III), and (2,2-dichlorotrifluoroethyl)trifluorosilane, (IV), have been prepared and their thermal decompositions studied. The pyrolyses of certain trichloro(polyhalogenoalkyl)silanes have also been investigated.

RESULTS AND DISCUSSION

Trifluorosilyl Compounds.—The silane (III) was obtained in high yield (90%) by reaction of the corresponding trichlorosilyl compound with antimony trifluoride. Thermal decomposition (140 °C) of silane (III) gave silicon tetrafluoride (100%) and 1,2-difluoroethylene (98%). This shows unambiguously that α elimination [equation (4)] is involved, since β elimination [equation (5)] would have afforded vinylidene fluoride. The fluoro(fluoromethyl)carbene (V) was trapped by decomposition of

$$\underset{(\mathrm{III})}{\mathrm{CH_2F{\cdot}CF_2{\cdot}SiF_3}} - \begin{cases} \xrightarrow{(4)} \mathrm{SiF_4} + \underset{(\mathrm{V})}{\mathrm{CH_2F{\cdot}\ddot{C}F}} \xrightarrow[\text{migration}]{\mathrm{H}} \mathrm{CHF{:}CHF} \\ \xrightarrow{(5)} \mathrm{SiF_4} + \mathrm{C_2H{:}CF_2} \end{cases}$$

(III) at 140 °C in the presence of an excess of isobutene, to give silicon tetrafluoride (99%), 1,2-difluoroethylene (19%), and 1-fluoro-1-fluoromethyl-2,2-dimethylcyclopropane, (VI) (79%).

$$(\mathrm{V}) + \mathrm{CH_2{:}CMe_2} \longrightarrow \underset{(\mathrm{VI})}{\overline{\mathrm{CH_2{\cdot}CMe_2{\cdot}C}}\mathrm{F{\cdot}CH_2F}} \qquad (6)$$

Photochemical chlorination of silane (III) gave the dichloro-compound (IV) (92%) which, at 140 °C, afforded

$$\underset{(\mathrm{IV})}{\mathrm{CFCl_2{\cdot}CF_2{\cdot}SiF_3}} \longrightarrow \mathrm{SiF_4} + \underset{(\mathrm{VII})}{\mathrm{CFCl_2{\cdot}\ddot{C}F}} \xrightarrow[\text{migration}]{\mathrm{Cl}} \mathrm{CFCl{:}CClF} \qquad (7)$$

silicon tetrafluoride (100%), 1,2-dichlorodifluoroethylene (90%), and 1,1-dichlorodifluoroethylene (8%). The major olefin is considered to arise *via* α elimination [equation (7)]. The minor olefin could have arisen by fluorine migration [equation (8)] in (dichlorofluoromethyl)fluorocarbene, (VII), competing with the major chlorine migration, or, more likely, by β elimination [equation (9)] in (IV) competing with α elimination.

$$\left.\begin{matrix} (\mathrm{VII}) \xrightarrow{(8)} \\ (\mathrm{IV}) \xrightarrow{(9)} \end{matrix}\right] \longrightarrow \mathrm{CF_2{:}CCl_2}$$

Such β-elimination processes have been clearly established in cases where halogen is absent on the β-carbon atom, *e.g.* $\mathrm{CHF_2{\cdot}CH_2{\cdot}SiF_3}$.[9]

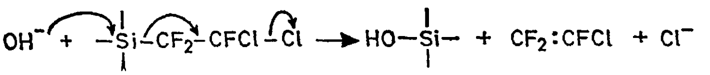
The hydrolyses of silanes (III) and (IV) with aqueous sodium hydroxide gave differing results in that the former silane afforded 1,1,2-trifluoroethane (95%) and 1,1-difluoroethylene (1%) [equation (10)] while the latter gave chlorotrifluoroethylene (100%) exclusively.

$$(\mathrm{III}) \xrightarrow{\mathrm{OH^-}} \mathrm{CH_2F{\cdot}\bar{C}F_2} - \begin{cases} \xrightarrow{\mathrm{H_2O}} \mathrm{CH_2F{\cdot}CHF_2} \\ \xrightarrow{-\mathrm{F^-}} \mathrm{CH_2{:}CF_2} \end{cases} \qquad (10)$$

