Polyfluoroalkyl Derivatives of Silicon. Part XV.[1] The Preparation and Pyrolysis of 1-Trifluoromethyl-1,2,2-trifluoroethyl-, 1-Trifluoromethyl-1,2,3,3,3-pentafluoropropyl-, 2*H*-Hexafluorocyclobutyl-, 3*H*-Pentafluoropropyl-, and 1,2,2-Trifluoroethyl-trihalogenosilanes

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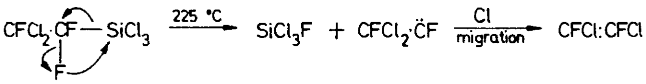
The trichloro(polyfluoroalkyl)silanes are formed in high yield by the photochemical reaction of trichlorosilane with the appropriate fluoro-olefin and they are readily converted into the trifluorosilyl analogues by reaction with antimony(III) fluoride. The reaction of trichlorosilane with hexafluorocyclobutene gives exclusively the *trans*-adduct. All the trihalogeno(polyfluoroalkyl)silanes and trihalogeno(2*H*-hexafluorocyclobutyl)silanes except trichloro(3*H*-pentafluoropropyl)silane decompose thermally by β-elimination processes; the latter silane partly decomposes by an α-elimination process *via* an intermediate carbene and it partly undergoes rearrangement by exchange of fluorine on the α-carbon by chlorine on silicon.

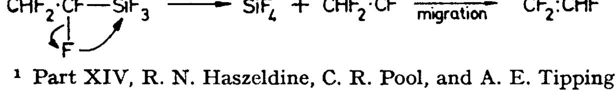
TRICHLORO(FLUOROALKYL)SILANES $RCF_2{\cdot}SiCl_3$ and $RCFCl{\cdot}SiCl_3$ on pyrolysis give products which depend on the size of the group R and the temperature employed.[2] At moderate temperature (<180 °C) and when the group R is small (Me or CH_2Cl) halogen exchange is the preferred reaction,[3-6] *e.g.*

$$CF_2Me{\cdot}SiCl_3 \xrightarrow{100\ ^\circ C} [CFClMe{\cdot}SiFCl_2] \longrightarrow CCl_2Me{\cdot}SiF_2Cl$$

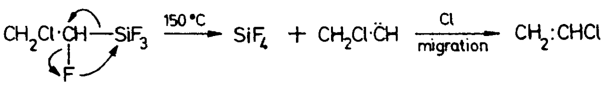
At higher temperature and as the size of the R group increases, α-elimination of fluorine to give a carbene becomes the major or even exclusive reaction,[3-7] *e.g.*



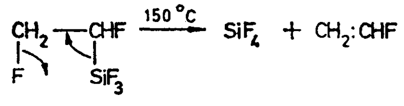
The trifluorosilyl analogues decompose at lower temperature (120—140 °C),[4-6,8] *e.g.*



However, although (2-chloro-1-fluoroethyl)trifluorosilane decomposes by an α-elimination process,[9] *i.e.*



trichloro(1,2-difluoroethyl)silane and (1,2-difluoroethyl)trifluorosilane both decompose *via* β-elimination,[9] *e.g.*



In an extension to this work the effect of chain-branching at the α-carbon atom on the mode of thermal decomposition of trihalogeno(polyfluoroalkyl)silanes has been

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[1] Part XIV, R. N. Haszeldine, C. R. Pool, and A. E. Tipping, *J.C.S. Dalton*, 1975, 2292.

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

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

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

[6] W. I. Bevan, R. N. Haszeldine, J. Middleton, and A. E. Tipping, *J.C.S. Dalton*, 1975, 620.

[7] R. N. Haszeldine and J. C. Young, *Proc. Chem. Soc.*, 1959, 394; W. I. Bevan, R. N. Haszeldine and J. C. Young, *Chem. and Ind.*, 1961, 789.

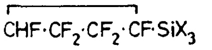
[8] G. Fishwick, R. N. Haszeldine, C. Parkinson, P. J. Robinson, and R. F. Simmons, *Chem. Comm.*, 1965, 382.

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

investigated and the silanes (I)—(V) have been prepared and pyrolysed.

