

## Fluoro-olefin Chemistry. Part 16.<sup>1</sup> Reaction of Hexafluoropropene with n-Butane and n-Pentane

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Thermal reaction of hexafluoropropene with n-butane at *ca.* 300 °C gives 1 : 1 and 2 : 1 adducts [major products  $\text{CF}_3\text{CHFCF}_2\text{R}$ ; R =  $\text{Bu}^n$  (11),  $\text{Bu}^s$  (12), and  $\text{CHMeCH}_2\text{CH}_2\text{CF}_2\text{CHF}_2$  (14)], together with lower alkane adducts  $\text{H}[\text{C}_3\text{F}_6]\text{R}$  (R = Me, Et, Pr<sup>n</sup>, and Pr<sup>i</sup>) and 1,1,1,2,3,3-hexafluoropropane (4). The 1 : 1 adducts are precursors of the 2 : 1 adducts and the lower alkane adducts, and the structures of the isolated 2 : 1 adducts indicate that C-H bonds  $\alpha$ - and  $\beta$ - to the fluoroalkyl group in the 1 : 1 adducts are deactivated towards hydrogen abstraction. It is proposed that the 1 : 1 and 2 : 1 adducts arise by a radical-chain mechanism initiated by hydrogen abstraction from n-butane and the 1 : 1 adducts, respectively, and that the lower alkane adducts are formed *via* interaction between the 1 : 1 adducts and excited hexafluoropropene resulting in C-C bond fission. The photochemical and peroxide-initiated reactions give much higher yields of 1 : 1 and 2 : 1 adducts at the expense of the lower alkane adducts. Analogous products are formed in the thermal reaction with n-pentane [major 1 : 1 and 2 : 1 adducts  $\text{CF}_3\text{CHFCF}_2\text{R}$ ; R =  $\text{CHMePr}^n$  (16),  $\text{CHEt}_2$  (17),  $\text{CHMeCH}_2\text{CHMeCF}_2\text{CHF}_2$  (18), and  $\text{CHMe}(\text{CH}_2)_3\text{CF}_2\text{CHF}_2$  (19)], but, surprisingly, 2 : 1 adducts formed *via* hydrogen abstraction from the  $\gamma$ -C-H bonds ( $\text{CH}_3$ ) of the 1 : 1 adduct (17) are absent.

Thermal reaction of hexafluoropropene with alkanes,<sup>2</sup> alkylbenzenes,<sup>3,4</sup> certain halogenoalkanes,<sup>5</sup> and dialkyl sulphides<sup>6</sup> gives 1 : 1 adducts considered to be formed by a radical-chain mechanism initiated by hydrogen atom abstraction by excited hexafluoropropene molecules (Scheme 1).

### Results and Discussion

The reaction of hexafluoropropene with n-butane at 325 °C was reported<sup>2</sup> to give 1 : 1 and 2 : 1 adducts, together with unidentified products. In the present work the reactions of hexafluoropropene with (i) n-butane under thermal, photochemical and peroxide-initiated conditions, and (ii) n-pentane under thermal conditions, have been investigated. The results of the present work are compared with those obtained previously<sup>2</sup> in Table 1.

(a) *Thermal reactions with n-butane.* The results obtained from experiments 1 and 2 confirm the original report (experiment 3) that both 1 : 1 and 2 : 1 hexafluoropropene-n-butane adducts are formed, but two additional 1 : 1 adducts (9) and (10), a further 2 : 1 adduct (15), and a number of lower-boiling products have been isolated and identified.

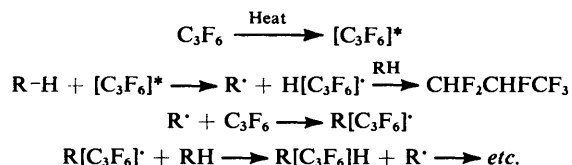
The 1 : 1 adducts are considered to be formed *via* the chain mechanism shown in Scheme 1 (where  $\text{R} \cdot = \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 \cdot$  and  $\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HCH}_3$ ); the isolation of 1,1,1,2,3,3-hexafluoropropane (4) is strong evidence for the proposed initiation step.

It is also apparent that, as expected, formation of s-butyl

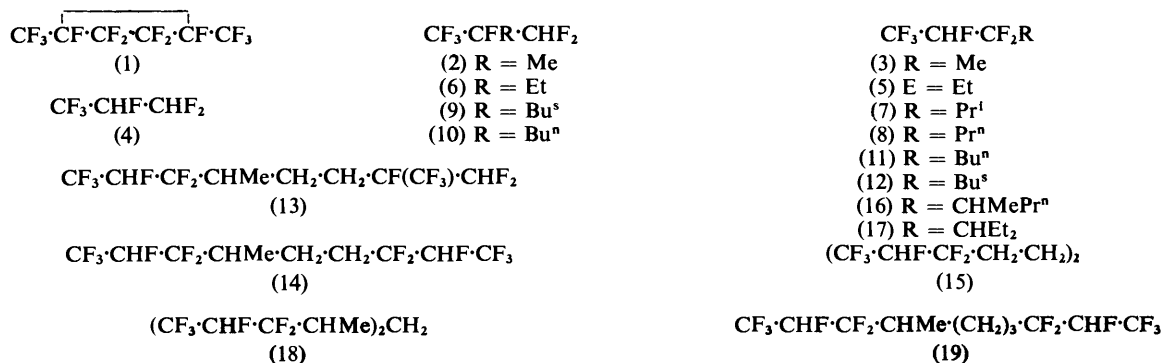
radicals to give the 1 : 1 adducts (9) and (12) is favoured over that of n-butyl radicals to give adducts (10) and (11).