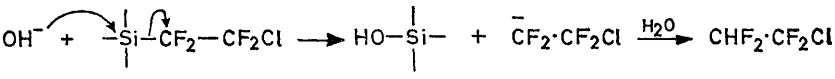
Hydrolysis of silane (IV) could similarly involve the formation of carbanion $\mathrm{CFCl_2{\cdot}\bar{C}F_2}$ which loses chloride before it abstracts a proton, but a concerted mechanism could also be involved [*cf.* hydrolysis of trichloro(2-chloroethyl)silane].[10] The formation of chlorotrifluoroethylene in the hydrolysis of silane (IV) contrasts with that of trichloro(2-chlorotetrafluoroethyl)silane which affords 1-chloro-1,1,2,2-tetrafluoroethane exclusively.[11]

Trichlorosilyl Compounds.—The pyrolysis of trichloro(trichloromethyl)silane in the presence of an excess of cyclohexene (1 : 5 molar ratio) at 250—260 °C gave silicon tetrachloride and 7,7-dichloronorcarane, (VIII) (60%) [equation (13)].

The thermal decompositions of trichloro(2-chlorotetrafluoroethyl)silane, (IX), and trichloro(1,1,2,2-tetrafluoroethyl)silane, (X), at 220 °C were amongst the first studied.[11] The former gave a mixture of chlorofluorosilanes and chlorotrifluoroethylene (90%) while the latter afforded a mixture of chlorofluorosilanes, trifluoroethylene (34%), and 1-chloro-2,2-difluoroethylene (49%). The formation of chlorotrifluoroethylene and trifluoroethylene can be explained by α elimination [equations (14) and (15)], but not the major olefin, $\mathrm{CF_2{\cdot}CHCl}$, formed on pyrolysis of silane (X). It will be noted that this olefin contains a carbon–chlorine bond whereas (X) does not.



$$\mathrm{OH^-} + -\mathrm{Si}-\mathrm{CF_2}-\mathrm{CFCl}-\mathrm{Cl} \longrightarrow \mathrm{HO}-\mathrm{Si}- + \mathrm{CF_2{:}CFCl} + \mathrm{Cl^-} \qquad (11)$$



$$\mathrm{OH^-} + -\mathrm{Si}-\mathrm{CF_2}-\mathrm{CF_2Cl} \longrightarrow \mathrm{HO}-\mathrm{Si}- + \mathrm{\bar{C}F_2{\cdot}CF_2Cl} \xrightarrow{\mathrm{H_2O}} \mathrm{CHF_2{\cdot}CF_2Cl} \qquad (12)$$

Thermal decomposition of the related trichloro(1,1,2-trifluoroethyl)silane, (XI), at 225 °C gave a mixture of

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[7] R. N. Haszeldine, A. E. Tipping, and R. O'B. Watts, *Chem. Comm.*, 1969, 1364.

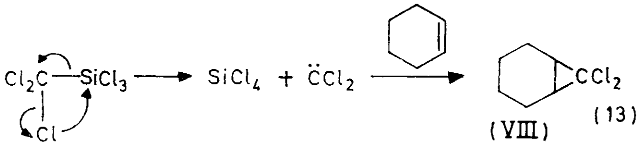
[8] R. N. Haszeldine, C. Parkinson, and P. J. Robinson, *J.C.S. Perkin II*, 1973, 1018.

[9] R. N. Haszeldine, P. J. Robinson, and R. F. Simmons, *J. Chem. Soc.*, 1964, 1890.

[10] L. H. Sommer, G. M. Goldberg, E. Dorfman, and F. C. Whitmore, *J. Amer. Chem. Soc.*, 1946, **68**, 1083.

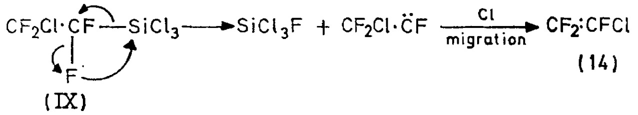
[11] R. N. Haszeldine and R. J. Marklow, *J. Chem. Soc.*, 1956, 962.

chlorofluorosilanes, 1,2-difluoroethylene (19%), 1-chloro-2-fluoroethylene (7%), and vinylidene chloride (60%).