$CHF_2 \cdot CF(CF_3) \cdot SiCl_3$ (I)

$CF_3 \cdot CHF \cdot CF(CF_3) \cdot SiX_3$ (II) X = Cl (III) X = F


$CHF \cdot CF_2 \cdot CF_2 \cdot CF \cdot SiX_3$

(IV) X = Cl

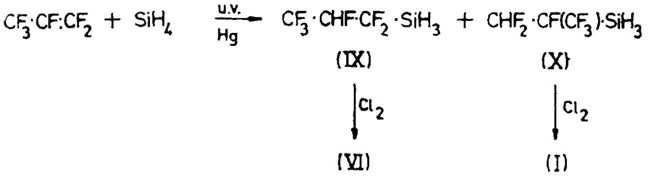
(V) X = F

The pyrolysis of trichloro(1,1,2,3,3,3-hexafluoropropyl)silane (VI) has also been carried out in order to compare the results with those obtained from pyrolysis of the isomeric compound (I) and further silanes of type $R_fCHF \cdot SiX_3$, *i.e.* (VII) and (VIII), have been thermally decomposed.

$CF_3 \cdot CHF \cdot CF_2 \cdot SiCl$ (VI)

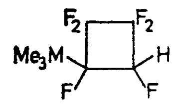
$CHF_2 \cdot CHF \cdot SiX_3$ (VII) $X_3 = Cl_3$ (VIII) $X_3 = MeCl_2$

Preparation of the Silanes.—The mercury-photosensitised reaction of an excess of silane with hexafluoropropene (1.6 : 1.0 molar ratio) gave a mixture (85%) of (1,1,2,3,3,3-hexafluoropropyl)silane (IX) and (1,2,2-trifluoro-1-trifluoromethylethyl)silane (X) in the ratio 60 : 40.[10] These were separated by g.l.c. and allowed to react separately with chlorine (1 : 3 molar ratio) to afford the silanes (VI) (84%) and (I) (89%), respectively.[10]

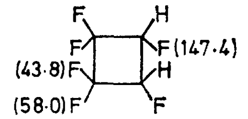


A mixture of trichlorosilane and octafluorobut-2-ene (4 : 1 molar ratio) on irradiation gave trichloro(2*H*-1-trifluoromethylpentafluoropropyl)silane (II) (91%) which was shown by n.m.r. spectroscopy to be a mixture of two diastereoisomers in the ratio 60 : 40 but attempts to separate the two isomers were unsuccessful. Fluorination (SbF_3–$SbCl_5$) of silane (II) gave the trifluorosilyl analogue (III) (87%).

The photochemical reaction of trichlorosilane with hexafluorocyclobutene (3 : 1 molar ratio) gave trichloro-(2*H*-hexafluorocyclobutyl)silane (IV) (80%), exclusively as one isomer as indicated by g.l.c. and n.m.r. spectroscopy. The similarity of the ^1H n.m.r spectrum of adduct (IV) to those of the adducts of hexafluorocyclobutene with the compounds Me_3SiH, Me_3GeH, and Me_3SnH reported by Cullen and Styan[11] indicates strongly that they all have the same stereochemistry. The latter adducts were tentatively identified as the compounds (XI) arising from *cis*-addition on the basis of the magnitudes of the H–F coupling constants derived from the ^1H spectra.

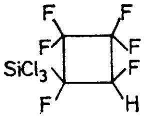


(XI) M = Si, Ge, and Sn



(XII)

For the $SiHCl_3$ adduct (IV) the ^{19}F n.m.r. spectrum has been recorded, chemical shifts obtained, and the magnitudes and assignments of H–F coupling constants confirmed. The product of catalytic hydrogenation of hexafluorocyclobutene, 1*H*,2*H*-hexafluorocyclobutane[12] (XXI) (chemical shifts shown), has been used as a model of known stereochemistry. The ^{19}F n.m.r. spectrum of adduct (IV) shows two AB-type multiplets at 40.5 and 55.7 p.p.m. (J_{AB} 228 Hz) and at 41.3 and 48.3 p.p.m. (J_{AB} 235 Hz), assigned, respectively, to the CF_2 groups adjacent to H and to $SiCl_3$, the lower field absorptions in each case being assigned to the fluorines *cis* to the substituent. It also shows band systems at 115.0 p.p.m. ($CF \cdot Si \lessdot$) and at 130.5 p.p.m. (CHF) the latter containing the characteristic geminal HF coupling (50.6 Hz). The low-field shift of this latter band, when compared with the shift of the CHF absorption in compound (XII), suggests strongly that the fluorine in the CHF group of adduct (IV) has an adjacent *cis*-$SiCl_3$ rather than a *cis*-fluorine, *i.e.* the adduct has structure (IVa).



