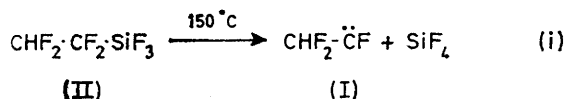


Carbene Chemistry. Part X.¹ Insertion Reactions of 1,2,2-Trifluoroethylidene into C-H bonds of Alkanes containing the t-Butyl Group and Some Addition and Insertion Reactions of 2-Chloro-1,2,2-trifluoroethylidene

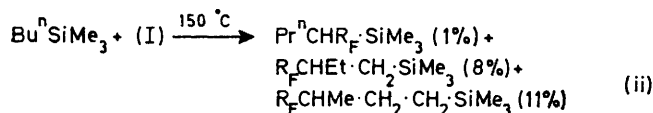
By Robert N. Haszeldine,* Colin R. Pool, Anthony E. Tipping, and Richard O'B. Watts, Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD

1,2,2-Trifluoroethylidene, generated by pyrolysis of trifluoro-(1,1,2,2-tetrafluoroethyl)silane, inserts exclusively into the tertiary C-H bond of the alkane $\text{Me}_2\text{CH}\cdot\text{CMe}_3$, into both the primary and secondary C-H bonds (ratio 1 : 2) of the ethyl group in the alkane EtCMe_3 , and into both the tertiary and secondary C-H bonds (ratio *ca.* 8 : 1) of the isobutyl group in the alkane $\text{Me}_2\text{CH}\cdot\text{CH}_2\cdot\text{CMe}_3$. (2-Chloro-1,1,2,2-tetrafluoroethyl)trifluorosilane is best prepared by fluorination of trichloro-(1,1,2,2-tetrafluoroethyl)silane followed by vapour-phase photochemical chlorination. On pyrolysis the silane affords 2-chloro-1,2,2-trifluoroethylidene, which inserts into the Si-H bond of trimethylsilane and reacts with allene to afford 1-chlorodifluoromethyl-1-fluoro-2-methylenecyclopropane. Stereospecific addition of the carbene to the double bond of *trans*-but-2-ene takes place to give *r*-1-chlorodifluoromethyl-1-fluoro-*c*-2,*t*-3-dimethylcyclopropane, but reaction with *cis*-but-2-ene is not stereospecific and affords a mixture of the *c*-2,*c*-3- and *t*-2,*t*-3-dimethylcyclopropanes and the *c*-2, *t*-3-dimethylcyclopropane in the ratio 63 : 18.

THE reactions of the carbene (I), formed by pyrolysis of trifluoro-(1,1,2,2-tetrafluoroethyl)silane (II), with various alkanes,² alkyltrimethylsilanes,³ and silanes containing Si-H and/or silicon-halogen bonds^{4,5} have been investigated previously in this department. It was found that



the reactivity of the C-H bonds towards carbene insertion is in the order tertiary > secondary > primary and that with the alkyltrimethylsilanes C-H bonds α to the silicon atom were somewhat deactivated towards attack, *e.g.* equation (ii), where $\text{R}_F = \text{CHF}_2\cdot\text{CHF}$.



An investigation of the reactions of the carbene (I) with the alkanes EtCMe_3 , $\text{Me}_2\text{CH}\cdot\text{CMe}_3$, and $\text{Me}_2\text{CH}\cdot\text{CH}_2\cdot\text{CMe}_3$ was undertaken in order that a comparison of the reactivities of the various C-H bonds towards insertion could be made with those of the same bonds in the trimethylsilyl analogues EtSiMe_3 , $\text{Me}_2\text{CH}\cdot\text{SiMe}_3$, and $\text{Me}_2\text{CH}\cdot\text{CH}_2\cdot\text{SiMe}_3$.

The reactions of the alkanes were investigated by means of the gas-phase decomposition of the carbene precursor (II) at 150 °C (6 h) in the presence of an excess of the alkane (3 : 1 molar ratio) at a maximum total pressure of *ca.* 0.8 atm.