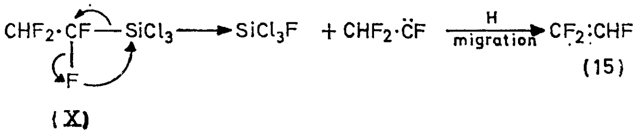
(VIII) (13)

The unusual formation of two chlorine-containing olefins was also observed during reinvestigation of the pyrolysis



(14)

(IX)



(15)

(X)

(225 °C) of compound (X) to give 1,1-dichloro-2-fluoroethylene (22%) as well as the trifluoroethylene (29%) and 1-chloro-2,2-trifluoroethylene (21%) observed previously.[11] It will again be noted that silicon compounds that contained no C–Cl bonds have produced olefins on pyrolysis containing one or two such bonds.

The chlorine-free olefins formed by pyrolysis of (X) or (XI) are still considered to arise *via* α elimination to give (fluoroalkyl)carbenes which then rearrange, *e.g.* as in equation (16). Three possibilities have to be considered

$$\underset{\text{(XI)}}{CH_2F{\cdot}CF_2{\cdot}SiCl_3} \longrightarrow \underset{\text{(V)}}{CH_2F{\cdot}\ddot{C}F} \longrightarrow CHF{:}CHF \qquad (16)$$

for the formation of the chloro-olefins. (*a*) The initial pyrolysis products react further with fluorine–chlorine

$$\text{(X)} \longrightarrow CF_2{:}CHF + SiCl_3F \longrightarrow CF_2{:}CHCl + SiCl_2F_2 \qquad (17)$$

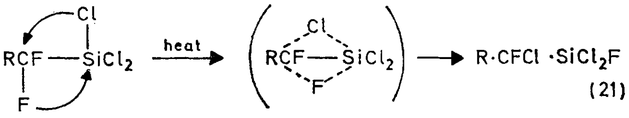
$$\text{(XI)} \longrightarrow CHF{:}CHF + SiCl_3F \longrightarrow CHF{:}CHCl + SiCl_2F_2 \qquad (18)$$

exchange as suggested earlier, *e.g.*[11] as in equations (17) and (18). Such an exchange process now seems unlikely because trifluoroethylene or 1,2-difluoroethylene fails to react with an excess of silicon tetrachloride at 225 °C [equations (19) and (20)] and such exchange would not

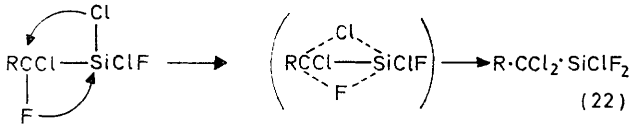
$$CHF{:}CF_2 + SiCl_4 \nrightarrow CF_2{:}CHCl + SiCl_3F \qquad (19)$$

$$CHF{:}CHF + SiCl_4 \nrightarrow CHF{:}CHCl + SiCl_3F \qquad (20)$$

explain the formation of vinylidene chloride from (XI). (*b*) Carbene insertion into Si–Cl, *e.g.* as in Scheme 1. This possibility must also be discounted since when silanes (III) and (XI) were separately pyrolysed in the presence of a large excess of silicon tetrachloride the olefinic products were formed in almost identical yields to those obtained when the silanes were pyrolysed alone. Carbene (II) can insert into Si–Cl bonds, but only in low yield (2—15%, *e.g.* 4% from $SiCl_4$).[7] (*c*) Concurrent nucleophilic attack by chlorine on carbon and nucleophilic attack by fluorine on silicon would lead to fluorine–chlorine exchange between carbon and silicon *via* a four-centre transition state [equation (21)]. A second fluorine–chlorine exchange could then occur, *i.e.* as in (22).



