

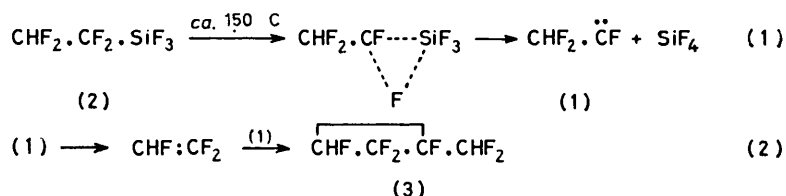
Carbene Chemistry. Part 11.¹ Insertion Reactions of 1,2,2-Trifluoroethylidene into Carbon-Hydrogen Bonds of Alkanes, Cycloalkanes, and Diethyl Ether²

By Robert N. Haszeldine,* Ronald Rowland, James G. Speight, and Anthony E. Tipping, Chemistry Department, University of Manchester Institute of Science and Technology, Manchester M60 1QD

1,2,2-Trifluoroethylidene, $\text{CHF}_2\cdot\ddot{\text{C}}\text{F}$, readily inserts into C-H bonds in alkanes and cycloalkanes in the order tertiary > secondary > primary. The ease of insertion into C-H bonds of the same type varies according to their environment and is dependent on the number of β hydrogen atoms present; an adjacent oxygen atom is also effective in this respect as shown by the high reactivity of the secondary C-H bonds in diethyl ether. In a number of reactions cyclopropanes are also formed as minor products *via* dehydrogenation of the alkane to the corresponding alkene by the carbene, followed by addition of the carbene to the alkene.

1,2,2-TRIFLUOROETHYLIDENE (1) is readily prepared by the pyrolysis of trifluoro-(1,1,2,2-tetrafluoroethyl)silane (2) in the gas phase in the absence of solvents; the reaction is a first-order process which proceeds *via* a three-centre transition state [equation (1)].³ In the absence of a substrate the carbene (1) rearranges to trifluoroethylene, some of which undergoes carbene attack to give the *cis*- and *trans*-isomers of the cyclopropane (3) [equation (2)].

available for n.m.r.) and the two diastereoisomers of structure (5f) which could not be resolved by g.l.c. and so were examined as a mixture (¹⁹F n.m.r. spectrum of mixture showed the presence of the diastereoisomers). In all cases the ¹H n.m.r. spectra showed distinct absorption regions for methyl, methylene, and methine hydrogens, and the integrations and observed couplings were consistent with the proposed structures. The mass spectrum of compound (4d) showed a weak parent ion



The carbene (1) reacts with various olefins to give the corresponding cyclopropanes,²⁻⁴ and inserts into Si-H bonds in trialkylsilanes,⁵ Si-halogen bonds in alkylchloro- and alkylbromo-silanes,⁵ Si-H and Si-Cl bonds in the silanes Cl_3SiH and MeCl_2SiH ,⁵ and C-H bonds in the alkyl groups R of the silanes RSiMe_3 ⁶ and alkanes RCMe_3 .¹ The carbene (1) as generated [equation (1)] is considered to be in the singlet state as shown by exclusive stereospecific addition to *cis*- or *trans*-but-2-ene² and insertion into the tertiary C-H bond of the optically active ether $\text{L-CH}_3\cdot[\text{CH}_2]_5\cdot\text{CHMe}\cdot\text{OMe}$ with complete retention of configuration.⁷

The present work reports the results of a reinvestigation and extension of C-H insertion reactions of the carbene (1) with alkanes, cycloalkanes, and diethyl ether previously reported in a preliminary communication.² The reactions were all carried out by the gas-phase decomposition of the carbene precursor in the presence of an excess of the substrate [10 : 1 ratio except with ethane and the cycloalkanes (15 : 1)] at 150 °C (18 h, maximum pressure *ca.* 1 atm) and the results obtained are shown in Table 1.

The structures of the insertion products (4)–(6) were established from the n.m.r. spectra of the separated compounds (g.l.c.), except for compound (4d) (mass spectral evidence only, since insufficient material

and a base peak at m/e 43 (C_3H_7^+) indicative of an $\text{Me}_2\text{-CH}$ group, *cf.* spectrum of compound (5e) which also shows a base peak at m/e 43.

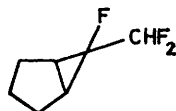
In Table 2 the ratios for primary : secondary : tertiary C-H insertion by carbene (1) are shown, allowance having been made for the different numbers of hydrogen atoms of each type.

