

Fluoro-olefin Chemistry. Part 17.¹ Thermal Reaction of Hexafluoropropene with 2-Trifluoromethylbutane and 1,1,1-Trifluoropentane

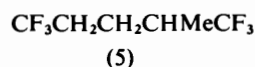
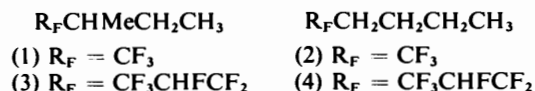
Terry Davies, Robert N. Haszeldine, and Anthony E. Tipping *

Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD

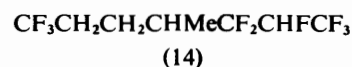
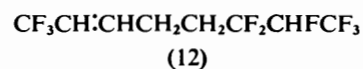
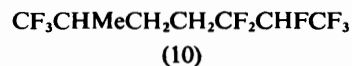
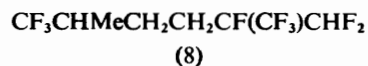
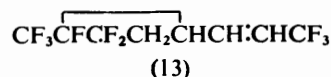
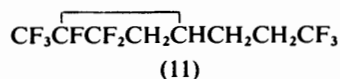
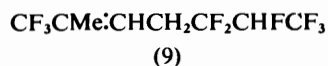
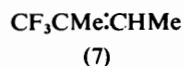
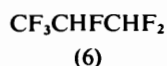
Reaction of hexafluoropropene with 2-trifluoromethylbutane (1) and 1,1,1-trifluoropentane (2) in the range 260–295 °C gives as major products the 1:1 adducts $\text{CF}_3\text{CHMeCH}_2\text{CH}_2\text{CF}_2\text{CHF}_3$ (10) and $\text{CF}_3\text{CH}_2\text{CH}_2\text{CHMeCF}_2\text{CHF}_3$ (14), respectively, formed *via* hydrogen abstraction from C–H bonds γ to the CF_3 group. However, dehydrogenation to give 1*H*,2*H*-hexafluoropropene (6) and the alkenes $\text{CF}_3\text{CMe:CHMe}$ (7) [from (1)] and $\text{CF}_3\text{CH}_2\text{CH}_2\text{CH:CH}_2$ (22) [from (2)] is a competing reaction which is more important the higher the temperature. The alkene (7) reacts further to give $\text{CF}_3\text{CMe:CHCH}_2\text{CF}_2\text{CHF}_3$ (9) and the cyclopentane $\text{CF}_3\text{CMeCH}_2\text{CH}_2\text{CF}_2\text{CF}_3$ (18) while the alkene (22) undergoes cyclodimerisation with hexafluoropropene to afford $\text{CF}_3\text{CFCF}_2\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CF}_3$ (11) and then the dehydrogenation product $\text{CF}_3\text{CFCF}_2\text{CH}_2\text{CHCH:CHCF}_3$ (13). A further product from the alkane (2) is the olefin $\text{CF}_3\text{CH:CHCH}_2\text{CH}_2\text{CF}_2\text{CHF}_3$ (12) formed *via* hydrogen abstraction from a δ -C–H bond. Reaction does not occur between 1,1,1-trifluoro-4-trifluoromethylpentane and hexafluoropropene at 295 °C.

Thermal and photochemical reaction of hexafluoropropene with *n*-butane gives both 1:1 and 2:1 adducts;^{1,2} the former compounds are precursors of the 2:1 adducts. The structures of the 2:1 adducts indicated that the C_3HF_6 group in the 1:1 adducts had a strong deactivating influence on the reactivities of C–H bonds in the α - and β -positions to the group.

The CF_3 group has a comparable electron-withdrawing $-I$ effect to that of the C_3HF_6 group, but being less bulky should sterically hinder reaction at the α - and β -C–H bonds to a lesser extent. Therefore the reactions of hexafluoropropene with 2-trifluoromethylbutane (1) and 1,1,1-trifluoropentane



(2), the CF_3 analogues of the major *n*-butane-hexafluoropropene 1:1 adducts (3) and (4), were investigated under thermal conditions. In addition the thermal reaction of hexafluoropropene with 1,1,1-trifluoro-4-trifluoromethylpentane (5) was also carried out in order to determine the effect of two CF_3



groups in the alkane on the reactivities of the various C–H bonds.