(21)

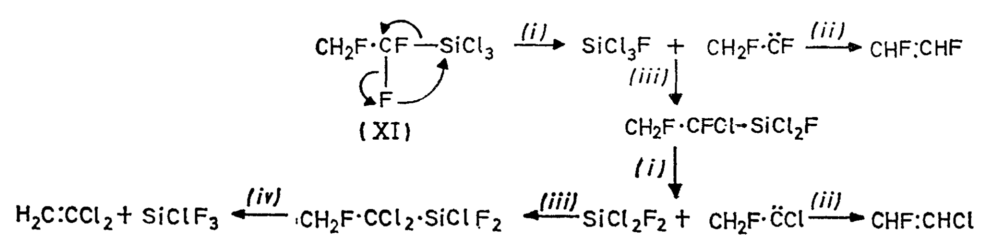


(22)

Such an exchange process is energetically favourable [equation (23)].[12] Relatively slow decomposition of the

$$\geqslant C{-}F + \geqslant Si{-}Cl \longrightarrow \geqslant C{-}Cl + \geqslant Si{-}F + ca.\ 40\ \text{kJ mol}^{-1} \qquad (23)$$

products of the exchange reaction could then proceed at 225 °C by α- or β-elimination processes. This is the most satisfactory explanation for the pyrolyses of silanes (X) and (XI) (Scheme 2).



SCHEME 1 (*i*), α Elimination; (*ii*), H migration; (*iii*), Si–Cl insertion; and (*iv*), β elimination

It will be noted that α elimination of fluorine predominates over β elimination and over α elimination of chlorine; β elimination of fluorine is preferred to α elimination of chlorine. That trichloro(polyfluoroalkyl)-silanes decompose at *ca.* 220 °C, whereas the corresponding trifluorosilanes decompose at a much lower temperature (*ca.* 140 °C) is attributed to the fluorine atoms bonded directly to silicon rendering the silicon atom particularly susceptible to intramolecular nucleophilic attack by a neighbouring fluorine. The variations in proportions of the olefins from the thermal decompositions of silanes

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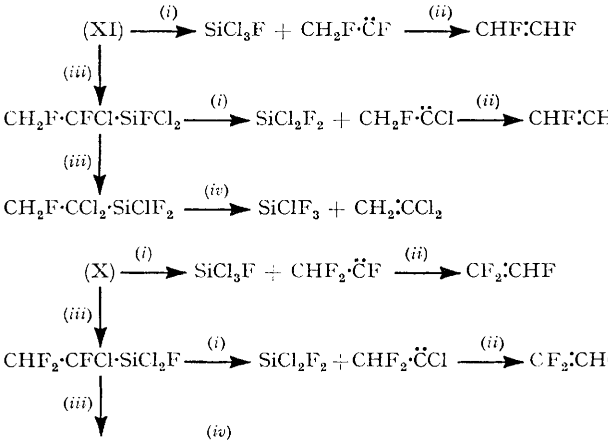
[12] T. L. Cottrell, 'The Strengths of Chemical Bonds,' 2nd edn., Butterworths, London, 1958.

(X) and (XI) may be due to steric rather than electronic factors, *i.e.* the larger β group (CHF_2) will hinder the exchange reaction more than the smaller (CH_2F); the larger the β group, the lower the yield of chlorine-containing olefins. Later work in which certain chlorine–fluorine exchange compounds were isolated [3,13] showed that chlorine–fluorine exchange plays an important part in thermal decompositions of trichloro(polyfluoroalkyl)-silanes. A somewhat related reaction subsequently reported [14] involves thermal rearrangement of α-substituted benzylsilanes $Ph{\cdot}CHY{\cdot}SiPh_3$ to $Ph_2CH{\cdot}SiPh_2Y$ (Y = $MeCO{\cdot}O$, p-$MeC_6H_4SO_2{\cdot}O$, Cl, or F).