(IVa)

The *vicinal* $^3J_{HF}$ coupling depends largely upon dihedral and bond angle[13] and the electronegativity of adjacent groups.[14] Cullen and Styan[11] concluded that the two largest $^3J_{HF}$ couplings (*ca.* 22 and *ca.* 13 Hz) observed in the ^1H n.m.r. spectra of adducts (XI) were due to coupling of axial substituents in a cyclobutane ring, from which their structural assignment followed. However, few unequivocal analyses of the spectra of fluorinated cyclobutanes have been made[15] and the following assignments made from the ^1H n.m.r. spectrum of adduct (IV) (d mult at τ 4.8), in which the larger $^3J_{HF}$ couplings correspond to a small dihedral angle (*ca.* 27°), are equally acceptable. Also the assignment made by Cullen and Styan requires that for each CF_2 group the high-field absorption should be *trans* to the adjacent substituent H and MMe_3, and this is unlikely.[16]

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[10] G. W. Cross, Ph.D. Thesis, Manchester, 1963.

[11] W. R. Cullen and G. E. Styan, *J. Organometallic Chem.*, 1966, **6**, 633.

[12] I. L. Knunyants, M. P. Krasuskaya, E. I. Misov, and I. A. Mukhtarov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1962, 2141.

[13] K. L. Williamson, Y-F. L. Hsu, F. H. Hall, S. Swager, and M. S. Coulter, *J. Amer. Chem. Soc.*, 1968, **90**, 6717.

[14] A. M. Ihrig and S. L. Smith, *J. Amer. Chem. Soc.*, 1970, **92**, 759; K. L. Williamson, S. Mosser, and D. E. Stedman, *ibid.*, 1971, **93**, 7208; R. J. Abraham and R. H. Kemp, *J. Chem. Soc.* (*B*), 1971, 1240.

[15] See for example, J. D. Park, R. O. Michael, and R. A. Newmark, *J. Org. Chem.*, 1969, **34**, 2525; R. K. Harris and V. J. Robinson, *J. Magnetic Resonance*, 1969, **1**, 362.

[16] J. W. Emsley and L. Phillips, *Progr. N.M.R. Spectroscopy*, 1971, **7**, 91.

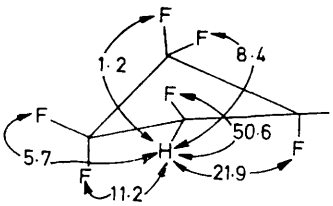
TABLE 1

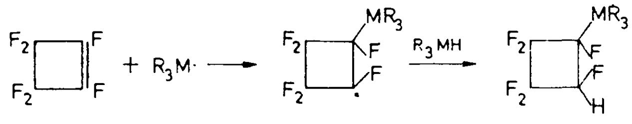
Thermal decompositions of silanes

Silane	Pyrolysis temp. (θ_c/°C)	Conditions time (h)	Olefinic products		Products (%)	
(I)	250	24	CF_3·CF:CHF	82		
(II)	225	16	*trans*-CF_3·CH:CF·CF_3	70	71 *	
			cis-CF_3·CH:CF·CF_3	8	7	
			CF_3·CHF·CF:CF_2	21	14	
(III)	165	6	*trans*-CF_3·CH:CF·CF_3	81	82 *	85 †
			cis-CF_3·CH:CF·CF_3	11	12	12
(IV)	265	16	CF_2·CH:CF·CF_2	92	90 *	
			CHF·CF:CF·CF_2	7	6	
(V)	200	14	CF_2·CH:CF·CF_2	86		87 †
			CHF·CF:CF·CF_2	9		10
(VI)	250—270	24	CF_3·CF:CHF	68		
			CF_3·CF:CHCl	18		
			CF_3·CH:CCl_2	3		
(VII) ‡	250—255	18	CHF:CHF	50		
(VIII) §	225	16	CHF:CHF	94		
			CH_2:CF_2	5		

* Pyrolysis carried out in the presence of an excess of isobutene. † Pyrolysis carried out in the presence of an excess of *cis*-but-2-ene. ‡ As a mixture of (VII) (95%) and (XIII) (5%). § As a mixture of (VIII) (85%) and (XIV) (15%).

The thermal additions[11] of trimethylsilane (250 °C), trimethylgermane (230 °C), and trimethyltin hydride (20 °C) and the photochemical addition of trichlorosilane to hexafluorocyclobutene are thus all stereospecific *trans*-additions, *i.e.*





It has similarly been reported[17] that the photochemical- or peroxide-initiated additions of hydrogen bromide to 1-alkylcylohexenes afford *cis*-1-bromo-2-alkylcyclohexanes.

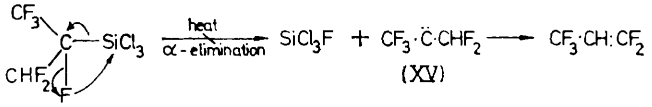
Fluorination (SbF_3–$SbCl_5$) of adduct (IV) gave the corresponding *trans*-trifluorosilyl compound (V) (90%).