Results and Discussion

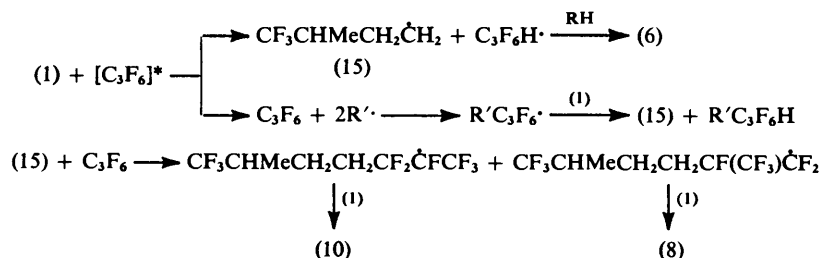
Initial reactions involving the alkanes (1) and (2) at *ca.* 290 °C (4d) prompted an investigation at lower temperature and the results obtained are given in Tables 1 and 2.

All the reactions gave tar and multicomponent mixtures from which only the major components were isolated.

The major products from the reactions of both alkanes were 1:1 adducts, but a totally unexpected observation was that dehydrogenation to give 1*H*,2*H*-hexafluoropropene (6) and alkenes was a competing reaction, the extent of which increased with increasing temperature.

(a) 2-Trifluoromethylbutane (1).—The 1:1 adducts (8) and (10) are considered to be formed by a chain mechanism initiated either by C–C bond cleavage or hydrogen abstraction from a γ -C–H bond in the alkane (1) involving thermally activated hexafluoropropene as postulated previously^{1,3} [Scheme 1, where R' is any radical formed by C–C bond cleavage of (1)].

The intermediate radical (15) undergoes bidirectional addition to hexafluoropropene with major attack occurring on the terminal CF_2 group (ratio *ca.* 3:1) as found for other



Scheme 1.

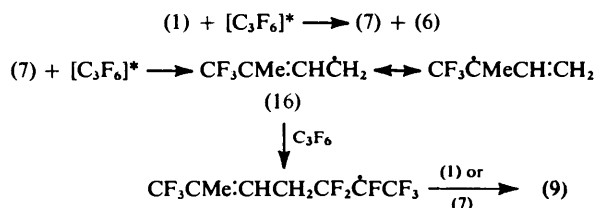
Table 1. Reaction of hexafluoropropene with 2-trifluoromethylbutane (1) (1 : 3 molar ratio; 96 h)

Temp. (°C)	Recovered (1) (%)	Recovered C ₃ F ₆ (%)	Products (%) *					
			(6)	(7)	(8)	(C ₈ H ₇ F ₉)†	(9)	(10)
292	83	27	33	16	3.5	4.5	4	10
280	82	42	12	6.5	14	7.5	6	43
260	94	86	2	Trace	22	2	2	70

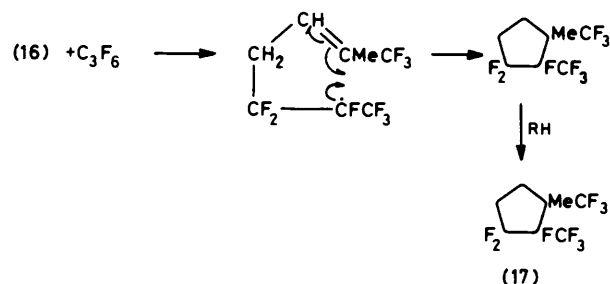
* Based on C₃F₆ consumed. † Compound not fully characterised.

Table 2. Reaction of hexafluoropropene with 1,1,1-trifluoropentane (2) (1 : 3 molar ratio; 96 h)

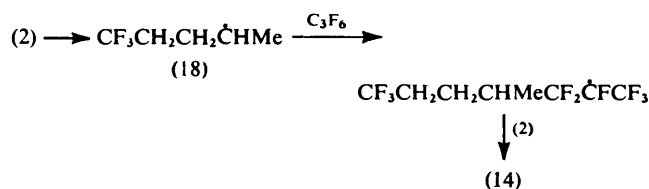
Temp. (°C)	Recovered (2) (%)	Recovered C ₃ F ₆ (%)	Products (%) *				
			(6)	(11)	(12)	(13)	(14)
295	78	35	27	16	6	1	35
277	82	62	20	10	3	3	52
260	93	80	15	6	3	3	64

* Based on C₃F₆ consumed.