From Table 2 it can be seen that the C-H bond reactivities are in the order tertiary > secondary > primary in agreement with the results obtained for insertion of carbene (1) into alkyltrimethylsilanes⁶ and *t*-butylalkanes.¹ It is also apparent that the relative reactivity of a primary, secondary, and tertiary C-H bond relates to the number of β hydrogens present and, presumably, thereby to its bond order and bond dissociation energy. Thus in the *n*-alkane series all the primary hydrogens are in the same environment (methyl adjacent to methylene) but there are three distinct methylene groups dependent on the number of β -hydrogens, *i.e.* CH_2 in propane (6 β hydrogens), CH_2 in the MeCH_2 groupings of butane, pentane, and hexane (5 β hydrogens), and CH_2 in the $\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2$ groupings of pentane and hexane (4 β hydrogens) with secondary to primary C-H bond reactivity ratios of *ca.* 19 : 1, 15 : 1, and 8 : 1, respectively (Table 2). Also the secondary C-H bonds in diethyl ether, which are adjacent to oxygen, are far more reactive (secondary to primary

TABLE 1
 C-H Insertion reactions of the carbene (1)

| Substrate | Insertion products | Cyclopropanes (%) | C-H Insertion reactions of the carbene (1) | | | | | |
|--|--|-------------------|--|----------------------|-------------------------|---|---------|---------|
| | | | (%) | SiF ₄ (%) | CHF:CF ₂ (%) | CHF ₂ :CH ₂ F (%) | (3) (%) | |
| C ₂ H ₄ | EtCHF·CHF ₂ (4a) | 16 | $\overline{\text{CH}_2\text{-CH}_2\text{-CF}\cdot\text{CHF}_2}$ (7) | 3 | 98 | 65 | Present | 12 |
| C ₃ H ₈ | Pr ⁿ CHF·CHF ₂ (4b) | 5 | $\overline{\text{CH}_2\text{-CHMe}\cdot\text{CF}\cdot\text{CHF}_2}$ †, a | 6 | 98 | 36 | 4 | 16 †, a |
| | Pr ⁱ CHF·CHF ₂ (5a) | 32 | | | | | | |
| n-C ₄ H ₁₀ | Bu ⁿ CHF·CHF ₂ (4c) | 4 | $\overline{\text{CHMe}\cdot\text{CHMe}\cdot\text{CF}\cdot\text{CHF}_2}$ †, b | 4 | 99 | 49 | Present | 3 |
| | EtCHMe·CHF·CHF ₂ * (5b) | 37 | | | | | | |
| Me ₃ CH | Bu ⁱ CHF·CHF ₂ (6a) | 59 | $\overline{\text{CH}_2\cdot\text{CMe}_2\cdot\text{CF}\cdot\text{CHF}_2}$ | <1 | 96 | 32 | <1 | 6 †, b |
| | Pr ⁱ CH ₂ ·CHF·CHF ₂ (4d) | 1.4 | | | | | | |
| n-C ₅ H ₁₂ | Me[CH ₂] ₄ ·CHF·CHF ₂ (4e) | 2.5 | $\overline{\text{CHMe}\cdot\text{CHEt}\cdot\text{CF}\cdot\text{CHF}_2}$ †, c | 1 | 96 | 53 | 1 | 5 †, a |
| | Et ₃ CH·CHF·CHF ₂ (5c) | 8 | | | | | | |
| | Pr ⁿ CHMe·CHF·CHF ₂ * (5d) | 26 | | | | | | |
| Me ₂ CHEt § | Me ₂ CEt·CHF·CHF ₂ (6b) | 32 | | | 99 | 52 | Trace | 7 |
| | Pr ⁱ CHMe·CHF·CHF ₂ * (5e) | 7 | | | | | | |
| n-C ₆ H ₁₄ | Me[CH ₂] ₅ ·CHF·CHF ₂ (4f) | 3 | | | 99 | 40 | Trace | 12 |
| | Pr ⁿ CHEt·CHF·CHF ₂ * (5f) | 15 | | | | | | |
| | Bu ⁿ CHMe·CHF·CHF ₂ * (5g) | 27 | | | | | | |
| Pr ⁱ ₂ CH ₂ § | Pr ⁱ ₂ CH·CHF·CHF ₂ (5h) | 3 | | | 99 | 47 | Trace | 17 |
| | Pr ⁱ CH ₂ ·CMe ₂ ·CHF·CHF ₂ (6c) | 31 | | | | | | |
| $\overline{\text{CH}_2\cdot[\text{CH}_2]_3\cdot\text{CH}_2}$ | $\overline{\text{CH}_2\cdot[\text{CH}_2]_3\cdot\text{CH}\cdot\text{CHF}\cdot\text{CHF}_2}$ (5j) | 55 | (12) | 0.5 | 99 | 30 | Trace | 12 |
| $\overline{\text{CH}_2\cdot[\text{CH}_2]_4\cdot\text{CH}_2}$ | $\overline{\text{CH}_2\cdot[\text{CH}_2]_4\cdot\text{CH}\cdot\text{CHF}\cdot\text{CHF}_2}$ (5k) | 44 | | | 99 | 41 | Trace | 12 †, b |
| Et ₂ O | EtO·CHMe·CHF·CHF ₂ * (5l) | 64 | | | 97 | 22 | | 9 |
| | Et·O·CH ₂ ·CH ₂ ·CHF·CHF ₂ (4g) | 1 | | | | | | |

* Two diastereoisomers formed. † Isomers formed, (a) two (ratio 1:1), (b) three, (c) two (ratio 3:7). ‡ (a) Two minor unidentified products also formed (<0.5%), (b) one minor unidentified product also produced (<0.5%). § Primary insertion products although expected in low yield (<2%) were not detected.