Bidirectional butyl radical addition to hexafluoropropene is observed with major attack by both n-butyl and s-butyl radicals at the terminal  $\text{CF}_2$  group of the olefin, as found previously for a variety of other radical additions to hexafluoropropene. The ratios of attack at the  $\text{CF}_2$  group relative to the  $\text{CF}_3\text{CF}$  group for the n-butyl and s-butyl radicals are *ca.* 4 : 1 and *ca.* 16 : 1, respectively (based on the 1 : 1 adducts isolated), or *ca.* 6.5 : 1 and *ca.* 24 : 1, respectively (based on the 1 : 1 and 2 : 1 adducts isolated). Thus, n-butyl radical attack at the central carbon atom is more favoured than attack by the s-butyl radical. This is probably due to greater steric hindrance to attack caused by the branched radical at the central carbon atom and/or the lower electrophilicity of the s-butyl radical relative to the n-butyl radical.

The 2 : 1 adducts could be formed by insertion of hexafluoropropene into C-H bonds of the 1 : 1 adducts (*via* an analo-



Scheme 1

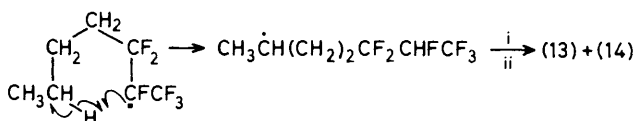


**Table 1.** Reaction of hexafluoropropene with n-butane and n-pentane (1 : 3 molar ratio)

Experiment	1 <sup>b,c</sup>	2 <sup>b</sup>	3 <sup>b,d</sup>	4	5	6	7 <sup>b</sup>	
Alkane	C <sub>4</sub> H <sub>10</sub>	C <sub>4</sub> H <sub>10</sub>	C <sub>4</sub> H <sub>10</sub>	C <sub>4</sub> H <sub>10</sub>	C <sub>4</sub> H <sub>10</sub>	C <sub>4</sub> H <sub>10</sub>	C <sub>5</sub> H <sub>12</sub>	
Conditions	Thermal (tube)	Thermal (autoclave)	Thermal (autoclave)	u.v. (static)	u.v. (shaken)	Peroxide-initiated	Thermal (autoclave)	
Temp. (°C)	295	310	325	ca. 40	ca. 40	130	300	
Time (h)	120	132	72	72	144	70	120	
Olefin (% recovered)	20	15	28	85	50	60	22	
Alkane (% recovered)	84	61	70	93	86	85	75	
Products (%) <sup>a</sup>	(1)	0.5	0.5			1	<0.5	
	(2)	0.5	0.5			0.5		
	(3)	1	1			2	1	
	(4)	0.5	0.5		1	Trace	0.5	
	(5)	9	10			2.5	4	
	(6)	0.5	1				0.5	
	(7)	3.5	1.5				1	
	(8)	3	2.5				3	
	(9)	1.5	2		4	1	0.5	
	(10)	1.5	1.5		4	1.5	0.5	
	(11)	5	6	8	10.5	8	1.5	3.5
	(12)	26	32	40	58	47	27	2
	(13)	1	2	4	1.5	4	5	
	(14)	8.5	16	27	16	33	60	
	(15)	<0.5	0.5		<0.5	0.5	1	
	(16)							29
	(17)							11
	(18)							16
	(19)							7.5

<sup>a</sup> In order of g.l.c. retention time and based on consumed olefin (given to nearest 0.5%). <sup>b</sup> Charred residue also formed. Compound (C<sub>3</sub>HF<sub>6</sub>)<sub>2</sub> (trace) also detected. <sup>d</sup> Previous investigation (ref. 2). <sup>e</sup> Di-t-butyl peroxide (2 mol %) used; small amount of acetone also isolated. A non-condensable product at -196 °C presumed to be methane was formed in all the thermal reactions

gous mechanism to that put forward for 1 : 1 adduct formation) or *via* rearrangement of the radical precursors to the 1 : 1 adducts followed by reaction of the rearranged radicals with hexafluoropropene, *e.g.*



Reagents: i, C<sub>3</sub>F<sub>6</sub>; ii, RH

The latter possibility is considered less likely because rearrangement gives less stabilised radicals and the formation of the 2 : 1 adduct (15) would require rearrangement of the radical CH<sub>3</sub>(CH<sub>2</sub>)CF<sub>2</sub>CF<sub>3</sub> to give  $\dot{\text{C}}\text{H}_2(\text{CH}_2)_3\text{CF}_2\text{CHF}\text{CF}_3$  *via* an unfavourable seven-centre transition state.