In each reaction a quantitative yield of silicon tetrafluoride was obtained, indicating complete breakdown of the precursor (II), and the expected carbene rearrangement products trifluoroethylene and the cyclopropanes *cis*- and *trans*- $\text{CHF}_2\text{CF}\cdot\text{CHF}\cdot\text{CF}_2$ were observed as well

¹ Part IX, J. M. Birchall, R. N. Haszeldine, and P. Tissington, *J.C.S. Perkin I*, 1975, 1638.

² R. N. Haszeldine and J. G. Speight, *Chem. Comm.*, 1967, 995.

as C-H insertion products. The ratios of isomeric insertion products were determined by g.l.c. and by repeated integration of certain of the n.m.r. signals. The results are shown in Table 1.

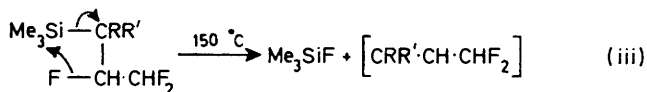
TABLE 1
Reaction of alkanes with the carbene (I)

R in RCMe_3	Insertion products *	Yield (%)	Statistical yield (%) †
$\text{CH}_3\cdot\text{CH}_2$	$\text{R}_F\text{CHMe}\cdot\text{CMe}_3$	8	4
	$\text{R}_F\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}_3$	4	1.3
$(\text{CH}_3)_2\text{CH}$	$\text{R}_F\text{CMe}_2\cdot\text{CMe}_3$	21	21
$(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2$	$\text{R}_F\text{CMe}_2\cdot\text{CH}_2\cdot\text{CMe}_3$	25	25
	$\text{R}_F\text{CH}(\text{CHMe}_2)\cdot\text{CMe}_3$	3	1.5

* $\text{R}_F = \text{CHF}_2\cdot\text{CHF}$. † % Yield divided by number of C-H bonds of type involved.

The C-H insertion products were identified on the basis of an n.m.r. investigation of the adduct fractions. The ¹H n.m.r. spectra of the insertion products showed signals at τ *ca.* 4.4 (1 H, tdd, CHF_2) and *ca.* 5.6 (1 H, dm, CHF); signals due to the Me_3C group (τ *ca.* 9.2) and other alkyl groups (τ 8.2–9.2) were also present. The ¹⁹F n.m.r. spectra showed signals at *ca.* 48 (2F, ABddd, CHF_2) and *ca.* 125 p.p.m. (1F, dm, CHF) relative to external trifluoroacetic acid.

In these reactions, products formed by the decomposition of the adducts under the reaction conditions were not observed, in contrast to the reactions of the carbene (I) with alkyltrimethylsilanes³ where the products of α -C-H carbene insertion decomposed by a β -elimination



process to yield fluorotrimethylsilane, *i.e.* equation (iii). Adducts formed by insertion of the carbene (I) into the

³ R. N. Haszeldine, A. E. Tipping, and R. O'B. Watts, *J.C.S. Perkin I*, 1975, 996.

⁴ R. N. Haszeldine, A. E. Tipping, and R. O'B. Watts, *Chem. Comm.*, 1969, 1364.

⁵ R. N. Haszeldine, A. E. Tipping, and R. O'B. Watts, *J.C.S. Perkin I*, 1974, 2391.

C-H bonds of the CMe₃ group were not detected; similarly carbene insertion into the C-H bonds of the Me₃Si group in the silane analogues was not observed.³

The total yields of the insertion products obtained are compared in Table 2 with those of the insertion products

TABLE 2

Reaction of the carbene (I) with alkanes Me₃CR and silanes Me₃SiR

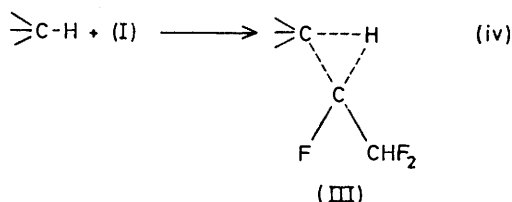
R	Alkane insertion products (%)	Silane insertion products (%)
CH ₃ ·CH ₂	α-Insertion, 8 β-Insertion, 4	α-Insertion, 7 β-Insertion, 6
Me ₂ CH	α-Insertion, 21 β-Insertion, not detected	α-Insertion, 17 β-Insertion, 1
Me ₂ CH·CH ₂	α-Insertion, 3 β-Insertion, 25	α-Insertion, not detected β-Insertion, 24

obtained from the trimethylsilyl analogues. The total yields obtained indicate that the alkanes are slightly more susceptible to C-H insertion than their silane analogues.