Scheme 2.



Scheme 3.



Scheme 4.

alkyl radicals, e.g. n-butyl (ratio *ca.* 4 : 1).¹ 1 : 1 Adducts formed *via* hydrogen abstraction from C-H bonds α or β to the CF₃ group were not detected. This observation is in agreement with the results obtained from reaction of the n-butane-hexafluoropropene adduct (3) with hexafluoropropene and indicates that the deactivation of the α - and β -C-H bonds in compounds (1) and (3) is due to the -I effect of the fluoroalkyl groups and steric effects are relatively unimportant.

The other identified products, 2-trifluoromethylbut-2-ene 7⁴ and 5,5,6,7,7,7-hexafluoro-2-trifluoromethylhept-2-ene (9), are probably formed *via* dehydrogenation of alkane (1) by thermally excited hexafluoropropene (Scheme 2).

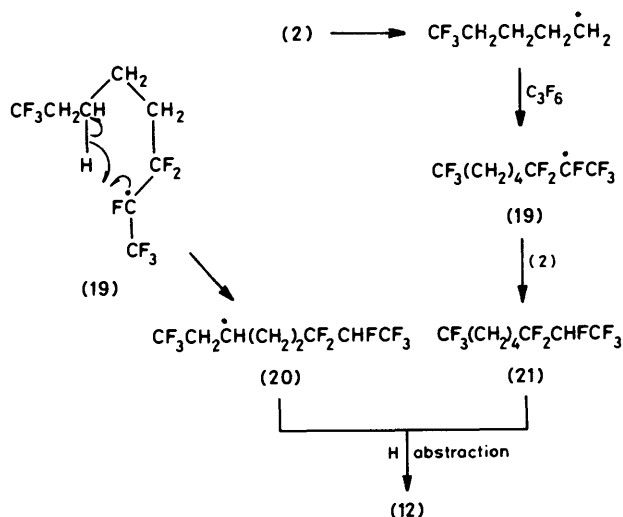
The remaining product C₈H₇F₉ is almost certainly the cyclopentane (17) as indicated by its ¹⁹F n.m.r. spectrum; $\delta_F +6.4$ br (s, 3 F, CF₃), -0.5 (td, 3 F, CF₃CFCF₂), -32.6 and -38.4 (AB, 2 F, CF₂, *J* 252 Hz), and -102.7 p.p.m. (mult, 1 F, CF). The groups CHF and CHF₂ were absent and the AB coupling observed was of the magnitude expected for a cyclopentane but not for a cyclobutane (*ca.* 220 Hz). The

¹H n.m.r. spectrum was uninformative although it confirmed the absence of CHF and CHF₂ groups.

Cyclopentane (17) is an expected product from reaction of the allyl radical (16) with hexafluoropropene (*cf.* reaction of the allyl radicals CH₂:CMe \dot{C} H₂, CHMe:CMe \dot{C} H₂, and CMe₂:CMe \dot{C} H₂⁵), *i.e.* Scheme 3. An attempted photochemical reaction surprisingly gave only unchanged reactants.

(b) 1,1,1-Trifluoropentane (2).—The only 1 : 1 adduct isolated was compound (14) formed *via* hydrogen abstraction from a γ -C-H bond to give the intermediate radical (18), *i.e.* Scheme 4.

1 : 1 Adducts formed by insertion into α -, β -, or δ -C-H bonds were not detected although it is considered that alkene (12) is formed *via* abstraction of hydrogen from a δ -C-H bond. Such δ -hydrogen abstraction was expected because the reaction of hexafluoropropene with the n-butane adduct (4) at 300 °C gave 2 : 1 adducts resulting from γ - and δ -hydrogen



Scheme 5.

abstraction in the ratio 7 : 1.¹ This ratio is in close agreement with the product ratio (14) : (12) = ca. 6 : 1 for reaction at 295 °C (Table 2).