The autoclave reaction gave comparable results to those obtained from the tube reaction, but less tar was formed and higher yields of compounds (12) and (14) were obtained in agreement with those reported.<sup>2</sup>

To determine if the 1 : 1 adducts were precursors of the 2 : 1 adducts, the major 1 : 1 adducts (11) and (12) were each heated with hexafluoropropene (3 : 1 molar ratio at 300 °C, 72 h); the results obtained are shown in Table 2.

A further reaction of a mixture of 1 : 1 adducts (9)–(12) with hexafluoropropene at 320 °C (120 h) gave similar results except that compounds (2) (1%) and (6) (2%) were also formed.

The 2 : 1 adducts (13), (14), and (15) were formed in the ratio *ca.* 3 : 25 : 1 in the reaction with n-butane (Table 1) and in the ratio *ca.* 3 : 27 : 1 from the reaction of the 1 : 1 adducts

with hexafluoropropene [Table 2, with due allowance being made for the relative amounts of the 1 : 1 adducts (11) and (12) available for further reaction with hexafluoropropene (*ca.* 1 : 5)]. It is therefore concluded that the 2 : 1 adducts are formed mainly from the 1 : 1 adducts in the n-butane reaction.

It is also apparent (Table 2) that the hydrogen atoms  $\alpha$ - and  $\beta$ - to the CF<sub>2</sub>CHF<sub>2</sub>CF<sub>3</sub> group are deactivated towards abstraction, and insertion of hexafluoropropene occurs into  $\gamma$ - and  $\delta$ -C-H bonds in the adduct (11) and  $\gamma$ -C-H bonds in the adduct (12). This is due to the strongly negative inductive effect of the fluoroalkyl group which renders the  $\alpha$ - and  $\beta$ -hydrogen atoms somewhat acidic and their abstraction unfavourable and possibly also to the steric requirements of the C<sub>3</sub>HF<sub>6</sub> group. A similar deactivating effect on the ease of abstraction of the hydrogen atoms  $\alpha$ - and  $\beta$ - to a CF<sub>3</sub> group has been reported in the chlorination of 1,1,1-trifluoropentane.<sup>7</sup>

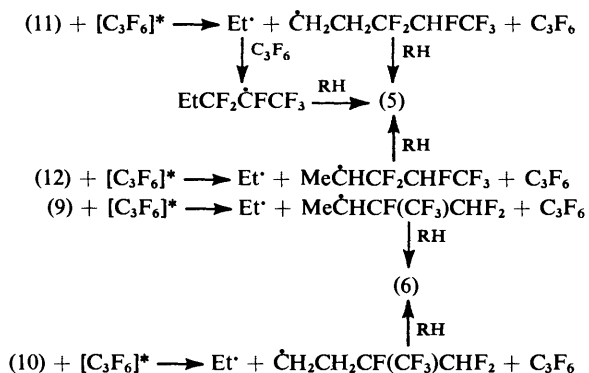
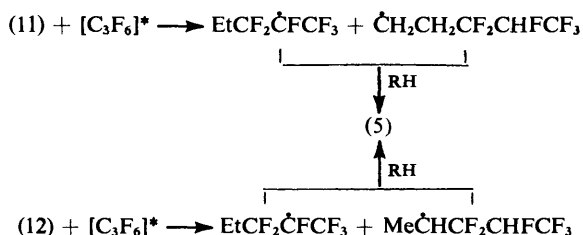
Apart from compound (1), the cyclodimer of hexafluoropropene,<sup>8</sup> the remaining products from both the n-butane and 1 : 1 adduct reactions are the lower alkane-hexafluoropropene 1 : 1 adducts R[C<sub>3</sub>F<sub>6</sub>]H (R = Me, Et, Pr<sup>n</sup>, and Pr<sup>i</sup>). Since these products are formed in both reactions it is possible that they are formed exclusively by further reaction of the 1 : 1 adducts (9)–(12). The 1 : 1 adducts are thermally stable under the reaction conditions employed and so the lower molecular weight compounds are considered to arise *via* interaction between the adducts and excited hexafluoropropene. Such interaction could involve two distinct mechanisms A and B as shown for the formation of the ethane-hexafluoropropene 1 : 1 adducts (5) and (6) in Schemes 2 and 3, respectively.

Mechanism A involves transfer of energy by collision from the excited hexafluoropropene to the 1 : 1 adduct which results

**Table 2.** Reaction of the 1 : 1 adducts (11) and (12) with hexafluoropropene

Reactant adduct	Recovered adduct (%)	Recovered C <sub>3</sub> F <sub>6</sub> (%)	Products (% yield) <sup>a</sup>							
			(3)	(4)	(5)	(7)	(8)	(13)	(14)	(15)
(11)	74	63	1	2	14		7			5
(12)	78	71	1.5	3	23	9	9	4		33

<sup>a</sup> Based on 1 : 1 adduct consumed; tar and three further unidentified products (ca. 5% total) with comparable g.l.c. retention times to those of the 2 : 1 adducts were also formed in each reaction.