The statistical yields of the alkane C-H insertion products (Table 1) indicate that insertion is preferred in the order tertiary > secondary > primary, as found previously for the insertions of the carbene (I) into the C-H bonds of alkyltrimethylsilanes³ and other alkanes.²

A comparison of the yields of products formed by insertion of the carbene (I) into the C-H bonds in the alkanes and the corresponding silanes indicates that α-insertion is more preferred in the alkanes than in the silanes, possibly because of steric hindrance by SiMe₃ to approach of the carbene.

The carbene insertions into the C-H bonds of the alkanes are considered to involve singlet carbene and occur *via* a transition state (III) of the type postulated previously⁶ for insertion of singlet methylene into C-H bonds, *i.e.* equation (iv).

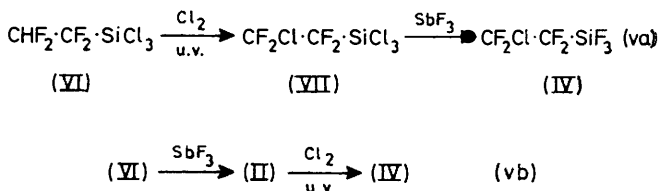


Certain reactions of the carbene (I) have shown that it is generated in the singlet state, *i.e.* stereospecific addition to *cis*- or *trans*-but-2-ene² and insertion into the tertiary C-H bond of the alcohol, 1-CH₃·[CH₂]₅·CHMe·OH, with complete retention of configuration.⁷

In the present work the preparation of (2-chloro-1,1,2,2-tetrafluoroethyl)trifluorosilane (IV) and its thermal decomposition in the presence of carbene traps have been carried out in order to compare such reactions of 2-

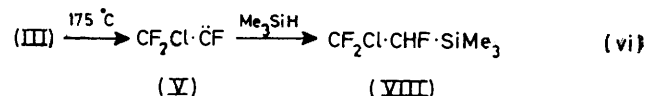
chloro-1,2,2-trifluoroethylidene (V) with those reported previously for the carbene (I).

Two routes to the carbene precursor (IV) from trichloro-(1,1,2,2-tetrafluoroethyl)silane (VI)⁸ were

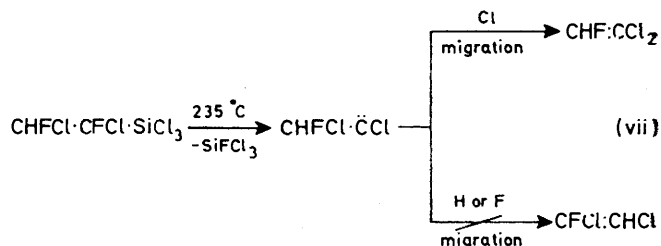


investigated [equations (va) and (vb)]. Both methods were suitable but method (vb) gave the higher overall conversion. The two fluorination steps afforded comparable yields of products, but the chlorination of the silane (II) [to (IV)] went in 90% conversion, while that of (VII) [to (IV)] went in 72% conversion only. The probable reason for this difference is that chlorination of (I) (b.p. *ca.* 6 °C) is a homogeneous gas-phase reaction, whereas that of (VI) (b.p. 85 °C) occurs with a high proportion of the silane in the liquid phase.