The absence of adducts formed *via* α - or β -hydrogen abstraction is further confirmation that the deactivation of the α - and β -C-H bonds in the *n*-butane adducts (3) and (4) is a result of electronic rather than steric factors. Deactivation of the α - and β -C-H bonds in the alkane (2) towards abstraction by chlorine atoms has been reported previously.⁶

Initial abstraction of a δ -hydrogen atom could give alkene (12) by two distinct mechanisms (Scheme 5). Of the two mechanisms that involving rearrangement of the intermediate radical (19) to radical (20) is perhaps more likely, because there appears to be no sound reason why adduct (21) should undergo dehydrogenation while the major 1 : 1 adduct (14) apparently does not.

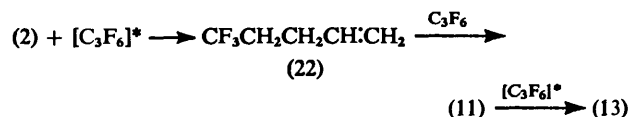
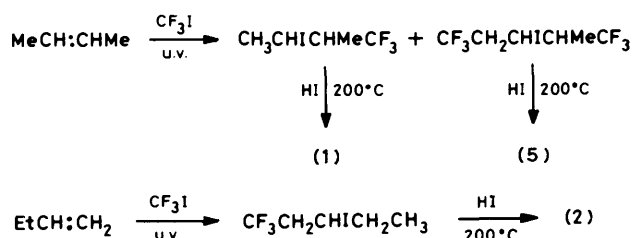
The remaining two products, the cyclobutanes (11) and (13), are considered to arise *via* initial dehydrogenation to give the alkene (22), *i.e.* Scheme 6.

(c) 1,1,1-Trifluoro-4-trifluoromethylpentane (5).—An attempted reaction between the alkane (5) and hexafluoropropene at 295 °C (91 h) gave only unchanged reactants. The C-H bonds in this alkane are all either α or β to a CF_3 group and hydrogen abstraction by thermally excited hexafluoropropene is not favourable.

Experimental

The techniques used are as described previously.¹ N.m.r. Chemical shifts quoted as positive are to low field of the references [external $\text{CF}_3\text{CO}_2\text{H}$ (^{19}F) and SiMe_4 (^1H)]. Molecular weights were determined by Regnault's method.

The reactant alkanes were prepared⁴ by the following routes:



Scheme 6.

Reaction of Hexafluoropropene with 2-Trifluoromethylbutane (1).—(a) At 280 °C. A mixture of the alkane (4.10 g, 33.0 mmol) and hexafluoropropene (1.65 g, 11.0 mmol), heated *in vacuo* in a Pyrex tube (ca. 300 cm³) at 280 °C (96 h), gave (i) a low-boiling fraction (0.64 g, 4.8 mmol; *M*, 152) which was shown by i.r. spectroscopy and g.l.c. (4 m Kel-F at 20 °C) to be unchanged hexafluoropropene (0.63 g, 4.7 mmol, 42% recovered) contaminated with traces of 1*H*,2*H*-hexafluoropropane (6) and *cis*- and *trans*-perfluoro(1,2-dimethylcyclobutane), (ii) an intermediate fraction (3.54 g), shown by g.l.c. (8 m TXP at 40 °C) to consist of four components (ratio; trace : 3 : 42 : 1) identified as a mixture of *cis*- and *trans*-perfluoro(1,2-dimethylcyclobutane) (trace), (6) (0.11 g, 0.72 mmol, 12%), unchanged (1) (3.40 g, 27.0 mmol, 82% recovered), and 2-trifluoromethylbut-2-ene⁴ (7) (0.005 g, 0.4 mmol, 7% on alkane) by their g.l.c. retention times and the i.r. and ^1H and ^{19}F n.m.r. spectra of the mixture; δ_{H} (*Z*- $\text{CF}_3\text{CMe}^a=\text{CH}^c\text{Me}^b$) 1.22 (3 H, s, H_a), 1.18 (3 H, mult, H_b), 5.63 (1 H, mult, H_c), and (*E*- $\text{CF}_3\text{CMe}^a=\text{CH}^c\text{Me}^b$) 1.28 (3 H, s, H_a), 1.20 (3 H, mult, H_b), and 5.24 (1 H, mult, H_c) p.p.m., (iii) a higher-boiling fraction (1.44 g) shown by g.l.c. (8 m TXP at 60 °C) to contain four major components (A—D) in the ratio 11 : 6 : 5 : 32 and a number of minor components, and (iv) a tarry carbonaceous residue which was not examined further.