**Scheme 2. Mechanism A**

and analogous reactions for adducts (9) and (10)

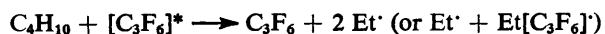
**Scheme 3. Mechanism B**

in C-C bond fission, while mechanism B is a displacement reaction at carbon.

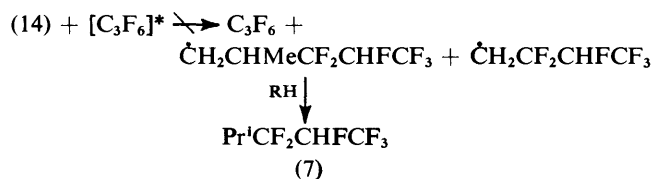
If mechanism A is correct it is perhaps surprising that products arising *via* addition of the radicals Me', Et', and Pr' to the central carbon atom of hexafluoropropene were not detected in the reactions of the 1 : 1 adducts (11) and (12). Such compounds were found, however, in the products from the reaction of the 1 : 1 adduct mixture and so it is concluded that they arise by decomposition of the minor 1 : 1 adducts (9) and (10).

The major objection to mechanism B is that the adducts of methane and propane with hexafluoropropene should be formed in equal amounts which clearly does not occur [ratio 1 : 7 with adduct (11) and 1 : 12 with adduct (12)]. On balance therefore it is considered that mechanism A is more likely with the methyl radicals produced reacting mainly by hydrogen abstraction to give methane (the presumed non-condensable product) while the ethyl and propyl radicals react mainly by addition.

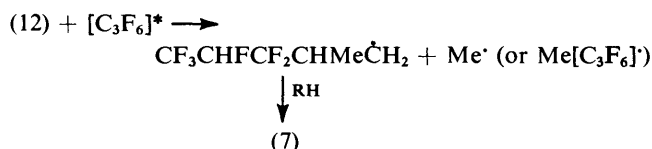
Hydrocarbon chain fission to give the ethane-hexafluoropropene adducts is favoured over fission to give methane- and propane-hexafluoropropene adducts. Although similar reactions to those shown in Schemes 2 and 3 could take place with n-butane, *e.g.*



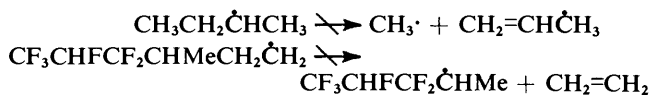
they do not apparently occur with the 2 : 1 adducts. Thus, although the 2 : 1 adduct (14) is the major product from the reaction of both the 1 : 1 adducts (11) and (12), only in the latter reaction is compound (7) formed, *i.e.*



Compound (7) is considered to arise by the reaction sequence:



One noteworthy feature of the reactions was the apparent unimportance of β-scission reactions involving intermediate radicals, *e.g.*



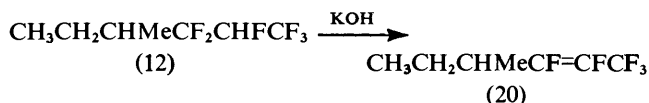
Neither olefins nor their cyclodimers with hexafluoropropene were detected in the products.

(b) *Photochemical reactions with n-butane.* These were cleaner than the thermal reactions in that tar was not observed, higher yields of the 1 : 1 and 2 : 1 adducts were obtained, and decomposition reactions to give lower alkane-hexafluoropropene adducts were relatively unimportant. Shaking of the reaction tube favoured 2 : 1 adduct formation by giving better mixing between the gas and liquid phases.

(c) *Peroxide-initiated reaction with n-butane.* This was again a clean reaction, but in contrast to both the thermal and photochemical reactions a 2 : 1 adduct (14) was the major product. This is presumably due to slow decomposition of the t-butyl peroxide in the liquid phase which, as the reaction progresses, becomes rich in 1 : 1 adduct.

The only lower alkane-hexafluoropropene adducts detected were the methane adducts (2) and (3), which are considered to arise *via* decomposition of t-butoxy-radicals to acetone and methyl radicals.

Dehydrofluorination of the major 1 : 1 adduct (12) with powdered potassium hydroxide gave a mixture (64%) of (*Z*)- and (*E*)-1,1,1,2,3,-pentafluoro-4-methylhex-2-ene (20) in the ratio 85 : 15, *i.e.*



It has been observed previously in a number of dehydrohalogenations giving the alkenes  $\text{RCF}=\text{CFR}'$  that the *cis*-isomer predominated even when the groups R and R' were bulky.<sup>9</sup>

(d) *Thermal reaction with n-pentane*.—The major products (Table 1) were the 1:1 adducts (16) and (17) and the 2:1 adducts (18) and (19); lower alkane-hexafluoropropene adducts were also formed. All of these products are considered to arise *via* analogous reactions to those discussed previously for the n-butane products. In contrast to the thermal n-butane reactions, 1:1 and 2:1 adducts resulting from radical addition to the central carbon atom of hexafluoropropene were not isolated although minor 1:1 and 2:1 adducts were detected. This is presumably a consequence of more bulky intermediate radicals produced in this reaction. The two major 2:1 adducts (18) and (19) are formed *via* hydrogen atom abstraction from  $\gamma$ - (secondary) and  $\delta$ - (primary) C-H bonds, respectively, in the 1:1 adduct (16). 2:1 Adducts resulting from abstraction of a  $\gamma$ - (primary) hydrogen atom in the 1:1 adduct (17) were not detected. Since compounds (16), (18), and (19) arise from the reaction of the pentan-2-yl radical and compound (17) arises from the reaction of the pentan-3-yl radical, the ease of abstraction of hydrogen from the 2- and 3-positions of n-pentane is in the ratio *ca.* 4:1 rather than the statistical ratio 2:1. Products formed from the intermediacy of the pentan-1-yl radical were not detected.