Pyrolysis of the silane (IV) at 170 °C afforded silicon tetrafluoride (98%) and chlorotrifluoroethylene (98%). That the reaction involved the intermediacy of the carbene (V) was demonstrated by heating the silane (IV) at 175 °C in the presence of an excess of trimethylsilane. The products were silicon tetrafluoride (99%), chlorotrifluoroethylene (6.5%), and (2-chloro-1,1,2-trifluoroethyl)trimethylsilane (VIII) (92%). The silane (II)



undergoes a similar reaction with trimethylsilane to afford silicon tetrafluoride (100%), the insertion product CHF₂·CHF·SiMe₃ (99%), and trifluoroethylene (1%). Thus olefin formation is more preferred in the reaction with the silane (IV) than that with the silane (II). This is as expected, since it has been observed⁹ that in carbenes where either a hydrogen or a chlorine atom can migrate to form an olefin it is the chlorine atom which migrates, *e.g.*⁹ equation (vii)



The structure of the product was established as (VIII) on the basis of its n.m.r. spectra; the ¹⁹F spectrum

⁶ P. S. Skell and R. C. Woodworth, *J. Amer. Chem. Soc.*, 1956, **78**, 4496; W. von E. Doering and L. H. Knox, *ibid.*, 1961, **83**, 1989.

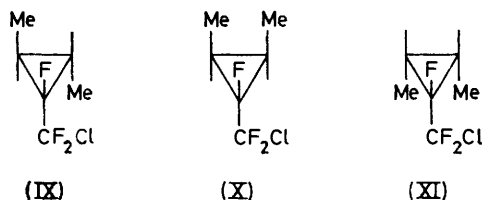
⁷ J. M. Birchall, T. K. Dempsey, and R. N. Haszeldine, unpublished results.

⁸ R. N. Haszeldine and R. J. Marklow, *J. Chem. Soc.*, 1956, 962.

⁹ W. I. Bevan and R. N. Haszeldine, unpublished results; W. I. Bevan, R. N. Haszeldine, J. Middleton, and A. E. Tipping, *J.C.S. Dalton*, 1975, 620.

showed peaks at -20.6 (2F, AB, CF_2Cl) and 144 p.p.m. (1F, ddd, CHF) (relative to $\text{CF}_3\cdot\text{CO}_2\text{H}$ reference) and the major splitting observed (45 Hz) in the latter peak was of the magnitude expected for a geminal H,F-coupling. Thus the adduct was formed by a carbene insertion reaction; other adducts which could have been formed by addition of trimethylsilane across the olefin $\text{CF}_2\cdot\text{CFCl}$ or by radical abstraction of hydrogen by excited chlorotrifluoroethylene followed by rapid radical combination were not detected.

Pyrolysis of the silane (IV) in the presence of an excess of *trans*-but-2-ene gave silicon tetrafluoride (99%), chlorotrifluoroethylene (11%), and *r*-1-chlorodifluoromethyl-1-fluoro-*c*-2,*t*-3-dimethylcyclopropane (IX)



(86%), formed by stereospecific addition of the carbene (V) to the olefin. However, a corresponding reaction with *cis*-but-2-ene did not result in stereospecific addition; the products were silicon tetrafluoride (99%), chlorotrifluoroethylene (18%), cyclopropane (IX) (19%), *r*-1-chlorodifluoromethyl-1-fluoro-*t*-2,*t*-3-dimethylcyclopropane (X) (48%), and *r*-1-chlorodifluoromethyl-1-fluoro-*c*-2,*c*-3-dimethylcyclopropane (XI) (15%). The assignments were based on a comparison of the ^{19}F spectra with those of the corresponding adducts formed by reaction of 1,2,2-trifluoroethylidene (I) with *cis*- and *trans*-but-2-ene.¹⁰ Compounds (X) and (XI) were differentiated on the basis that the fluorines in the CF_2Cl group were expected to absorb at higher field in the *c*-2,*c*-3- than in the *t*-2,*t*-3-isomer, as found for the corresponding CHF_2 compounds.