Photochemical reaction of trichlorosilane with trifluoroethylene (5 : 1 molar ratio) gave a mixture (70%) of the 1 : 1 adducts trichloro(1,2,2-trifluoroethyl)silane (VII) and trichloro(1,1,2-trifluoroethyl)silane (XIII) in the ratio 95 : 5,[18] and a comparable reaction of dichloromethylsilane with trifluoroethylene afforded a mixture (75%) of the corresponding 1 : 1 adducts (VIII) and (XIV) in the ratio 85 : 15.[18]

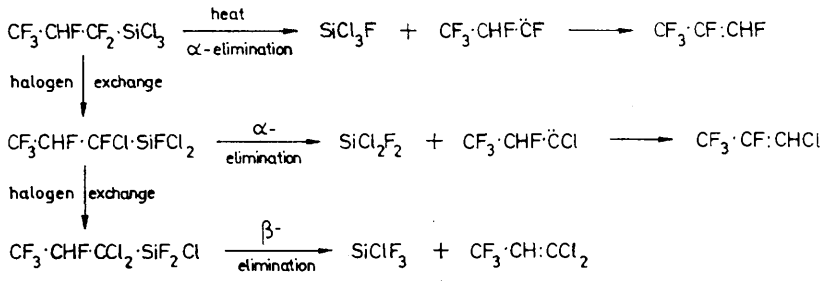
$CH_2F·CF_2·SiCl_3$ (XIII)

$CH_2F·CF_2·SiMeCl_2$ (XIV)

Pyrolysis of the Silanes.—The conditions used and the products formed in the pyrolyses of silanes (I)—(VIII) are shown in Table 1. The exclusive formation of 1*H*-pentafluoropropene in the pyrolysis of silane (I) shows unambiguously that a β-elimination process is involved. An α-elimination mechanism would have given the



intermediate carbene (XV) and, since hydrogen migration in such carbenes occurs in preference to fluorine migration,[4,6] the product would have been 2*H*-pentafluoropropene. In contrast the isomer (VI) decomposed *via* α-elimination and halogen exchange as found for other polyfluoroalkyltrichlorosilanes containing the $-CF_2·SiCl_3$ grouping,[2-4,8,19] *i.e.*



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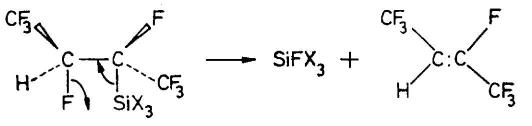
[17] H. L. Goering, P. I. Abell, and B. G. Aycock, *J. Amer. Chem. Soc.*, 1952, **74**, 3588; H. L. Goering and L. L. Sims, *ibid.*, 1955, **77**, 3465.

[18] C. J. Attridge, Ph.D. Thesis, Manchester, 1967.

[19] J. T. Maynard, *J. Org. Chem.*, 1963, **28**, 112.

The silanes (II)—(V) are all considered to decompose thermally by β-elimination processes since comparable yields of the same olefinic products were formed irrespective of whether the pyrolyses were carried out in the presence or absence of hydrocarbon olefins (carbene traps). If such β-eliminations were completely *cisoid*, the *erythro*-isomers of silanes (II) and (III) would afford the *trans*-olefin and the *threo*-isomers the corresponding *cis*-olefin. Stereoselective elimination does not occur, however, since the ratio of isomers in silanes (II) and (III) was *ca.* 60 : 40 and the yields of *trans*-olefin obtained from the pyrolyses were *ca.* 70% and *ca.* 83%, respectively; the olefins did not isomerise under the reaction conditions.

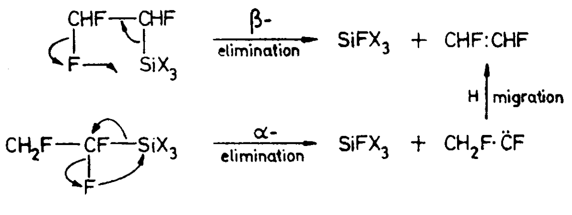


The absence of 3*H*-heptafluorobut-1-ene in the products from pyrolysis of silane (III) can be accounted for by the smaller steric requirements of the SiF_3 group as compared to the $SiCl_3$ group, which enhances elimination of the internal β-fluorine atom at the expense of a terminal β-fluorine atom.