## Experimental

Thermal reactions were carried out *in vacuo* in sealed Pyrex tubes (*ca.* 300 cm<sup>3</sup> unless stated otherwise) or in Hastelloy autoclaves, while photochemical reactions employed silica tubes (*ca.* 300 cm<sup>3</sup>) which were irradiated with a Hanovia S 500 medium-pressure lamp at a distance of *ca.* 20 cm. Volatile products were partially separated by fractional condensation under reduced pressure and individual components were separated from the resulting fractions by g.l.c. [Pye 104 or Perkin-Elmer F 21 instruments; columns of trixylyl phosphate (TXP), Silicone SE 30 oil, or Kel-F 10 oil (30% on Celite)] and were examined by i.r. spectroscopy (Perkin-Elmer 257 spectrophotometer with sodium chloride optics), n.m.r. spectroscopy (Perkin-Elmer R 10 spectrometer operating at 60 MHz for <sup>1</sup>H and 56.46 MHz for <sup>19</sup>F or a Varian HA-100 spectrometer operating at 100 MHz for <sup>1</sup>H and 94.1 MHz for <sup>19</sup>F with external tetramethylsilane and trifluoroacetic acid as the respective references; chemical shifts to low field of reference are positive), and mass spectrometry (A.E.I. MS 902 spectrometer). B.p.s were determined by Siwoloboff's method.

*Reaction of Hexafluoropropene with Alkanes*.—(a) *n-Butane under thermal conditions (autoclave)*. A mixture of n-butane (18.1 g, 0.312 mol) and hexafluoropropene (15.6 g, 0.104 mol), heated *in vacuo* in a rocked autoclave (*ca.* 250 cm<sup>3</sup>) at 310 °C (132 h), gave (i) a non-condensable gas at -196 °C (1.0 mmol) probably methane [i.r. 3.34  $\mu\text{m}$  (C-H str.)]; (ii) a low-boiling fraction (14.1 g, 0.22 mmol; *M*, 68) consisting of unchanged n-butane (11.2 g, 0.190 mol, 61% recovered), unchanged hexafluoropropene (2.25 g, 15.0 mmol, 15% recovered), and lesser amounts of 1,1,1,2,3,3-hexafluoropropane (4) and low molecular weight hydrocarbons (total 0.65 g) as shown by i.r. spectroscopy and g.l.c. (4-m Kel-F at 20 °C); (iii) an intermediate fraction (10.84 g), shown by g.l.c. (8-m TXP at 60 °C) to contain twelve components (A)—(H), (J)—(M) in the ratio 1:1:5:3:52:3:9:13:12:8:36:192; (iv) a higher-boiling fraction (3.10 g), shown by g.l.c. (8-m TXP at 130 °C) to contain three major components (N)—(P) in the ratio

4:35:1 and several minor components; and (v) a tarry carbonaceous residue (5.5 g) which was not examined further.