(12)

reactivity ratio 96:1) than those in a MeCH₂·CH₂ grouping (ca. 15:1).

The only compound for which a tertiary to primary

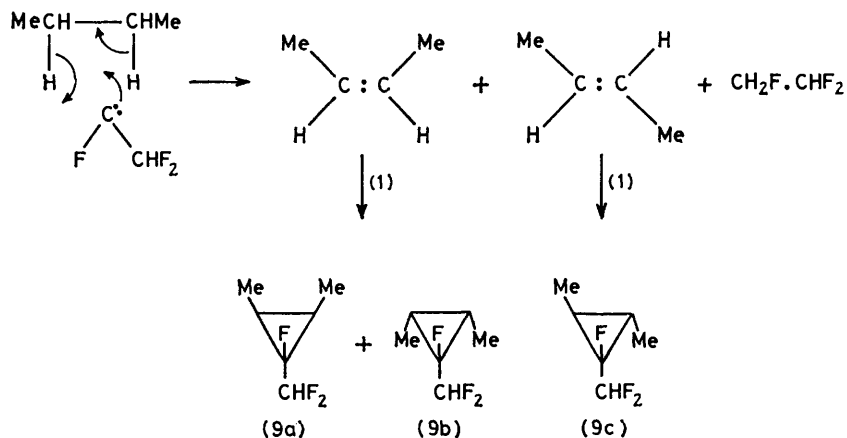
C-H bond reactivity ratio could be obtained was 2-methylpropane (380:1); primary C-H bond insertion into the compounds Me₂CHEt and Prⁱ₂CH₂ was not

 TABLE 2
 Experimental and statistical C-H bond insertion ratios

| Alkane | Experimental ratios | | | | Statistical ratios | | | |
|---|---------------------|--------|--------|------|--------------------|--------|--------|------|
| | 1° | 2° (A) | 2° (B) | 3° | 1° | 2° (A) | 2° (B) | 3° |
| C ₃ H ₈ | 1 | 6.5 | | | 1 | 19.5 | | |
| n-C ₄ H ₁₀ | 1 | 9.5 | | | 1 | 14 | | |
| n-C ₅ H ₁₂ | 1 | 10.5 | 3 | | 1 | 16 | 9 | |
| n-C ₆ H ₁₄ | 1 | 9 | 5 | | 1 | 13.5 | 7.5 | |
| Me ₃ CH | 1 | | | 42 | 1 | | | 380 |
| Me ₂ CHEt | | 1 | | 4.5 | | 1 | | 9 |
| (Me ₂ CH) ₂ CH ₂ | | | 1 | 10.5 | | | 1 | 10.5 |
| Et ₂ O | 1 | 64 | | | 1 | 96 | | |

A, CH₂ adjacent to methyl. B, CH₂ not adjacent to methyl. Figures rounded off to nearest 0.5.

detected. This high ratio (380:1) relates to the nine β -hydrogens present for tertiary C-H bond insertion as against only one β -hydrogen present for primary C-H bond insertion. With the alkane Me_2CHEt tertiary C-H bond insertion (eight β -hydrogens) is preferred over secondary C-H bond insertion (four β -hydrogens)



by the ratio 9:1, whereas with the alkane Pr_i^2CH_2 tertiary insertion (eight β -hydrogens) is favoured over secondary C-H bond insertion (two β -hydrogens) by the ratio 10.5:1, *i.e.* the secondary C-H bonds in the alkane Me_2CHEt are, perhaps, slightly more reactive than those in the alkane Pr_i^2CH_2 .

Insertion into a primary C-H bond (two β -hydrogens) of diethyl ether is much less favourable than insertion into a secondary C-H bond (three β -hydrogens and adjacent oxygen atom).

Ethane with only primary C-H bonds is, as expected, less reactive (16% insertion) than the other alkanes investigated ($\geq 34\%$ insertion) and insertion into methane under comparable conditions was not observed. n-Pentane (37% insertion) was less reactive than n-butane (41% insertion) or n-hexane (45% insertion) and cyclohexane (44% insertion) was less reactive than cyclopentane (55% insertion).