The four components (A—D) were separated by g.l.c. (3.5 m TXP at 100 °C) to give 1,1,2-trifluoro-2,5-bis(trifluoromethyl)hexane (8) (0.27 g, 1.0 mmol, 14% on C_3F_6) (Found: C, 35.0; H, 3.1%; *M*, 276. $\text{C}_8\text{H}_9\text{F}_9$ requires C, 34.8; H, 3.3%; *M*, 276, b.p. 120 °C, *m/z* 276 (trace, M^+) and 207 [100%, ($M - \text{CF}_3$)⁺], n.m.r. bands for $\text{CF}_3^a\text{CH}^b\text{Me}^c\text{CH}_2^d\text{CH}_2^e\text{CF}^f(\text{CF}_3)^g\text{CH}^h\text{F}^i\text{F}^j$ at δ_{F} +2.9 (3 F, d, F_a , J_{ba} 8 Hz), -1.0 (3 F, mult, F_g), -55.8 and -57.1 (2 F, AB mult, F_i and F_j) and -109.2 (1 F, mult, F_f) and δ_{H} 0.90 (3 H, d, H_c , J_{bc} 6.2 Hz), 1.6 to 2.1 (4 H, mult, H_d and H_e), 2.60 (1 H, mult, H_b), and 5.68 (1 H, td, H_h , J_{AB-h} 54.0, J_{fh} 4.0 Hz); a compound tentatively identified as 1,1,2-trifluoro-2,3-bis(trifluoromethyl)-3-methylcyclopentane (18) (0.14 g, 0.50 mmol, 7.5%) (Found: C, 34.9; H 2.7%; M^+ , 274. $\text{C}_8\text{H}_7\text{F}_9$ requires C, 35.0; H, 2.6%; *M*, 274), b.p. 124 °C, *m/z* 274 (12%, M^+) and 173 [100, ($M - \text{C}_2\text{HF}_4$)⁺]; 5,5,6,7,7-hexafluoro-2-trifluoromethylhept-2-ene (9) (0.12 g, 0.45 mmol, 6%) (Found: C, 34.7; H, 2.7%; M^+ , 274), b.p. 126 °C, *m/z* 274 (34%, M^+) and 123 [100, $\text{C}_5\text{H}_6\text{F}_3^+$], n.m.r. bands for $\text{CF}_3^a\text{CMe}^b\text{CH}^c\text{CH}_2^d\text{CF}^e\text{F}^f\text{CH}^g\text{F}^h\text{CF}_3^i$ at δ_{F} +5.9 (3 F, s, F_a), +1.6 (3 F, mult, F_g), -30.1 and -33.4 (2 F, AB mult, F_i and F_h , J_{AB} 280 Hz), and -134.0 (1 F, dmult, F_f , J_{ef} 44 Hz) and δ_{H} 1.16 (3 H, s, H_b), 2.65 (2 H, td, H_d , J_{AB-d} 17, J_{cd} 7 Hz), 4.44 (1 H, ddquin, H_e , J_{fe} 44, J_{Ac} 12, $J_{Be} \approx J_{ge}$ 6 Hz), and 5.90 (1 H, tmult, H_c , J_{dc} 7 Hz); and 1,1,1,2,3,3-hexafluoro-6-trifluoromethylheptane (10) (0.87 g, 3.15 mmol, 43%) (Found: C, 34.7; H, 3.1%; M^+ , 276), b.p. 129 °C, *m/z* 276 (trace, M^+) and 65 [100%, $\text{C}_2\text{H}_3\text{F}_2^+$], n.m.r. bands for $\text{CF}_3^a\text{CH}^b\text{Me}^c\text{CH}_2^d\text{CH}_2^e\text{CF}^f\text{F}^g\text{CH}^h\text{F}^i\text{CF}_3^j$ at δ_{F} +3.0 (3 F, d, F_a , J_{ba} 8.4 Hz), +1.8 (3 F, qd, F_h , $J_{gh} \approx J_{Ah}$ 11, J_{fh} 6 Hz), -32.1 and -34.5 (2 F, AB mult, F_i and F_j , J_{AB} 272 Hz), and -134.0 (1 F, dmult, F_g , J_{fg} 44 Hz) and δ_{H} 0.92 (3 H, d, H_c , J_{bc} 7.8 Hz), 1.6 to 2.1 (4 H, mult, H_d and H_e), 2.6 (1 H, mult, H_b), and 4.48 (1 H, ddquin, H_f , J_{gf} 44, J_{Bf} 11, $J_{Af} \approx J_{Bf}$ 6 Hz).