The twelve components from (iii) above were separated by g.l.c. (7.5-m TXP at 90 °C) to give: (A) a 1:1 mixture of *cis*- and *trans*-perfluoro-(1,2-dimethylcyclobutane) (1) (0.03 g, 0.1 mmol, 0.5%) was shown by a comparison of its i.r., n.m.r., and mass spectra with those reported;<sup>8</sup> (B) 1,1,1,2,3,3-hexafluoro-2-methylpropane (2) (0.04 g, 0.26 mmol, 0.5%) (Found: C, 28.6; H, 2.7%; *M*, 166. C<sub>4</sub>H<sub>4</sub>F<sub>6</sub> requires C, 28.9; H, 2.4%; *M*, 166); *m/e* 151 [8%, (*M* - Me)<sup>+</sup>], 65 (64, C<sub>2</sub>H<sub>3</sub>F<sub>2</sub><sup>+</sup>), and 51 (100, CHF<sub>2</sub><sup>+</sup>); (C) 1,1,1,2,3,3-hexafluorobutane (3) (0.16 g, 1.0 mmol, 1%) (Found: C, 29.0; H, 2.7%; *M*, 166); *m/e* 166 (trace, *M*<sup>+</sup>), 151 [22%, (*M* - Me)<sup>+</sup>], and 65 (100, C<sub>2</sub>H<sub>3</sub>F<sub>2</sub><sup>+</sup>); (D) 1,1,1,2,3,3-hexafluoropropane (4) (0.10 g, 0.32 mmol, 0.5%) as shown by a comparison of its i.r., n.m.r., and mass spectra with those of an authentic sample; (E) 1,1,1,2,3,3-hexafluoropentane (5) (1.61 g, 8.92 mmol, 10%) (Found: C, 33.4; H, 3.3%; *M*, 181. Calc. for C<sub>5</sub>H<sub>5</sub>F<sub>6</sub>: C, 33.3; H, 3.3%; *M*, 180); *m/e* 161 [1%, (*M* - F)<sup>+</sup>], and 79 (100, EtCF<sub>2</sub><sup>+</sup>); (F) 1,1,2-trifluoro-2-trifluoromethylbutane (6) (0.11 g, 0.6 mmol, 1%) (Found: C, 33.6; H, 3.3%; *M*, 180); b.p. 49 °C; *m/e* 160 [1%, (*M* - HF)<sup>+</sup>], 129 (60, EtCF<sub>2</sub>F<sub>3</sub><sup>+</sup>) 109 (100, C<sub>4</sub>H<sub>4</sub>F<sub>3</sub><sup>+</sup>), and 51 (53, CHF<sub>2</sub><sup>+</sup>); (G) 1,1,1,2,3,3-hexafluoro-4-methylpentane (7) (0.27 g, 1.41 mmol, 1.5%) (Found: C, 37.2; H, 4.2%; *M*<sup>+</sup>, 194. Calc. for C<sub>6</sub>H<sub>8</sub>F<sub>6</sub>: C, 37.1; H, 4.2%; *M*, 194), *m/e* 194 (1%, *M*<sup>+</sup>), 93 (56, C<sub>3</sub>H<sub>7</sub>CF<sub>2</sub><sup>+</sup>), 78 (56, C<sub>3</sub>H<sub>4</sub>F<sub>2</sub><sup>+</sup>), and 43 (100, C<sub>3</sub>H<sub>7</sub><sup>+</sup>); (H) 1,1,1,2,3,3-hexafluorohexane (8) (0.40 g, 2.1 mmol, 2.5%) (Found: C, 37.4; H, 4.3%; *M*, 194); *m/e* 194 (trace, *M*<sup>+</sup>), 93 (26%, C<sub>3</sub>H<sub>7</sub>CF<sub>2</sub><sup>+</sup>), 64 (37, C<sub>2</sub>H<sub>2</sub>F<sub>2</sub><sup>+</sup>), and 43 (100, C<sub>3</sub>H<sub>7</sub><sup>+</sup>); (J) 1,1,2-trifluoro-3-methyl-2-trifluoromethylpentane (9) (0.38 g, 1.8 mmol, 2%) (Found: C, 40.1; H, 4.8%; *M*, 208. C<sub>7</sub>H<sub>10</sub>F<sub>6</sub> requires C, 40.4; H, 4.8%; *M*, 208), b.p. 99 °C; *m/e* 208 (trace, *M*<sup>+</sup>), 57 (100%, C<sub>4</sub>H<sub>9</sub><sup>+</sup>), and 51 (13, CHF<sub>2</sub><sup>+</sup>); (K) 1,1,2-trifluoro-2-trifluoromethylhexane (10) (0.26 g, 1.24 mmol, 1.5%) (Found: C, 40.1; H, 4.6%; *M*, 208), b.p. 98 °C, *m/e* 208 (1%, *M*<sup>+</sup>), 57 (12, C<sub>4</sub>H<sub>9</sub><sup>+</sup>), and 43 (100, C<sub>3</sub>H<sub>7</sub><sup>+</sup>); (L) 1,1,1,2,3,3-hexafluoroheptane (1) (1.09 g, 5.2 mmol, 6%) (Found: C, 40.3; H, 4.8; F, 55.0%; *M*, 208. C<sub>7</sub>H<sub>10</sub>F<sub>6</sub> requires C, 40.4; H, 4.8; F, 54.8%; *M*, 208), b.p. 100.5 °C; *m/e* 208 (trace, *M*<sup>+</sup>), 65 (12%, C<sub>2</sub>H<sub>3</sub>F<sub>2</sub><sup>+</sup>), and 43 (100, C<sub>3</sub>H<sub>7</sub><sup>+</sup>); (M) 1,1,1,2,3,3-hexafluoro-4-methylhexane (12) (5.76 g, 27.6 mmol, 32%) (Found: C, 40.7; H, 4.8; F, 54.9%; *M*, 209), b.p. 104.5 °C (lit.,<sup>2b</sup> b.p. 104—105 °C); *m/e* 208 (trace, *M*<sup>+</sup>), 87 (17%, C<sub>5</sub>H<sub>8</sub>F<sup>+</sup>), 65 (17, C<sub>2</sub>H<sub>3</sub>F<sub>2</sub><sup>+</sup>), 59 (17, C<sub>3</sub>H<sub>4</sub>F<sup>+</sup>), and 57 (100%, C<sub>4</sub>H<sub>9</sub><sup>+</sup>).