The apparent non-stereospecific addition to *cis*-but-2-ene contrasts with the reaction of the carbene (I) with this olefin. It is possible that the reason for the non-stereospecific addition is steric in origin, but this is unlikely because the *trans*-but-2-ene reaction was stereospecific. Thermal isomerisation of the olefin or of the cyclopropanes (X) and (XI) under the reaction conditions was shown not to occur. However, the presence of a small amount of *trans*-but-2-ene in the recovered olefin suggests that olefin isomerisation has taken place to some degree. This could occur by the formation of radicals in the system (possibly chlorine atoms) in low concentration which cause some of the *cis*-olefin to isomerise to the more stable *trans*-olefin. Carbene addition then occurs stereospecifically with the

olefin mixture. In support of this, reaction of the silane (IV) with tetrafluoroethylene was observed not to give any of the expected cyclopropane, $\overline{\text{CF}_2\cdot\text{CF}_2}\cdot\text{CF}\cdot\text{CF}_2\text{Cl}$ [contrast reaction of the carbene (I)], and the products were a solid assumed to be polytetrafluoroethylene (95%), silicon tetrafluoride (99%), and chlorotrifluoroethylene (99%).

Reaction of the silane (IV) with allene at 170°C gave silicon tetrafluoride (99.5%) and 1-chlorodifluoromethyl-1-fluoro-2-methylenecyclopropane, $\text{CH}_2\cdot\overline{\text{C}}\cdot\text{CH}_2\cdot\text{CF}\cdot\text{CF}_2\text{Cl}$ (98%); a 2 : 1 adduct (a spiro-pentane) was not observed.

The evidence thus suggests that the carbene (V), as generated, is in the singlet state, as previously found for the corresponding carbene (I).

EXPERIMENTAL

Reactants and products were manipulated, where possible, in a conventional vacuum system in order to avoid contamination with air or moisture. Reactions involving the thermal decomposition of trifluoro-(1,1,2,2-tetrafluoroethyl)silane^{11,12} were carried out *in vacuo* in Pyrex bulbs (capacities ca. 5 l) fitted with a side arm and at maximum pressures of ca. 0.8 atm. Pure compounds were isolated by repeated fractional condensation *in vacuo* or by preparative scale g.l.c. [Pye 105 or Perkin-Elmer 452 instrument with columns (4, 8, or 12 m) packed with Silicone SE30 oil (20%) or MS550 oil (20%) on Celite]. The identities of products were established by molecular weight determination (Regnault's method), elemental analysis, i.r. spectroscopy (Perkin-Elmer spectrophotometer model 452 with sodium chloride optics), and n.m.r. spectroscopy (Perkin-Elmer R10 instrument operating at 60.0 MHz for ^1H and 56.46 MHz for ^{19}F or a Varian HA-100 spectrometer operating at 100 MHz for ^1H and 94.1 MHz for ^{19}F and with internal tetramethylsilane or external trifluoroacetic acid as the respective references). N.m.r. data (^1H and ^{19}F) for compounds indicated with an asterisk are available as Supplementary Publication No. SUP 21629 (11 pp., 1 microfiche).†

The alkanes were commercial samples which were carefully purified before use. Trichloro-(1,1,2,2-tetrafluoroethyl)silane was prepared by the photochemical reaction of trichlorosilane with tetrafluoroethylene⁸ and was converted into the trifluorosilyl analogue (93%) by reaction with antimony trifluoride *in vacuo*.^{11,12}

Reactions of Trifluoro-(1,1,2,2-tetrafluoroethyl)silane with Alkanes.—(a) *2,2-Dimethylbutane.* A mixture of the silane (5.58 g, 30.0 mmol) and the alkane (7.74 g, 90.0 mmol), pyrolysed as described previously, gave (i) a mixture (4.25 g, 43.8 mmol) of silicon tetrafluoride and trifluoroethylene (i.r.), which on hydrolysis with water (10 ml, 30 min) *in vacuo* gave trifluoroethylene (1.13 g, 13.8 mmol, 46%), thus allowing the amount of silicon tetrafluoride (3.12 g, 30.0 mmol, 100%) originally present to be estimated; (ii) a mixture (8.42 g, 92.2 mmol) (Found: *M*, 91) of unchanged alkane (7.40 g, 86.0 mmol, 95% recovered) and *cis*- and *trans*-1-difluoromethyl-1,2,2,3-tetrafluorocyclopropane (1.02 g, 6.2 mmol, 42%) which was characterised by i.r. spectroscopy and g.l.c. (4 m SE30 column at 35°C); and (iii) a higher-boiling mixture (0.62 g, 3.7 mmol, 12%)

¹² W. I. Bevan, R. N. Haszeldine, and J. C. Young, *Chem. and Ind.*, 1961, 789; G. Fishwick, R. N. Haszeldine, C. Parkinson, P. J. Robinson, and R. F. Simmons, *Chem. Comm.*, 1965, 382.