SCHEME 2 (*i*), α Elimination; (*ii*), H migration, (*iii*), halogen exchange; and (*iv*), β elimination

EXPERIMENTAL

Reactants and products were manipulated, where possible, in a conventional high-vacuum apparatus to avoid contact with air or moisture. Photochemical reactions were carried out *in vacuo* in sealed silica tubes (*ca.* 380 cm^3) at a distance of *ca.* 15 cm from a Hanovia S500 medium-pressure lamp. Thermal reactions were carried out *in vacuo* in sealed Dreadnought glass tubes (*ca.* 250 cm^3 unless stated to the contrary). Products were separated by repeated fractional condensation *in vacuo*, or by preparative gas–liquid chromatography (g.l.c.) [columns 2 or 4 m packed with 40% by weight of squalane or 30% by weight of dinonyl phthalate (dnp) on Celite]. Identities of products were established by elemental analysis, molecular-weight determination (Regnault's method), and i.r. spectroscopy (Perkin-Elmer model 21 spectrometer with sodium-chloride optics).

Trichloro(1,1,2-trifluoroethyl)silane (36%) and trichloro-(1,1,2,2-tetrafluoroethyl)silane (50%) were prepared by photochemical reactions of trichlorosilane with chlorotrifluoroethylene [15] (5 : 1 molar ratio) and tetrafluoroethylene [11] (5 : 1 molar ratio), respectively. Trichloro(trichloromethyl)-silane (75% conversion, 95% yield) was prepared by photochemical chlorination of trichloro(methyl)silane according to the method of Runge and Zimmerman.[16]

Preparation of Trifluoro(1,1,2-*trifluoroethyl*)*silane*, (III).—Trichloro(1,1,2-trifluoroethyl)silane, (XI) (5·0 g, 23·0 mmol), repeatedly passed *in vacuo* through a tube packed with a large excess of antimony trifluoride, gave unchanged (XI) (0·3 g, 1·15 mmol, 5% recovered) and *trifluoro*(1,1,2-*trifluoroethyl*)*silane* (3·3 g, 19·6 mmol, 90%) (Found: C, 14·7; H, 1·6, hydrolysable F, 34·2; *M*, 168. Calc. for $C_2H_2F_6Si$: C, 14·3; H, 1·2, hydrolysable F, 34·0%; *M*, 168), b.p. 4—5 °C.

Reactions of Silane (III).—(a) *Photochemical chlorination.* A mixture of (III) (1·40 g, 8·35 mmol) and chlorine (2·50 g, 35·0 mmol), when irradiated (3 d), gave a mixture of hydrogen chloride and unreacted chlorine and a higher-boiling fraction identified as (2,2-*dichloro*-1,1,2-*trifluoroethyl*)*trifluorosilane*, (IV) (1·85 g, 7·8 mmol, 92%) (Found: C, 10·0; H, 0·2; *M*, 238. Calc. for $C_2Cl_2F_6Si$: C, 10·1; H, 0·0%; *M*, 237), b.p. 38 °C.

(b) *Pyrolysis.* Compound (III) (0·15 g, 0·89 mmol), sealed in a Dreadnought tube (150 cm^3) and heated at 140 °C (3 h), gave silicon tetrafluoride (0·093 g, 0·89 mmol, 100%) (Found: *M*, 103. Calc. for SiF_4: *M*, 104) and 1,2-difluoroethylene (0·056 g, 0·88 mmol, 98%) (Found: C, 37·8; H, 3·3; *M*, 63·5. Calc. for $C_2H_2F_2$: C, 36·5; H, 3·1%; *M*, 64). The absence of 1,1-difluoroethylene was confirmed by i.r. spectroscopy and g.l.c.

(c) *Pyrolysis in the presence of isobutene.* A mixture of compound (III) (0·57 g, 3·4 mmol) and isobutene (1·90 g, 34·0 mmol), heated *in vacuo* at 140 °C (3 h), gave (*i*) silicon tetrafluoride (0·34 g, 3·35 mmol, 99%), (*ii*) unchanged isobutene (1·78 g, 31·9 mmol, 92% recovered), (*iii*) 1,2-difluoroethylene (0·042 g, 0·65 mmol, 19%), and (*iv*) a higher-boiling fraction identified as 1-*fluoro*-1-*fluoromethyl*-2,2-*dimethylcyclopropane*, (VI) (0·33 g, 2·68 mmol, 79%) (Found: C, 60·1; H, 8·1; *M*, 120. Calc. for $C_6H_{10}F_2$: C, 60·0; H, 8·3%; *M*, 122), b.p. 102 °C.