Ethylidene, $\text{CH}_3\cdot\dot{\text{C}}\text{H}$, generated by photolysis or pyrolysis of diazoethane⁸ or by photolysis of methylketene,⁹ does not apparently insert into the C-H bonds of hydrocarbons but undergoes rearrangement to ethylene.

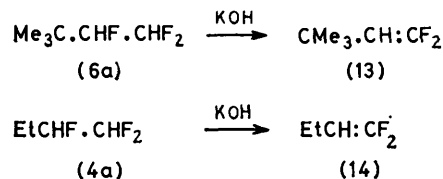
An interesting feature of a number of the alkane reactions was the formation of cyclopropanes, *i.e.* (7)—(12), with the concurrent production of 1,1,2-trifluoroethane. The cyclopropanes (7)—(10) were identified by a comparison of their g.l.c. retention times, mass spectra, and, in certain cases, n.m.r. spectra with those of authentic samples prepared in this Department. Two of the three possible isomers of cyclopropane (11) were tentatively identified by mass spectrometry as was the cyclopropane (12).

It is suggested that these compounds are formed *via* a concerted abstraction of hydrogen from the alkanes by singlet carbene (1) followed by a stereospecific addition of carbene (1) to the resultant olefins as shown above for n-butane.

A related intramolecular transfer of hydrogen atoms to a carbene centre has been postulated.¹⁰

With n-butane and n-pentane abstraction involves secondary and not primary hydrogens, although primary hydrogen abstraction can occur as shown with ethane, propane, and 2-methylpropane.

Dehydrofluorination of the carbene adduct (6a) with an excess of powdered potassium hydroxide at 95 °C (95 h) gave unchanged (6a) (5% recovered) and 1,1-difluoro-3,3-dimethylbut-1-ene (13) (95%); the adduct



(4a) was less easily dehydrofluorinated and reaction with potassium hydroxide at 95 °C (120 h) gave unchanged (4a) (58% recovered) and 1,1-difluorobut-1-ene (14) (39%).

EXPERIMENTAL

Reactants and products were manipulated, where possible, in a conventional vacuum system to avoid contact with air or moisture. Reactions were carried out *in vacuo* in Pyrex bulbs [capacities *ca.* 5 dm³ except with ethane, cyclopentane, and cyclohexane (*ca.* 3.7 dm³)] fitted with a side-arm and at maximum pressures of *ca.* 1 atm. Pure compounds were isolated by repeated fractional condensation *in vacuo* or by preparative scale g.l.c. [Pye 104 instrument with columns packed with Phasesep Q, dinonyl phthalate (DNP), or trixylyl phosphate (TXP) on Celite as indicated in the text]. 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), n.m.r. spectroscopy [Varian Associates HA 100 spectrometer operating at 100 MHz for ¹H and 94.1 MHz for ¹⁹F (SiMe₄ and CF₃CO₂H as the respective external references) or a Perkin-Elmer R12 instrument operating at 60.0 MHz for ¹H and 56.46 MHz for ¹⁹F (external SiMe₄ and 4-CF₂Cl-C₆H₄Cl as the respective references)], and mass spectrometry (MS 902 machine). All the spectroscopic

data for the products described are available as a Supplementary publication No. SUP 22490 (19 pp.).*

The reactant alkanes were commercial samples which were distilled carefully before use and their purities checked.

For all compounds containing the $\text{CHF}_2\text{-CHF-}$ group the CF_2 fluorines are magnetically non-equivalent and can give rise to an AB-type multiplet in the ^{19}F n.m.r. spectrum with J_{AB} ca. 300 Hz. However, only the spectra of compounds (4a), (4c), (5b; isomer 1), (5l; isomer 2), and (6a) showed a clear AB multiplet. In the spectra of the remaining compounds, the chemical shift difference between the geminal fluorines was rather small and the outer lines of the multiplet were too weak to be observed, although a separation of the inner lines was generally apparent.

Reactions of Trifluoro-(1,1,2,2-tetrafluoroethyl)silane with Hydrocarbons.—(a) *With ethane.* A mixture of the silane (1.86 g, 10 mmol) and the hydrocarbon (4.45 g, 148.4 mmol) heated at 150 °C (18 h) gave (i) a gaseous mixture shown by g.l.c. (4 m Phasesep Q at 100 °C) to contain silicon tetrafluoride (1.02 g, 9.8 mmol, 98%), trifluoroethylene (0.53 g, 6.5 mmol, 65%), unchanged ethane (4.35 g, 145.2 mmol, 98% recovered), and 1,1,2-trifluoroethane (present) and (ii) a volatile liquid mixture (0.32 g) which was separated by g.l.c. (2 m Phasesep Q at 150 °C) into its components *cis*- and *trans*-1-difluoromethyl-1,2,2,3-tetrafluorocyclopropane (3) (0.10 g, 0.6 mmol, 12%); 1,1,2-trifluorobutane (4a) (0.18 g, 1.6 mmol, 16%) (Found: C, 42.6; H, 5.9%; M , 112. $\text{C}_4\text{H}_7\text{F}_3$ requires C, 42.8; H, 6.3%; M , 112), b.p. (isoteniscope) 46.5 ± 0.5 °C; and three minor products one of which was shown to be 1-difluoromethyl-1-fluorocyclopropane (7) (ca. 0.03 g, 0.3 mmol, 3%); m/e 110 (4%, M^+), 59 [100%, ($M - \text{CHF}_2$) $^+$], and 51 (24%, CHF_2^+); the two other minor products (<0.5%) were not identified.