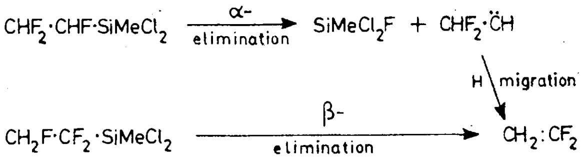
The *trans*-silanes (IV) and (V) on β-elimination would afford 1*H*- and/or 3*H*-pentafluorocyclobutene, while β-elimination from the corresponding *cis*-isomers could yield only the 3*H*-isomer. The observation that the preferred β-elimination occurs from the CHF group rather than from the β-CF_2 group finds a parallel with the products obtained from the pyrolyses of silanes (I)—(III).

The ready elimination of trimethyltin fluoride from adduct (XI; M = Sn) to give 1*H*-pentafluorocyclobutene was postulated[11] to involve an intermediate carbene formed by α-elimination; since the $SnMe_3$ group and the β-fluorine in the CHF group of the adduct are probably *cis* simple β-elimination now seems more plausible as with adduct (IV).

Pyrolysis of the silane (VII) containing isomer (XIII) (5%) gave only a low yield of 1,2-difluoroethylene (50%), the olefin expected by β-elimination from silane (VII) and α-elimination from silane (XIII), *i.e.* (where $X_3 = Cl_3$)



In contrast pyrolysis of a mixture of silane (VIII) (85%) and silane (XIV) (15%) gave a nearly quantitative yield of olefinic products (99%). The major product, 1,2-difluoroethylene (94%), is formed as shown in the above scheme (where $X_3 = MeCl_2$). However, the presence of 1,1-difluoroethylene (5%) in the products requires that a small proportion of silane (VIII) decomposes by α-elimination and/or a proportion of silane (XIV) decomposes by β-elimination, *i.e.*



The reported modes of decomposition of (polyfluoroalkyl)silanes are summarised in Table 2.

TABLE 2

Mode of thermal decomposition of (polyfluoroalkyl)silanes

Silane	Decomposition	Ref.
$>CF\cdot CF_2\cdot SiX_3$	α-	2—4, 7, 8
$>CF\cdot CFCl\cdot SiX_3$	α-	3, 6
$>CF\cdot CHF\cdot SiX_3$	β-	9, this work
$>CF\cdot CF(CF_3)\cdot SiX_3$	β-	This work
$\overline{CHF\cdot CF_2\cdot CF_2\cdot C}F\cdot SiX_3$	β-	This work
$>CCl\cdot CHF\cdot SiX_3$	α-	9
$>CF\cdot CCl_2\cdot SiX_3$	β-	3, 6

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 silica tubes (*ca.* 300 cm^3) which were shaken and irradiated at a distance of *ca.* 15 cm from a Hanovia S 500 medium-pressure u.v. lamp and thermal decompositions were carried out *in vacuo* in Pyrex or Dreadnought tubes (*ca.* 300 cm^3), unless stated to the contrary. The products from the thermal decompositions, consisting of mixtures of tetrahalogenosilanes and olefins, were shaken *in vacuo* with aqueous sodium hydroxide (*ca.* 10% w/v) and the resultant olefins were dried (P_2O_5). Products were separated by either fractional distillation, fractional condensation *in vacuo*, or g.l.c. (Perkin-Elmer 116, 154B, or 451 Fraktometers using columns as indicated in the text) and their identities were established by molecular-weight determination (Regnault's method), elemental analysis, i.r. spectroscopy (Perkin-Elmer model 21 spectrophotometer with sodium chloride optics), and n.m.r. spectroscopy (Perkin-Elmer R10 or Hitachi R20A spectrometers operating at 56.46 MHz for ^{19}F and 60.0 MHz for ^1H with external trifluoroacetic acid and internal tetramethylsilane as the respective references).

trans-2*H*-Heptafluorobutene was prepared by the fluorination of hexachlorobutadiene with potassium fluoride in *N*-methyl-2-pyrrolidone[19,20] and a sample of the corresponding *cis*-olefin was obtained by free-radical chlorination of the *trans*-olefin, dechlorination of the resultant adduct with zinc in ethanol, and separation of the *cis*-olefin from the mixture of isomers by g.l.c.[20]

Reaction of Octafluorobut-2-ene with Trichlorosilane.—The olefin (25.0 g, 0.125 mol) and trichlorosilane (68.5 g, 0.507 mol), irradiated (150 h), gave (i) hydrogen (*ca.* 0.5 mmol), (ii) unchanged olefin (6.40 g, 32.0 mmol, 26% recovered), and (iii) a higher-boiling fraction (87 g), which when distilled (30 cm Vigreux column) yielded unchanged

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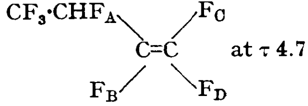
[20] R. D. Chambers and A. J. Palmer, *Tetrahedron*, **1969**, **25**, 4217.