(d) *Hydrolysis.* Compound (III) (0·33 g, 1·98 mmol) and degassed 10% aqueous sodium hydroxide (10 cm^3) reacted readily *in vacuo* to give volatile material which was dried by passage over P_2O_5 *in vacuo* and identified as 1,1-difluoroethylene (0·001 g, 0·02 mmol, 1%) and 1,1,2-trifluoroethane (0·16 g, 1·88 mmol, 95%) (Found: C, 28·5; H, 3·9; *M*, 83·5. Calc. for $C_2H_3F_3$: C, 28·6; H, 3·8%; *M*, 84) by comparison of their i.r. spectra with those of known pure samples.

(e) *Pyrolysis in the presence of silicon tetrachloride.* A mixture of compound (III) (0·37 g, 2·2 mmol) and silicon tetrachloride (2·65 g, 15·6 mmol), heated *in vacuo* at 225 °C (16 h), gave (*i*) silicon tetrafluoride (0·23 g, 2·2 mmol, 100%), (*ii*) 1,2-difluoroethylene (0·14 g, 2·17 mmol, 97%) (Found: *M*, 63. Calc. for $C_2H_2F_2$: *M*, 64), and (*iii*) unchanged silicon tetrachloride.

Reactions of Silane (IV).—(a) *Pyrolysis.* Compound (IV) (0·29 g, 1·22 mmol), sealed in a Dreadnought tube (150 cm^3) and heated at 140 °C (3 h), gave silicon tetrafluoride (0·13 g, 1·22 mmol, 100%) and a mixture (0·16 g, 1·20 mmol, 98%) (Found: C, 18·2; *M*, 133. Calc. for $C_2Cl_2F_2$: C, 18·1%; *M*, 133) which was shown by i.r. spectroscopy and g.l.c. (4 m squalane at room temperature) to consist of 1,2-dichlorodifluoroethylene (0·147 g, 1·10 mmol, 90%) and 1,1-dichlorodifluoroethylene (0·013 g, 0·10 mmol, 8%).

(b) *Hydrolysis.* Compound (IV) (0·26 g, 1·14 mmol) hydrolysed with 10% aqueous sodium hydroxide (10 cm^3) gave chlorotrifluoroethylene (0·13 g, 1·14 mmol, 100%) (Found: *M*, 116. Calc. for C_2ClF_3: *M*, 116·5).

Reactions of Silane (XI).—(a) *Pyrolysis.* Compound (XI) (1·19 g, 5·47 mmol) heated *in vacuo* at 225 °C (16 h) gave a

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[13] W. I. Bevan, R. N. Haszeldine, J. Middleton, and A. E. Tipping, *J. Organometallic Chem.*, 1970, **23**, C17.

[14] A. G. Brook and P. F. Jones, *Chem. Comm.*, 1969, 1324.

[15] R. N. Haszeldine and J. C. Young, *J. Chem. Soc.*, 1960, 4503.

[16] F. Runge and W. Zimmerman, *Chem. Ber.*, 1954, **87**, 282.

mixture (10·65 mmol) of chlorofluorosilanes and various olefins. The mixture was hydrolysed *in vacuo* with 10% aqueous sodium hydroxide (10 cm^3) and the volatile material (4·71 mmol, 86%) was dried (P_2O_5) and separated into two fractions. The major fraction was identified as vinylidene chloride (0·29 g, 3·0 mmol, 55%) (Found: C, 25·1; H, 2·1; *M*, 97. Calc. for $C_2H_2Cl_2$: C, 24·8; H, 2·1%; *M*, 97) by a comparison of its g.l.c. retention time and i.r. spectrum with those of a known pure sample. The minor fraction was separated by g.l.c. (2 m dnp at room temperature) into its three components which were identified by a comparison of their g.l.c. retention times and i.r. spectra with those of known pure samples as (*i*) vinylidene chloride (0·027 g, 0·28 mmol, 5%), (*ii*) 1-chloro-2-fluoroethylene (0·029 g, 0·36 mmol, 7%), and (*iii*) 1,2-difluoroethylene (0·069 g, 1·07 mmol, 19%) (Found: C, 37·2; H, 3·0; *M*, 64. Calc. for $C_2H_2F_2$: C, 37·5; H, 3·1%; *M*, 64).