† For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1975, Index issue.

¹⁰ J. Lee, C. Parkinson, P. J. Robinson, and J. G. Speight, *J. Chem. Soc. (B)*, 1967, 1125.

¹¹ R. N. Haszeldine, P. J. Robinson, and R. F. Simmons, *J. Chem. Soc.*, 1964, 1890.

(Found: C, 56.9; H, 9.3. Calc. for $C_8H_{15}F_3$: C, 57.2; H, 9.0%) which was shown by g.l.c. (12 m SE30 column at 90 °C) and n.m.r. spectroscopy to consist of 1,1,2-trifluoro-3,4,4-trimethylpentane * (0.42 g, 2.4 mmol, 8%) and 1,1,2-trifluoro-5,5-dimethylhexane * (0.2 g, 1.2 mmol, 4%).

(b) 2,2,4-*Trimethylpentane*. A mixture of the silane (5.58 g, 30.0 mmol) and the alkane (10.30 g, 90.0 mmol), pyrolysed as described previously, gave (i) a mixture of silicon tetrafluoride (3.12 g, 30.0 mmol, 100%) and trifluoroethylene (0.96 g, 11.7 mmol, 39%) estimated as described in experiment (a); (ii) a mixture of *cis*- and *trans*-1-difluoromethyl-1,2,2,3-tetrafluorocyclopropane (0.81 g, 4.9 mmol, 33%) (Found: *M*, 164. Calc. for $C_4H_2F_6$: *M*, 164); (iii) unchanged alkane (9.30 g, 81.6 mmol, 91% recovered); and (iv) a higher-boiling fraction (1.65 g, 8.4 mmol, 28%) (Found: C, 61.2; H, 9.6. Calc. for $C_{10}H_{19}F_3$: C, 61.4; H, 9.7%), which was shown by g.l.c. (12 m SE30 column at 165 °C) and n.m.r. spectroscopy to consist of 1,1,2-trifluoro-3,3,5,5-tetramethylhexane * (1.47 g, 7.5 mmol, 25%) and 1,1,2-trifluoro-3-isopropyl-4,4-dimethylpentane * (0.18 g, 0.9 mmol, 3%); the two isomers were present in the ratio 8.3 : 1.

(c) 2,2,3-*Trimethylbutane*. A mixture of the silane (5.58 g, 30.0 mmol) and the alkane (9.0 g, 90.0 mmol), pyrolysed as described previously, gave (i) a mixture of silicon tetrafluoride (3.12 g, 30.0 mmol, 100%) and trifluoroethylene (1.01 g, 12.3 mmol, 41%); (ii) a mixture of *cis*- and *trans*-1-difluoromethyl-1,2,2,3-tetrafluorocyclopropane (0.93 g, 5.7 mmol, 38%); (iii) unchanged alkane (8.50 g, 85.0 mmol, 94% recovered); and (iv) 1,1,2-trifluoro-3,3,4,4-tetramethylpentane * (1.15 g, 6.3 mmol, 21%) (Found: C, 59.1; H, 9.6. $C_9H_{17}F_3$ requires C, 59.4; H, 9.4%), b.p. 156 °C.

Chlorination of Trichloro-(1,1,2,2-tetrafluoroethyl)silane.—A mixture of chlorine (8.3 g, 0.117 mol) and the silane (27.0 g, 0.115 mol), sealed in two silica ampoules (ca. 500 ml capacity) and irradiated at 15 cm from a Hanovia S500 medium-pressure u.v. lamp (24 h), gave a low-boiling mixture of hydrogen chloride and the excess of chlorine and a higher-boiling mixture which was distilled through a vacuum-jacketed column (30 cm) to afford unchanged trichloro-(1,1,2,2-tetrafluoroethyl)silane (7.2 g, 30.6 mmol, 27% recovered), b.p. 85–86 °C, and (2-chloro-1,1,2,2-tetrafluoroethyl)trichlorosilane (22.6 g, 83.8 mmol, 99%) (Found: C, 9.2%. Calc. for $C_2Cl_4F_4Si$: C, 9.0%), b.p. 103–104 °C, identified by i.r. and n.m.r. spectroscopy.