trichlorosilane (53.8 g, 0.40 mol, 79% recovered), an intermediate fraction (2.0 g), b.p. 35—118 °C, *trichloro*(2H-1-*trifluoromethylpentafluoropropyl*)*silane* (28.1 g, 84.0 mmol, 91%) (Found: C, 14.1; H, 0.4; Cl, 31.5. $C_4HCl_3F_8Si$ requires C, 14.3; H, 0.3; Cl, 31.7%), b.p. 118—119 °C, and a residue (3 g), b.p. >119 °C. The ^{19}F n.m.r. spectrum of the adduct showed the presence of two diastereoisomers in the ratio 60 : 40; bands for major isomer at δ −5.9 (3F, complex, CF_3), −4.2 (3F, complex, CF_3), 110.7 (1F, d mult, CHF, *J ca.* 50 Hz), and 111.3 p.p.m. (1F, complex, $CF{\cdot}SiCl_3$) and bands for minor isomer at δ −9.6 (3F, complex, CF_3), −3.2 (3F, complex, CF_3), 110.8 (1F, d mult, *J ca.* 50 Hz), and 111.7 p.p.m. (1F, complex, $CF{\cdot}SiCl_3$); g.l.c. (4 m Silicone column at 100 °C) failed to resolve the isomers.

Reactions of Trichloro(2*H*-1-*trifluoromethylpentafluoropropyl*)*silane*.—(a) *Fluorination*. The silane (1.56 g, 4.7 mmol), passed several times *in vacuo* through a tube packed with a mixture of antimony trifluoride (*ca.* 75 g) and antimony pentachloride (*ca.* 1 g), gave *trifluoro*(2*H*-1-*trifluoromethylpentafluoropropyl*)*silane* (1.17 g, 4.1 mmol, 87%) (Found: C, 16.5; H, 0.5%; *M*, 288. $C_4HF_{11}Si$ requires C, 16.7; H, 0.5%; *M*, 286), b.p. 41—42 °C. The ^{19}F n.m.r. spectrum showed the presence of two isomers in the ratio 60 : 40; bands for major isomer at δ −2.2 (6F, complex, $2CF_3$), 65.8 (3F, s, SiF_3), 120 (1F, d mult, CHF), and 136.5 p.p.m. (1F, complex, $C\mathit{F}{\cdot}SiF_3$) and bands for minor isomer at δ −5.3 (3F, complex, CF_3), −2.0 (3F, complex, CF_3), 65.8 (3F, s, SiF_3), 130 (1F, d mult, CHF), and 132.5 p.p.m. (1F, complex, $C\mathit{F}{\cdot}SiF_3$).

(b) *Pyrolysis*. The silane (1.21 g, 3.6 mmol), heated at 225 °C (16 h), gave a mixture (7.2 mmol, 100%) of chlorofluorosilanes and olefins. Hydrolysis of the mixture yielded an olefin mixture which was separated by g.l.c. (10 m Kel-F 10 oil at 20 °C) into its three components identified as (i) *trans*-2*H*-heptafluorobut-2-ene (0.46 g, 2.5 mmol, 70%) (Found: C, 26.5; H, 0.7%; *M*, 182. Calc. for C_4HF_7: C, 26.4; H, 0.6%; *M*, 182), the i.r. and n.m.r. spectra of which were identical with those of an authentic sample, (ii) *cis*-2*H*-heptafluorobut-2-ene (0.15 g, 0.8 mmol, 21%) (Found: C, 26.6; H, 0.8%; *M*, 182), the i.r. and n.m.r. spectra of which were identical with those of a pure sample prepared by chlorination of the *trans*-isomer and dechlorination of the resultant 1 : 1 adduct, and (iii) 3H-*heptafluorobut*-1-*ene* (0.15 g, 0.8 mmol, 21%) (Found: C, 26.6: H, 0.6%; *M*, 182); $\lambda_{max.}$ 5.58s ($>C{:}C<$ str.); ^1H n.m.r. band for



$CF_3{\cdot}CHF_A(F_B)C{=}C(F_C)F_D$

at τ 4.75 (ddqdd, CHF, J_{HF_A} 43.8, J_{HF_B} 22.8; J_{HCF_3} 5.9, J_{HF_C} 2.9, J_{HF_D} 1.7 Hz) and ^{19}F bands at 3.1 (3F, ddddd, CF_3, $J_{CF_3F_A}$ 14.1, $J_{CF_3F_B}$ 7.8; $J_{CF_3F_C}$ 2.1, $J_{CF_3F_D}$ 0.5 Hz), 17.8 (1F, ddddq, F_D, $J_{F_DF_C}$ 59.9, $J_{F_DF_B}$ 36.6, $J_{F_DF_A}$ 5.0 Hz), 116.9 (1F, ddddq, F_B, $J_{F_BF_C}$ 118.4, $J_{F_BF_A}$ 19.1 Hz), and 127.7 p.p.m. (1F, ddqdd, F_A).