(b) *With propane.* A mixture of the silane (3.72 g, 20.0 mmol) and the hydrocarbon (8.80 g, 200 mmol) heated at 150 °C (18 h) gave (i) a mixture of silicon tetrafluoride (2.03 g, 19.5 mmol, 98%), trifluoroethylene (0.59 g, 7.2 mmol, 36%), and 1,1,2-trifluoroethane (ca. 0.06 g, 0.7 mmol, 4%) [Found: M^+ , 84 (mass spec.). Calc. for $\text{C}_2\text{H}_3\text{F}_3$: M , 84], (ii) unchanged propane (8.27 g, 187.9 mmol, 94% recovered), and (iii) a liquid mixture (1.35 g) which was separated by g.l.c. (2 m DNP at 25 °C) into its components *cis*- and *trans*-1-difluoromethyl-1,2,2,3-tetrafluorocyclopropane (3) (0.26 g, 1.6 mmol, 16%); 1,1,2-trifluoro-3-methylbutane (5a) (0.81 g, 6.4 mmol, 32%) (Found: C, 47.3; H, 7.1%; M , 126. $\text{C}_5\text{H}_9\text{F}_3$ requires C, 47.6; H, 7.1%; M , 126), b.p. (Siwoloboff) 63 °C; 1,1,2-trifluoropentane (4b) (0.13 g, 1.03 mmol, 5%); *r*-1-difluoromethyl-1-fluoro-*t*-2-methylcyclopropane (8a) (0.08 g, 0.64 mmol, 3%); and *r*-1-difluoromethyl-1-fluoro-*c*-2-methylcyclopropane (8b) (0.07 g, 0.57 mmol, 3%).

(c) *With 2-methylpropane.* A mixture of the silane (1.86 g, 10.0 mmol) and the hydrocarbon (5.80 g, 100 mmol) heated at 150 °C (18 h) gave (i) a mixture of silicon tetrafluoride (1.0 g, 9.6 mmol, 96%), trifluoroethylene (0.26 g, 3.2 mmol, 32%), and 1,1,2-trifluoroethane (<1%), (ii) unchanged 2-methylpropane (5.20 g, 89.7 mmol, 90% recovered), and (iii) a liquid mixture (0.90 g) which was separated by g.l.c. (2 m DNP at 60 °C) into its components 1,1,2-trifluoro-3,3-dimethylbutane (6a) (0.82 g, 5.9 mmol, 59%) (Found: C, 51.2; H, 7.7%; M , 140. $\text{C}_6\text{H}_{11}\text{F}_3$ requires C, 51.4; H, 7.9%; M , 140), b.p. (Siwoloboff) 81.5 °C;

1,1,2-trifluoro-4-methylpentane (4d) (0.02 g, 0.14 mmol, 1.4%); 1-difluoromethyl-1-fluoro-2,2-dimethylcyclopropane (10) (<1%); and a minor product (<0.5%) which could not be identified. *cis*- and *trans*-1-Difluoromethyl-1,2,2,3-tetrafluorocyclopropane (3) (0.05 g, 0.3 mmol, 6%) were also identified amongst the reaction products.

(d) *With n-butane.* A mixture of the silane (3.72 g, 20 mmol) and the hydrocarbon (11.60 g, 200 mmol) heated at 150 °C (18 h) gave (i) a mixture of silicon tetrafluoride (2.05 g, 19.7 mmol, 99%) and trifluoroethylene (0.80 g, 9.8 mmol, 49%) contaminated with a small amount of 1,1,2-trifluoroethane, (ii) unchanged *n*-butane (11.0 g, 189.6 mmol, 95% recovered), and (iii) a liquid mixture (1.31 g) which was separated by g.l.c. (2 m DNP at 60 °C) into its components *cis*- and *trans*-1-difluoromethyl-1,2,2,3-tetrafluorocyclopropane (3) (0.09 g, 0.5 mmol, 3%); 1,1,2-trifluoro-3-methylpentane (5b) (1.01 g, 7.3 mmol, 37%) (Found: C, 51.2; H, 7.9%; M , 140. $\text{C}_6\text{H}_{11}\text{F}_3$ requires C, 51.4; H, 7.9%; M , 140) as two diastereoisomers in the ratio 56:44, isomer 1, b.p. (Siwoloboff) 87 °C; isomer 2, b.p. (Siwoloboff) 88–89 °C; 1,1,2-trifluorohexane (4c) (0.10 g, 0.7 mmol, 4%); and three isomeric products (0.11 g, 0.8 mmol, 4%) shown by comparison of their g.l.c. retention times and mass spectra with authentic samples to be *r*-1-difluoromethyl-1-fluoro-*t*-2,3-dimethylcyclopropane (9a), *r*-1-difluoromethyl-1-fluoro-*c*-2-*t*-3-dimethylcyclopropane (9c), and *r*-1-difluoromethyl-1-fluoro-*c*-2,3-dimethylcyclopropane (9b).