Fluorination of (2-Chloro-1,1,2,2-tetrafluoroethyl)trichlorosilane.—The silane (5.99 g, 22.2 mmol), passed repeatedly *in vacuo* through a column (20 cm) containing antimony trifluoride and antimony pentachloride (5% by weight), gave unchanged trichlorosilane (3.2 g, 11.4 mmol, 58% recovered) and (2-chloro-1,1,2,2-tetrafluoroethyl)trifluorosilane (2.21 g, 10.0 mmol, 92%) (Found: C, 10.7%; *M*, 222. C_2ClF_2Si requires C, 10.9%; *M*, 221), b.p. 37 °C; ^{19}F n.m.r. bands at -7.5 (2 F, t, *J* 8.7 Hz, CF_2Cl), 48.0 (2 F, t, CF_2), and 68.8 p.p.m. (3 F, s, SiF_3).

Chlorination of Trifluoro-(1,1,2,2-tetrafluoroethyl)silane.—A mixture of chlorine (2.4 g, 33.0 mmol) and the silane (6.2 g, 33.3 mmol), sealed *in vacuo* in a silica ampoule (ca. 250 ml) and irradiated (24 h), gave (i) a mixture of hydrogen chloride and the excess of chlorine, (ii) unchanged silane (0.59 g, 3.2 mmol, 9% recovered), and (iii) (2-chloro-1,1,2,2-tetrafluoroethyl)trifluorosilane (6.62 g, 30.0 mmol, 99%).

Pyrolyses of (2-Chloro-1,1,2,2-tetrafluoroethyl)trifluoro-

silane.—(a) *Alone*. The silane (0.40 g, 1.81 mmol), sealed in a Pyrex ampoule (ca. 100 ml) and heated at 175 °C (17 h) gave a mixture (0.39 g, 3.44 mmol, 98%) of silicon tetrafluoride and chlorotrifluoroethylene (i.r.) in a 1 : 1 molar ratio as determined by a molecular weight determination (Found: *M*, 110. Calc. for 1 : 1 mixture of SiF_4 and C_2ClF_3 : *M*, 110).

(b) *With trimethylsilane*. A mixture of trimethylsilane (1.85 g, 25.0 mmol) and (2-chloro-1,1,2,2-tetrafluoroethyl)trifluorosilane (1.20 g, 5.43 mmol), sealed in a Pyrex ampoule (ca. 250 ml) and heated at 175 °C (24 h), gave (i) a mixture (0.61 g) of silicon tetrafluoride and chlorotrifluoroethylene (i.r.), which after hydrolysis with aqueous sodium hydroxide (5% w/v; 10 ml) *in vacuo* gave chlorotrifluoroethylene (0.04 g, 0.35 mmol, 7%); (ii) unchanged trimethylsilane (ca. 1.5 g, ca. 80% recovered); and (iii) (2-chloro-1,2,2-trifluoroethyl)trimethylsilane * (0.96 g, 5.05 mmol, 99%) (Found: C, 31.6; H, 5.4%; *M*, 189. $C_5H_{10}ClF_3Si$ requires C, 31.5; H, 5.3%; *M*, 191), b.p. (Siwoloboff) 82 °C.

(c) *With trans-but-2-ene*. A mixture of the silane (1.20 g, 5.43 mmol) and the olefin (1.40 g, 25.0 mmol), sealed in a Pyrex ampoule (ca. 250 ml) and heated at 175 °C (24 h), gave (i) a mixture (0.63 g) of silicon tetrafluoride and chlorotrifluoroethylene (i.r.), which was hydrolysed (as before) to give chlorotrifluoroethylene (0.07 g, 0.59 mmol, 11%); (ii) unchanged olefin (ca. 1.1 g, ca. 79% recovered) which was shown to be exclusively the *trans*-isomer by i.r. spectroscopy and g.l.c.; and (iii) *r*-1-chlorodifluoromethyl-1-fluoro-*c*-2,3-dimethylcyclopropane * (0.80 g, 4.65 mmol, 86%) (Found: C, 41.8; H, 4.7%; *M*, 174. $C_8H_8ClF_3$ requires C, 41.8; H, 4.7%; *M*, 172.5), b.p. (Siwoloboff) 87 °C; g.l.c. (4 m MS550 at 85 °C) showed only one peak.