(b) *At other temperatures.* Two further reactions using the same quantities of reactants as in experiment (a) and heated at

292 and 260 °C (96 h), respectively, gave the results shown in Table 1.

(c) *Under photochemical conditions.* A mixture of alkane (1) (1.16 g, 9.15 mmol) and hexafluoropropene (0.46 g, 3.05 mmol), sealed *in vacuo* in a silica tube (*ca.* 15 cm³) and irradiated with a Hanovia S500 medium-pressure lamp at a distance of *ca.* 15 cm (160 h), gave only unchanged reactants.

Reaction of Hexafluoropropene with 1,1,1-Trifluoropentane (2).—(a) *At 295 °C.* A mixture of alkane (2) (3.91 g, 31.0 mmol) and hexafluoropropene (1.50 g, 10.0 mmol), heated *in vacuo* in a Pyrex tube (*ca.* 300 cm³) at 295 °C (96 h), gave (i) a low-boiling fraction (0.57 g, 3.7 mmol; *M*, 153) consisting of unchanged hexafluoropropene (0.53 g, 5.5 mmol, 55% recovered) and traces of 1*H*,2*H*-hexafluoropropane (6) and *cis*- and *trans*-perfluoro(1,2-dimethylcyclobutane) [*i.r.* and *g.l.c.* (4 m Kcl-F at 20 °C)]; (ii) an intermediate fraction (3.29 g), shown by *i.r.* spectroscopy and *g.l.c.* (8 m TXP at 40 °C) to consist of (6) (0.29 g, 1.8 mmol, 27%) and unchanged (2) (3.00 g, 23.8 mmol, 78% recovered); (iii) a high-boiling fraction (1.13 g) shown by *g.l.c.* (8 m TXP at 60 °C) to be a multi-component mixture containing four major components (E—H, ratio 10 : 4 : 1 : 21), and (iv) a carbonaceous residue which was not examined further.

Compounds (E—H) were separated by *g.l.c.* (3.5 m TXP at 95 °C) to give: 1,2,2-trifluoro-1-trifluoromethyl-4-(3,3,3-trifluoropropyl)cyclobutane (11) (0.29 g, 1.1 mmol, 16%) (Found: C, 35.3; H, 2.9; *M*, 274. C₈H₇F₉ requires C, 35.0; H, 2.6%; *M*, 274), b.p. 116 °C, *m/z* 274 (1%, *M*⁺) and 77 (100, C₃H₃F₂⁺),

n.m.r. bands for CF₃^aCF^bCF^aF^bCH₂^cCH^dCH₂^eCH₂^fCF₃^g at δ_F +11.9 (3 F, t, F_g, *J*_{fg} 10.2 Hz), +3.0 (3 F, mult, F_a), -31.0 and -34.0 (2 F, AB mult, F_A and F_B), and -106.1 (1 F, mult, F_b) and δ_H 1.7 (2 H, mult, H_e), 1.05 (4 H, complex, H_c + H_f), and 2.5 to 2.7 (1 H, mult, H_d); 1,1,1,6,6,7,8,8,8-nonafluoro-oct-2-ene (12) (0.12 g, 0.44 mmol, 6%) (Found: C, 35.3; H, 2.5%; *M*⁺, 274), λ_{max} 5.90 μm (C:C str.); *m/z* 274 (7%, *M*⁺) and 77 (100, C₃H₃F₂⁺), *n.m.r.* bands for CF₃^aCH^b:CH^cCH₂^dCH₂^eCF₂^fCH^gF^hCF₃ⁱ at δ_F +11.1 (3 F, d, F_a, *J*_{ba} 6.0 Hz), -3.0 (3 F, mult, F_i), -31.0 (2 F, mult, F_f), and -133.0 (1 F, dmult, F_h, *J*_{gh} 44 Hz) and δ_H 1.7 to 2.1 (2 H, complex H_d), 2.2 to 2.5 (2 H, mult, H_e), 4.60 (1 H, dmult, H_g, *J*_{hg} 44 Hz), 5.64 [1 H, dq, H_b, *J*_{cb} (*trans*) 16, *J*_{ab} 6.0 Hz], and 6.10 (1 H, mult, H_c); 1,2,2-trifluoro-1-trifluoromethyl-4-(3,3,3-trifluoro-