Pyrolysis of a mixture of the silane and isobutene (1 : 3 molar ratio) under identical conditions gave a mixture (99%) of unchanged isobutene, fluoro-olefins, and chlorofluorosilanes, which, after hydrolysis and removal of unchanged isobutene by reaction with moist phosphoric oxide, yielded (as estimated by g.l.c.) *trans*-2*H*-heptafluorobut-2-ene (71%), *cis*-2*H*-heptafluorobut-2-ene (7%), and 3*H*-heptafluorobut-1-ene (14%).

Pyrolysis of Trifluoro(2H-1-*trifluoromethylpentafluoropropyl*)*silane*.—The silane (0.52 g, 1.81 mmol), sealed in a Dreadnought tube (*ca.* 150 ml) *in vacuo* and heated at 165 °C (6 h) gave, after hydrolysis of the silicon tetrafluoride formed, *trans*-2*H*-heptafluorobut-2-ene (0.27 g, 1.47 mmol, 81%) and *cis*-2*H*-heptafluorobut-2-ene (0.04 g, 0.20 mmol, 11%).

Pyrolysis of a mixture of the silane and isobutene (1 : 3 molar ratio) under identical conditions gave, after removal of silicon tetrafluoride and unchanged isobutene, a mixture of *trans*-2*H*-heptafluorobut-2-ene (82%) and the *cis*-isomer (12%). Similarly pyrolysis of a mixture of the silane and *cis*-but-2-ene (1 : 3 molar ratio) under identical conditions, gave silicon tetrafluoride (100%), unchanged *cis*-but-2-ene (98% recovered), and a mixture of the *trans*- (85%) and *cis*- (12%) isomers of 2*H*-heptafluorobut-2-ene.

Reaction of Hexafluorocyclobutene with Trichlorosilane.—A mixture of the olefin (30.0 g, 0.185 mol) and trichlorosilane (79.9 g, 0.590 mol), sealed in a silica tube (*ca.* 360 ml) and irradiated (150 h), gave (i) hydrogen (*ca.* 0.5 mmol), (ii) unchanged olefin (15.4 g, 95.0 mmol, 51% recovered), (iii) unchanged trichlorosilane (64.1 g, 0.473 mol, 80%), (iv) an intermediate fraction (6.0 g), b.p. 35—116 °C, (v) trans-*trichloro*(2H-*hexafluorocyclobutyl*)*silane* (21.5 g, 72.2 mmol, 80%) (Found: C, 16.1; H, 0.5; Cl, 35.5%; *M*, 295. $C_4HCl_3F_6Si$ requires C, 16.1; H, 0.3; Cl, 35.7%; *M*, 298), b.p. 116—119 °C, and (vi) a residue (*ca.* 3 g), b.p. >119 °C.

Reactions of Trichloro(2H-*hexafluorocyclobutyl*)*silane*.—(a) *Fluorination*. The silane (1.77 g, 5.95 mmol), passed in the vapour phase *in vacuo* over an excess of powdered antimony trifluoride containing a small amount of phosphorus pentachloride, gave trans-*trifluoro*(2H-*hexafluorocyclobutyl*)*silane* (1.35 g, 5.35 mmol, 90%) (Found: C, 19.2; H, 0.5%; *M*, 246. C_4HF_9Si requires C, 19.3; H, 0.4%; *M*, 248), b.p. 38 °C.

(b) *Pyrolysis*. The silane (1.42 g, 4.8 mmol), heated at 265 °C (16 h), gave, after hydrolysis, a mixture (0.67 g, 4.66 mmol, 99%) (Found: C, 33.5; H, 0.7%; *M*, 144. Calc. for C_4HF_5: C, 33.3; H, 0.7%; *M*, 144), which was shown by g.l.c. (4m Kel-F 10 oil at 20 °C) and n.m.r. spectroscopy to consist of 3*H*-pentafluorocyclobutene (0.05 g, 0.34 mmol, 7%) and 1*H*-pentafluorocyclobutene (0.62 g, 4.32 mmol, 92%); the i.r. spectrum of the mixture contained the major absorption bands reported for the isomers.