(d) *With cis-but-2-ene*. A mixture of the silane (1.20 g, 5.43 mmol) and the olefin (1.40 g, 25.0 mmol), treated as in the previous experiment, gave (i) a mixture (0.67 g, 6.4 mmol) of silicon tetrafluoride and chlorotrifluoroethylene (i.r.), which on hydrolysis (as before) afforded chlorotrifluoroethylene (0.11 g, 0.98 mmol, 18%); (ii) unchanged olefin (ca. 1.15 g, ca. 82% recovered) which was shown to be almost exclusively the *cis*-isomer (<1% *trans*-isomer) by i.r. spectroscopy and g.l.c.; (iii) a mixture of cyclopropanes (0.76 g, 4.42 mmol, 82%) (Found: C, 42.0; H, 4.9%; *M*, 175. Calc. for $C_6H_8ClF_3$: C, 41.8; H, 4.7%; *M*, 172.5), b.p. (Siwoloboff) 88 °C, which was shown by ^{19}F n.m.r. spectroscopy to contain *r*-1-chlorodifluoromethyl-1-fluoro-*c*-2,3-dimethylcyclopropane (0.18 g, 1.01 mmol, 19%), *r*-1-chlorodifluoromethyl-1-fluoro-*t*-2,3-dimethylcyclopropane (0.45 g, 2.60 mmol, 48%) with ^{19}F n.m.r. bands at -14.2 (2 F, d, *J* 11.3 Hz, CF_2Cl) and 144.0 p.p.m. (1 F, tm), and *r*-1-chlorodifluoromethyl-1-fluoro-*c*-2,3-dimethylcyclopropane (0.14 g, 0.79 mmol, 15%) with ^{19}F n.m.r. bands at -22.2 (2 F, complex, CF_2Cl), and 123.0 p.p.m. (1 F, complex).

When the experiment was repeated under the same conditions, similar results were obtained. In separate experiments, isomerisation of *cis*-but-2-ene, the *c*-2,3-dimethylcyclopropane, or a mixture of the cyclopropanes did not occur at 200 °C (24 h).

(e) *With allene*. A mixture of allene (0.80 g, 20.0 mmol) and the silane (1.2 g, 5.4 mmol), sealed *in vacuo* in a Pyrex ampoule (ca. 250 ml) and heated at 180 °C (17 h), gave (i) silicon tetrafluoride (0.51 g, 4.95 mmol, 93%) contaminated with a trace of chlorotrifluoroethylene (i.r.), (ii) unchanged allene (0.59 g, 14.8 mmol, 74% recovered), and (iii) 1-chlorodifluoromethyl-1-fluoro-2-methylenecyclopropane *

(0.78 g, 4.9 mmol, 92%) (Found: C, 38.2; H, 3.0%; M , 153. $C_3H_4ClF_3$ requires C, 38.5; H, 2.6%; M , 156.5), b.p. (Siwoloboff) 71 °C.

(f) *With tetrafluoroethylene.* A mixture of tetrafluoroethylene (2.0 g, 20.0 mmol) and the silane (1.2 g, 5.4 mmol), treated as in the previous experiment, gave (i) an equimolar

mixture (1.19 g, 10.7 mmol, 99%) (Found: M , 111. Calc. for 1:1 mixture of SiF_4 and C_2ClF_3 : M , 110) of silicon tetrafluoride and chlorotrifluoroethylene contaminated with a trace of tetrafluoroethylene (i.r.), and (ii) a white solid residue (1.95 g) assumed to be polytetrafluoroethylene.

[5/377 Received, 24th February, 1975]