The three major components from the higher-boiling fraction [(iv) above] were separated by g.l.c. (4-m TXP at 120 °C) to give: (N) 1,1,2,6,6,7,8,8,8-nonafluoro-2-trifluoromethyl-5-methyloctane (13) (0.20 g, 0.8 mmol, 2%) (Found: C, 33.6; H, 2.9; F, 63.7%; *M*<sup>+</sup>, 358. C<sub>10</sub>H<sub>16</sub>F<sub>12</sub> requires C, 33.5; H, 2.8; F, 63.7%; *M*, 358), b.p. 164 °C; *m/e* 358 (trace, *M*<sup>+</sup>), 207 [100%, (*M* - C<sub>3</sub>HF<sub>6</sub>)<sup>+</sup>], and 51 (16, CHF<sub>2</sub><sup>+</sup>); (O) 1,1,1,2,3,3,7,7,8,9,9,9-dodecafluoro-4-methylnonane (14) (1.83 g, 7.0 mmol, 16%) (Found: C, 33.7; H, 2.9; F, 63.7%; *M*<sup>+</sup>, 358), b.p. 170 °C (lit.,<sup>2</sup> b.p. 170 °C); *m/e* 358 (0.5%, *M*<sup>+</sup>), 207 [100, (*M* - C<sub>3</sub>HF<sub>6</sub>)<sup>+</sup>], 187 (94, C<sub>7</sub>H<sub>8</sub>F<sub>5</sub><sup>+</sup>), 159 (46, C<sub>5</sub>H<sub>4</sub>F<sub>5</sub><sup>+</sup>), 77 (60, C<sub>2</sub>H<sub>3</sub>F<sub>2</sub><sup>+</sup>), and 65 (51, C<sub>2</sub>H<sub>3</sub>F<sub>2</sub><sup>+</sup>); (P) 1,1,1,2,3,3,8,8,9,10,10,10-dodecafluorodecane (15) (0.05 g, 0.20 mmol, 0.5%) (Found: C, 33.6; H, 2.9%; *M*<sup>+</sup>, 358 °C), b.p. 172 °C; *m/e* 358 (trace, *M*<sup>+</sup>), 237 (56%, C<sub>8</sub>H<sub>8</sub>F<sub>7</sub><sup>+</sup>), 192 (100, C<sub>6</sub>H<sub>6</sub>F<sub>6</sub><sup>+</sup>), and 91 (74, C<sub>4</sub>H<sub>5</sub>F<sub>2</sub><sup>+</sup>).

The <sup>1</sup>H and <sup>19</sup>F n.m.r. spectra of compounds (3), (5), (7), (8), (12), and (14) were identical with those obtained previously.<sup>10</sup>

(b) *n-Butane under thermal conditions (tube)*. A mixture of the alkane (1.64 g, 30.0 mmol) and hexafluoropropene (1.50 g, 10.0 mmol), heated at 295 °C (120 h), gave unchanged n-butane (1.45 g, 25.0 mmol, 84% recovered), unchanged hexa-

fluoropropene (0.30 g, 2.0 mmol, 20% recovered) and the products given in Table 1.

(c) *n*-Butane under photochemical conditions. In the first experiment a mixture of the alkane (3.60 g, 60.0 mmol) and hexafluoropropene (3.0 g, 20.0 mmol), contained in a silica tube (ca. 300 cm<sup>3</sup>) and irradiated (72 h), gave unchanged *n*-butane (3.25 g, 56.0 mmol, 93% recovered), unchanged hexafluoropropene (2.55 g, 17.0 mmol, 85% recovered) and the products shown in Table 1. In a second experiment a mixture of *n*-butane (6.96 g, 0.120 mol) and hexafluoropropene (6.0 g, 40.0 mmol) contained in two silica tubes (ca. 600 cm<sup>3</sup> total) were irradiated (144 h) with shaking to give unchanged *n*-butane (5.80 g, 0.103 mol, 86% recovered), unchanged hexafluoropropene (3.0 g, 20.0 mmol, 50% recovered), and the products shown in Table 1.

(d) *n*-Butane under peroxide-initiated conditions. A mixture of *n*-butane (3.13 g, 54.0 mmol), hexafluoropropene (3.0 g, 20.0 mmol), and di-*t*-butyl peroxide (0.30 g, 2 mol %), heated in a Pyrex tube (130 °C, 70 h), gave unchanged *n*-butane (2.67 g, 46.0 mmol, 85% recovered), unchanged hexafluoropropene (1.75 g, 12.0 mmol, 60% recovered), and the products shown in Table 1.

(e) *n*-Pentane under thermal conditions. A mixture of *n*-pentane (108 g, 1.46 mol) and hexafluoropropene (75.0 g, 0.50 mol), heated in a rocked autoclave (ca. 1 dm<sup>3</sup>) at 300 °C (120 h), gave (i) a non-condensable gas (1.5 mmol), probably methane; (ii) a low-boiling fraction (16.49 g, 0.105 mol; *M*, 157) consisting of unchanged hexafluoropropene (15.1 g, 0.101 mol, 22% recovered) and a lesser amount (1.39 g) of 1,1,1,2,3,3-hexafluoropropane (4) and low molecular weight saturated hydrocarbons, as shown by g.l.c. (4-m Kel-F at 20 °C) and i.r. spectroscopy; (iii) an intermediate fraction (131.2 g) shown by g.l.c. (8-m TXP at 75 °C) to contain unchanged *n*-pentane (80.1 g, 1.11 mmol, 75% recovered) and twelve other components (A), (C)—(H), (J), (L), (M), (R), and (S) in the ratio 1 : 2 : 1 : 13 : 2 : 4 : 10 : 1 : 11 : 6 : 94 : 39; (iv) a higher-boiling fraction (22.0 g) shown by g.l.c. (8-m TXP at 140 °C) to contain three major components; and (v) a tarry carbonaceous residue (ca. 13 g) which was not examined further.