(e) *With n-pentane.* A mixture of the silane (3.63 g, 19.5 mmol) and the hydrocarbon (14.04 g, 195 mmol) heated at 150 °C (18 h) gave (i) a mixture of silicon tetrafluoride (1.93 g, 18.6 mmol, 96%), trifluoroethylene (0.85 g, 10.4 mmol, 53%), and 1,1,2-trifluoroethane (ca. 0.02 g, 0.2 mmol, 1%), (ii) unchanged *n*-pentane (12.45 g, 172.9 mmol, 89% recovered) contaminated with *cis*- and *trans*-1-difluoromethyl-1,2,2,3-tetrafluorocyclopropane (3) (ca. 0.08 g, 0.5 mmol, 5%), and (iii) a liquid mixture (1.13 g) which was separated by g.l.c. (2m DNP at 80 °C) into its components 1,1,2-trifluoro-3-methylhexane (5d) (0.77 g, 5.0 mmol, 26%) (Found: C, 54.5; H, 8.5%; M , 153. $\text{C}_7\text{H}_{13}\text{F}_3$ requires C, 54.5; H, 8.4%; M , 154) as a pair of diastereoisomers in the ratio 59:41; isomer A, b.p. (Siwoloboff) 117–119 °C; and isomer B, b.p. (Siwoloboff) 116 °C; 3-ethyl-1,1,2-trifluoropentane (5c) (0.24 g, 1.6 mmol, 8%) (Found: C, 54.0; H, 8.5. $\text{C}_7\text{H}_{13}\text{F}_3$ requires C, 54.5; H, 8.4%, b.p. (Siwoloboff) 117 °C; 1,1,2-trifluoroheptane (4e) (0.07 g, 0.5 mmol, 2.5%); and four minor products (ca. 0.05 g) two of which were identified as isomers of 1-difluoromethyl-2-ethyl-1-fluoro-3-methylcyclopropane (11a) (ca. 0.02 g, 0.13 mmol, 0.7%), and (11b) (ca. 0.01 g, 0.06 mmol, 0.3%).

(f) *With n-hexane.* A mixture of the silane (3.72 g, 20 mmol) and the hydrocarbon (17.2 g, 200 mmol) heated at 150 °C (18 h) gave (i) silicon tetrafluoride (2.02 g, 19.4 mmol, 97%) and trifluoroethylene (0.65 g, 7.9 mmol, 40%) contaminated with a trace of 1,1,2-trifluoroethane, (ii) *cis*- and *trans*-1-difluoromethyl-1,2,2,3-tetrafluorocyclopropane (3) (ca. 0.1 g, 0.6 mmol, 12%), (iii) unchanged *n*-hexane (15.3 g, 177.9 mmol, 89% recovered), and (iv) a liquid mixture (1.50 g) which was separated by g.l.c. (2m TXP at 100 °C) into its components 1,1,2-trifluoro-3-methylheptane (5g) (0.90 g, 5.4 mmol, 27%) (Found: C, 56.8; H, 8.8. $\text{C}_8\text{H}_{15}\text{F}_3$ requires C, 57.1; H, 8.9%) as a pair of diastereoisomers in the ratio 54:46; isomer A, b.p. (Siwoloboff) 142 °C; and isomer B, b.p. (Siwoloboff) 140.5 °C; 3-ethyl-

* For details of the Supplementary publications scheme, see Notice to Authors No. 7, in *J.C.S. Perkin I*, 1978, Index issue.

1,1,2-trifluorohexane (5f) (0.50 g, 3.0 mmol, 15%) (Found: C, 56.8; H, 8.8. $C_6H_{11}F_3$ requires C, 57.1; H, 8.9%), b.p. (Siwoloff) 141–143 °C, as a pair of unresolved diastereoisomers; and 1,1,2-trifluoro-octane (4f) (0.10 g, 0.6 mmol, 3%).