Pyrolysis of a mixture of the silane and isobutene (1 : 3 molar ratio) under identical conditions gave a mixture (99%) which, after hydrolysis and polymerisation of unchanged isobutene, afforded 3*H*-pentafluorocyclobutene (6%) and 1*H*-pentafluorocyclobutene (90%).

Pyrolysis of Trifluoro(2*H*-*hexafluorocyclobutyl*)*silane*.—The silane (0.57 g, 2.30 mmol), sealed *in vacuo* in a Dreadnought tube (*ca.* 160 ml) and heated at 200 °C (14 h), gave a mixture (4.35 mmol, 95%) of silicon tetrafluoride and pentafluorocyclobutenes which, after hydrolysis, afforded 3*H*-pentafluorocyclobutene (0.03 g, 0.20 mmol, 9%) and 1*H*-pentafluorocyclobutene (0.19 g, 1.98 mmol, 86%). A second pyrolysis at 165 °C (14 h) gave a quantitative recovery of unchanged reactant.

Pyrolysis of a mixture of the silane and *cis*-but-2-ene (1 : 3 molar ratio) *in vacuo* at 200 °C (14 h) gave, after hydrolysis, unchanged *cis*-but-2-ene (98% recovered) and a mixture of 3*H*- (10%) and 1*H*-pentafluorocyclobutene (87%).

Pyrolysis of Trichloro(1-*trifluoromethyl*-1,2,2-*trifluoroethyl*)-*silane*.—The silane (0.292 g, 1.03 mmol), sealed *in vacuo* in a Pyrex tube (*ca.* 100 ml) and heated at 250 °C (24 h), gave a mixture of olefin and chlorofluorosilanes which, after hydrolysis, afforded 1*H*-pentafluoropropene (0.110 g, 0.84 mmol, 82%) (Found: *M*, 132. Calc. for C_3HF_5: *M*, 132), the g.l.c. retention time and i.r. spectrum of which were identical with those of an authentic sample.

Pyrolysis of Trichloro(1,1,2,3,3,3-*hexafluoropropyl*)*silane*.—The silane (0.438 g, 1.54 mmol), sealed *in vacuo* in a Pyrex tube (*ca*. 100 ml) and heated at 250—270 °C (24 h), gave a mixture of olefins and chlorofluorosilanes which, after hydrolysis, afforded a mixture (1.37 mmol, 89%) of olefins which were separated by g.l.c. (3.5 m D.N.P. at 50 °C) and identified as (i) 1*H*-pentafluoropropene (0.140 g, 1.06 mmol, 68%), (ii) 1-chloro-2,3,3,3-tetrafluoropropene (0.046 g, 0.27 mmol, 18%) by comparison of its g.l.c. retention time and i.r. spectrum with those of a synthesised sample, and (iii) a third olefin (0.04 mmol, 3%) probably 1,1-dichloro-3,3,3-trifluoropropene.

Pyrolysis of a Mixture of Trifluoroethylene–Trichlorosilane Adducts.—A mixture (0.326 g, 1.5 mmol) of trichloro-(1,2,2-trifluoroethyl)silane and the corresponding 1,1,2-trifluoroethyl isomer (ratio 95 : 5), sealed *in vacuo* in a silica tube (*ca*. 100 ml) and heated at 250—255 °C (18 h), gave a mixture (1.49 mmol, 50%) of olefin and chlorofluorosilane which, after hydrolysis, afforded 1,2-difluoroethylene (0.43 g, 0.75 mmol, 50%); a black non-volatile tar remained in the pyrolysis tube.

A second pyrolysis carried out at 225 °C (16 h) gave 1,2-difluoroethylene (47%).

Pyrolysis of a Mixture of Trifluoroethylene–Dichloro(*methyl*)*silane Adducts*.—A mixture (0.301 g, 1.53 mmol) of dichloro(methyl)(1,2,2-trifluoroethyl)silane and the corresponding1,1,2-trifluoroethyl isomer (ratio 85 : 15), sealed *in vacuo* in a silica tube (*ca*. 100 ml) and heated at 225 °C (16 h), gave a mixture (3.02 mmol, 99%) of olefins and chlorofluorosilanes which, after hydrolysis, afforded 1,2-difluoroethylene (0.09 g, 1.42 mmol, 94%) and 1,1-difluoroethylene (0.006 g, 0.09 mmol, 5%) present in the ratio 95 : 5 (g.l.c.).

We thank I.C.I. Limited (Nobel Division) and Midland Silicones Limited for gifts of chlorosilanes and the Science Research Council for Research Studentships (to J. M., C. J. A., D. C., and G. W. C.).

[5/592 *Received, 2nd April*, 1975]