prop-1-enyl)cyclobutane (13) (0.02 g, 0.08 mmol, 1%) (Found: C, 35.6; H, 2.0%; *M*⁺, 272. C₈H₅F₉ requires C, 35.3; H, 1.8%; *M*, 272), λ_{max} 5.90 μm (C:C str.), *m/z* 272 (1%, *M*⁺) and 122 (100, C₅H₅F₃⁺), *n.m.r.* bands for

CF₃^aCH^b:CH^cCH^dCH₂^eCF₂^fABCF^gCF₃^h at δ_F +11.0 (3 F, d, F_a, *J*_{ba} 6.0 Hz), +1.1 (3 F, td, F_g, *J*_{AB-g} 10.5, *J*_{fg} 6.0 Hz), -24.0 and -41.0 (2 F, AB mult, F_A and F_B), and -104 (1 F, complex, F_f), and δ_H 2.2 to 3.6 (2 H, complex, H_e), 2.6 to 3.1 (1 H, complex, H_d), 5.48 [1 H, dq, H_b, *J*_{cb} (*trans*) 16, *J*_{ab} 6.0 Hz], and 6.18 (1H, dd, H_c, *J*_{ac} 7.0 Hz); and 1,1,1,2,3,3,7,7,7-nonafluoro-4-methylheptane (14) (0.64 g, 2.32 mmol, 35%) (Found: C, 34.8; H, 3.2%; *M*⁺, 276. C₈H₉F₉ requires C, 34.8; H, 3.3%; *M*, 276), b.p. 130 °C, *m/z* 276 (trace, *M*⁺) and 65 (100%, C₅H₅⁺), *n.m.r.* bands for CF₃^aCH^bF^cCF₂^dCH^eMe^fCH₂^gCH₂^hCF₃ⁱ at δ_F +11 (3 F, mult, F_i), +3.0 (3 F, mult, F_a), -40.1 (2 F, complex, F_d), and -138 (1 F, dmult, F_c, *J*_{bc} 46 Hz) and δ_H 0.88 (3 H, d, H_f, *J*_{ef} 7.5 Hz), 1.6 to 2.2 (4 H, complex, H_g + H_h), 2.4 to 2.7 (1 H, complex, H_e), and 4.54 (1 H, dmult, H_b, *J*_{cb} 46 Hz).

(b) *At other temperatures.* Two further reactions were carried out at 277 and 260 °C (3 : 1 ratio of alkane: C₃F₆) and the results obtained are shown in Table 2.

Thermal Reaction of Hexafluoropropene with 1,1,1-Trifluoro-4-trifluoromethylpentane (5).—A mixture of the alkane (5) (0.44 g, 2.26 mmol) and hexafluoropropene (0.11 g, 0.75 mmol), sealed *in vacuo* in a Pyrex tube (*ca.* 25 cm³) and heated at 295 °C (91 h), gave only unchanged reactants (98% recovered) and a small carbonaceous residue which was not examined further.

References

- 1 Part 16, T. Davies, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc., Perkin Trans. 1*, 1983, 109.
- 2 R. N. Haszeldine and R. Rowland, U.S.P. 3917,725/1975.
- 3 R. N. Haszeldine, A. J. Mitchinson, R. Rowland, and A. E. Tipping, *J. Chem. Soc., Perkin Trans. 1*, 1976, 517.
- 4 T. Davies, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc., Perkin Trans. 1*, 1980, 927.
- 5 R. N. Haszeldine, C. M. Raynor, and A. E. Tipping, *J. Chem. Soc., Perkin Trans. 1*, 1982, 2219.
- 6 H. Singh and J. M. Tedder, *J. Chem. Soc.*, 1964, 4737.

Received 13th August 1982; Paper 2/1411