(g) *With 2-methylbutane.* A mixture of the silane (3.72 g, 20 mmol) and the hydrocarbon (14.4 g, 200 mmol) heated at 150 °C (18 h) gave (i) silicon tetrafluoride (2.06 g, 19.8 mmol, 99%) and trifluoroethylene (0.86 g, 10.5 mmol, 52%) contaminated with a trace amount of 1,1,2-trifluoroethane, (ii) *cis*- and *trans*-1-difluoromethyl-1,2,2,3-tetrafluorocyclopropane (3) (0.11 g, 0.7 mmol, 7%), (iii) unchanged 2-methylbutane (13.36 g, 185.6 mmol, 93% recovered), and (iv) a liquid mixture (1.20 g) (Found: C, 53.9; H, 8.3. Calc. for $C_7H_{13}F_3$: C, 54.5; H, 8.4%) which was separated by g.l.c. (2m TXP at 80 °C) into its components 1,1,2-trifluoro-3,3-dimethylpentane (6b) (0.99 g, 6.43 mmol, 32%), b.p. (Siwoloff) 118–119 °C; and 1,1,2-trifluoro-3,4-dimethylpentane (5e) (0.21 g, 1.36 mmol, 7%) as a pair of diastereoisomers A and B in the ratio *ca.* 54 : 46.

(h) *With 2,4-dimethylpentane.* A mixture of the silane (3.72 g, 20 mmol) and the hydrocarbon (20.0 g, 200 mmol) heated at 150 °C (18 h) gave (i) silicon tetrafluoride (2.07 g, 19.9 mmol, 99%) and trifluoroethylene (0.77 g, 9.4 mmol, 47%) contaminated with a trace amount of 1,1,2-trifluoroethane, (ii) *cis*- and *trans*-1-difluoromethyl-1,2,2,3-tetrafluorocyclopropane (3) (0.28 g, 1.7 mmol, 17%), (iii) unchanged 2,4-dimethylpentane (18.8 g, 188 mmol, 94% recovered), and (iv) a liquid mixture (1.23 g) (Found: C, 58.9; H, 9.0. Calc. for $C_9H_{17}F_3$: C, 59.2; H, 9.0%) which was separated by g.l.c. (2m TXP at 100 °C) into its components 1,1,2-trifluoro-3,3,5-trimethylhexane (6c) (1.11 g, 6.1 mmol, 31%), b.p. (Siwoloff) 152.0 °C; and 1,1,2-trifluoro-3-isopropyl-4-methylpentane (5h) (0.12 g, 0.66 mmol, 3%).

(i) *With cyclopentane.* A mixture of the silane (1.86 g, 10 mmol) and the hydrocarbon (10.4 g, 148.4 mmol) heated at 150 °C (18 h) gave (i) a mixture of silicon tetrafluoride (1.03 g, 9.9 mmol, 99%) and trifluoroethylene (0.25 g, 3.0 mmol, 30%) contaminated with a trace amount of 1,1,2-trifluoroethane, (ii) *cis*- and *trans*-1-difluoromethyl-1,2,2,3-tetrafluorocyclopropane (3) (0.1 g, 0.6 mmol, 12%), (iii) unchanged cyclopentane (9.88 g, 141.4 mmol, 95% recovered), and (iv) 1,2,2-trifluoroethylcyclopentane (5j) (0.83 g, 5.5 mmol, 55%) (Found: C, 55.0; H, 7.3%; *M*, 152. $C_7H_{11}F_3$ requires C, 55.2; H, 7.2%; *M*, 152), b.p. (Siwoloff) 131 °C; contaminated with two minor products one of which was tentatively identified as 6-difluoromethyl-6-fluorobicyclo[3.1.0]hexane (12) (*ca.* 0.01 g, 0.06 mmol, 0.6%).

(j) *With cyclohexane.* A mixture of the silane (1.86 g, 10 mmol) and the hydrocarbon (12.47 g, 148.4 mmol) heated at 150 °C (18 h) gave (i) silicon tetrafluoride (1.03 g, 9.9 mmol, 99%) and trifluoroethylene (0.34 g, 4.1 mmol, 41%) contaminated with a trace amount of 1,1,2-trifluoroethane, (ii) *cis*- and *trans*-1-difluoromethyl-1,2,2,3-tetrafluorocyclopropane (3) (0.1 g, 0.6 mmol, 12%), (iii) unchanged cyclohexane (12.02 g, 143.1 mmol, 96% recovered), (iv) 1,2,2-trifluoroethylcyclohexane (5k) (0.73 g, 4.4 mmol, 44%) (Found: C, 57.8; H, 7.5%; *M*, 165. $C_8H_{13}F_3$ requires C, 57.8; H, 7.8%; *M*, 166), b.p. (Siwoloff)

154.5 °C; and (v) a minor product (<0.5%) which was not 7-difluoromethyl-7-fluorobicyclo[4.1.0]heptane.