(b) *Pyrolysis in the presence of silicon tetrachloride.* A mixture of compound (XI) (1·20 g, 5·5 mmol) and silicon tetrachloride (2·70 g, 15·7 mmol), heated at 225 °C (16 h) *in vacuo*, gave a mixture of chlorofluorosilanes, silicon tetrachloride, and olefins. Hydrolysis of this mixture as in (*a*) afforded vinylidene chloride (0·32 g, 3·30 mmol, 60%), 1-chloro-2-fluoroethylene (0·027 g, 0·33 mmol, 6%), and 1,2-difluoroethylene (0·064 g, 0·99 mmol, 18%).

Pyrolysis of Trichloro(1,1,2,2-*tetrafluoroethyl*)*silane*, (X).—Compound (X) (1·80 g, 7·66 mmol), heated *in vacuo* at 225 °C (16 h), gave a mixture (13·4 mmol) of chlorofluorosilanes and olefins. Hydrolysis of this mixture, as described above, afforded (*i*) 1,1-dichlorofluoroethylene (0·132 g, 1·15 mmol, 20%) (Found: *M*, 115. Calc. for C_2HCl_2F: *M*, 115) which was identified by a comparison of its g.l.c. retention time and i.r. spectrum with those of a known pure sample, (*ii*) a mixture (0·031 g, 0·28 mmol) shown by g.l.c. (2 m squalane at room temperature) and i.r. spectroscopy to consist of 1,1-dichlorofluoroethylene (0·024 g, 0·21 mmol, 3%) and 2-chloro-1,1-difluoroethylene (0·007 g, 0·07 mmol, 1%), (*iii*) 2-chloro-1,1-difluoroethylene (0·136 g, 1·38 mmol, 18%) (Found: *M*, 98. Calc. for $CHClF_2$: *M*, 98·5), identified by a comparison of its g.l.c. retention time and i.r. spectrum with those of a known pure sample, (*iv*) a mixture (0·045 g, 0·50 mmol) shown by g.l.c. (as before) and i.r. spectroscopy to consist of 2-chloro-1,1-difluoroethylene (0·019 g, 0·19 mmol, 3%) and trifluoroethylene (0·026 g, 0·31 mmol, 4%), and (*v*) trifluoroethylene (0·16 g, 1·91 mmol, 25%) (Found: *M*, 83. Calc. for C_2HF_3: *M*, 83) which was identified by a comparison of its g.l.c. retention time and i.r. spectrum with those of a known pure sample.

Attempted Reaction of 1,2-*Difluoroethylene with Silicon Tetrachloride.*—A mixture of the olefin (0·14 g, 2·23 mmol) and the chlorosilane (2·65 g, 15·6 mmol), heated at 225 °C (16 h), gave unchanged olefin (0·14 g, 2·22 mmol, 99% recovered) and unchanged silicon tetrachloride.

Pyrolysis of Trichloro(*trichloromethyl*)*silane in the Presence of Cyclohexene.*—A mixture of the silicon compound (14·5 g, 56·2 mmol) and cyclohexene (22·8 g, 0·278 mol), heated *in vacuo* in a stainless-steel autoclave (300 cm^3) at 250—260 °C (10 h), gave a mixture of unchanged cyclohexene and silicon tetrachloride and higher-boiling material which, on distillation (15 cm Vigreux column fitted with a partial take-off head) at reduced pressure, afforded as the major fraction 7,7-dichlorobicyclo[4.1.0]heptane (5·6 g, 34·0 mmol, 60%) (Found: C, 51·1; H, 6·1; Cl, 43·0. Calc. for $C_7H_{10}Cl_2$: C, 50·9; H, 6·1; Cl, 43·0%), b.p. 78—79 °C at 15 mmHg, n_D^{21} 1·502 (lit.,[17] b.p. 78—79 °C at 15 mmHg, n_D^{23} 1·5014).

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