(k) *With diethyl ether.* A mixture of the silane (3.44 g, 18.5 mmol) and the ether (14.8 g, 200 mmol) heated at 150 °C (18 h) gave (i) a mixture of silicon tetrafluoride (1.86 g, 17.9 mmol, 97%) and trifluoroethylene (0.33 g, 4.0 mmol, 22%), (ii) *cis*- and *trans*-1-difluoromethyl-1,2,2,3-tetrafluorocyclopropane (3) (0.14 g, 0.9 mmol, 9%), (iii) unchanged diethyl ether (13.75 g, 185.8 mmol, 93% recovered), and (iv) a liquid mixture (1.87 g) which was separated by g.l.c. (2m DNP at 60 °C) into its components *ethyl 2,3,3-trifluoro-1-methylpropyl ether* (5l) (1.84 g, 11.8 mmol, 64%) (Found: C, 46.2; H, 7.3%; *M*, 156. $C_8H_{11}F_3O$ requires C, 46.2; H, 7.0%; *M*, 156), b.p. (Siwoloff) 112–114 °C, as a pair of diastereoisomers A and B in the ratio 53 : 47; and 3,4,4-trifluorobutyl ethyl ether.

Dehydrofluorination of 1,1,2-Trifluoro-3,3-dimethylbutane (6a).—The fluoroalkane (0.35 g, 2.5 mmol) and dry powdered potassium hydroxide (56.0 g, 1.0 mol), sealed in a Pyrex tube (*ca.* 150 cm³) *in vacuo* and heated at 95 °C (95 h), gave unchanged fluoroalkane (0.017 g, 0.121 mmol, 5% recovered) and 1,1-difluoro-3,3-dimethylbut-1-ene (13) (0.273 g, 2.26 mmol, 95%) (Found: C, 60.1; H, 8.6%; *M*, 120. $C_8H_{10}F_2$ requires C, 60.0; H, 8.3%; *M*, 120).

Dehydrofluorination of 1,1,2-Trifluorobutane (4a).—The fluoroalkane (0.45 g, 4.0 mmol) and dry powdered potassium hydroxide (95 g, 1.7 mol), sealed in a Pyrex tube (*ca.* 150 cm³) *in vacuo* and heated at 95 °C (120 h), gave unchanged fluoroalkane (0.26 g, 2.32 mmol, 58% recovered) and 1,1-difluorobut-1-ene (14) (0.06 g, 0.65 mmol, 39%) (Found: *M*, 93. Calc. for $C_4H_8F_2$: *M*, 92), b.p. (isoteniscope) 4.1 ± 0.5 °C (lit.,¹¹ 3.7 °C).

[7/1097 Received 24th June, 1977]

REFERENCES

- Part 10, R. N. Haszeldine, C. R. Pool, A. E. Tipping, and R. O'B. Watts, *J.C.S. Perkin I*, 1976, 513.
- Reported in part as a preliminary communication, R. N. Haszeldine and J. G. Speight, *Chem. Comm.*, 1967, 995, and in '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.
- G. Fishwick, R. N. Haszeldine, C. Parkinson, P. J. Robinson, and R. F. Simmons, *Chem. Comm.*, 1965, 382; R. N. Haszeldine, P. J. Robinson, and W. J. Williams, *J.C.S. Perkin II*, 1973, 1013.
- J. Lee, C. Parkinson, P. J. Robinson, and J. G. Speight, *J. Chem. Soc. (B)*, 1967, 1125.
- R. N. Haszeldine, A. E. Tipping, and R. O'B. Watts, *J.C.S. Perkin I*, 1974, 2391.
- R. N. Haszeldine, A. E. Tipping, and R. O'B. Watts, *J.C.S. Perkin I*, 1975, 966.
- J. M. Birchall, R. N. Haszeldine, and T. K. Dempsey, unpublished results.
- A. L. Glasebrook and F. O. Rice, *J. Amer. Chem. Soc.*, 1934, 56, 741; F. E. Blacet, R. K. Brinton, P. A. Leighton, and D. H. Volman, *J. Chem. Phys.*, 1950, 18, 203; R. K. Brinton and D. H. Volman, *ibid.*, 1951, 19, 1394; H. M. Frey, *Chem. and Ind.*, 1962, 81, 218; H. M. Frey, *J. Chem. Soc.*, 1962, 2293.
- G. B. Kistiakowsky and B. H. Mahan, *J. Chem. Phys.*, 1956, 24, 922; *J. Amer. Chem. Soc.*, 1957, 79, 2412.
- C. D. Gutsche, G. Buchmun, and R. S. Coffey, *Tetrahedron*, 1962, 18, 617.
- A. L. Henne and J. B. Hinkamp, *J. Amer. Chem. Soc.*, 1945, 67, 1197.