The two major components (R) and (S) of the intermediate fraction were separated by g.l.c. (7.5-m TXP at 90 °C) to give (R), 1,1,1,2,3,3-hexafluoro-4-methylheptane (16) (25.46 g, 0.115 mol, 29%) (Found: C, 43.1; H, 5.5; F, 51.1%; *M*<sup>+</sup>, 222. C<sub>8</sub>H<sub>12</sub>F<sub>6</sub> requires C, 43.3; H, 5.4; F, 51.3%; *M*, 222), b.p. 120 °C, and (S), 1,1,1,2,3,3-hexafluoro-4-ethylhexane (17) (9.75 g, 43.9 mmol, 11%) (Found: C, 43.2; H, 5.5%; *M*<sup>+</sup>, 222), b.p. 121 °C; the mass spectrum of the mixture of adducts showed peaks at *m/e* 222 (trace, *M*<sup>+</sup>), 69 (31%, CF<sub>3</sub><sup>+</sup>), and 43 (100, C<sub>3</sub>H<sub>7</sub><sup>+</sup>). The remaining components in the fraction were identified, by their g.l.c. retention times and their mass spectra [coupled g.l.c. (7.5-m TXP at 90 °C)—mass spectrometry], as (1) (0.03 g, 0.1 mmol, <0.5%); (3) (0.41 g, 2.4 mmol, 1%); (4) (0.10 g, 0.66 mmol, 0.5%); (5) (3.01 g, 15.9 mmol, 4%); (6) (0.22 g, 1.22 mmol, 0.5%); (7) (0.95 g, 4.90 mmol, 1%); (8) (2.37 g, 12.2 mmol, 3%); (9) (0.25 g, 1.22 mmol, 0.5%); (11) (2.79 g, 13.4 mmol, 3.5%); and (12) (1.52 g, 7.32 mmol, 2%).

Components (T) and (V) were separated from the higher-boiling fraction by g.l.c. (10-m SE 30 at 120 °C) and were identified as 1,1,1,2,3,3,7,7,8,9,9,9-dodecafluoro-4,6-dimethylnonane (18) (13.8 g, 37.1 mmol, 16%) (Found: C, 36.0; H, 3.4%; *M*<sup>+</sup>, 372. C<sub>11</sub>H<sub>12</sub>F<sub>12</sub> requires C, 35.5; H, 3.2%; *M*, 372), b.p. 180 °C; *m/e* 372 (trace, *M*<sup>+</sup>), 184 (42%, C<sub>7</sub>H<sub>5</sub>F<sub>2</sub><sup>+</sup>), 77 (100, C<sub>3</sub>H<sub>3</sub>F<sub>2</sub><sup>+</sup>), and 69 (44, CF<sub>3</sub><sup>+</sup>), and 1,1,1,2,3,3,8,8,9,10,10,10-dodecafluoro-4-methyldecane (19) (6.32 g, 17.3 mmol, 7.5%) (Found: C, 36.0; H, 3.3%; *M*<sup>+</sup>, 372), b.p. 183 °C; *m/e* 372 (trace, *M*<sup>+</sup>), 221 [38%, (*M* - C<sub>3</sub>HF<sub>6</sub>)<sup>+</sup>], 77 (91, C<sub>3</sub>H<sub>3</sub>F<sub>2</sub><sup>+</sup>), 69 (77, CF<sub>3</sub><sup>+</sup>), 65 (100, C<sub>2</sub>H<sub>3</sub>F<sub>2</sub><sup>+</sup>), 43 (67, C<sub>3</sub>H<sub>7</sub><sup>+</sup>), and 41 (72,

C<sub>3</sub>H<sub>5</sub><sup>+</sup>). Component (U) was another 2 : 1 adduct (ca. 0.5 g, ca. 1.3 mmol, 0.5%; *M*<sup>+</sup>, 372), but the remaining four minor components were not identified.

(f) *n*-Butane-hexafluoropropene 1 : 1 adducts. A mixture (1.97 g, 9.50 mmol) of the adducts (9)—(12) (ratio 1.4 : 1 : 4.2 : 22.3) and hexafluoropropene (0.60 g, 4.0 mmol), heated in a Pyrex tube (ca. 100 cm<sup>3</sup>) at 320 °C (120 h), gave (i) a non-condensable gas at -196 °C (0.11 mmol) probably methane; (ii) a low-boiling fraction consisting of unchanged hexafluoropropene (0.21 g, 1.40 mmol, 35% recovered) and small amounts of compound (4) and low molecular weight saturated hydrocarbons; (iii) an intermediate fraction (1.30 g) shown by g.l.c. (8-m TXP at 55 °C) to consist of compounds (1) (0.007 g, 0.022 mmol), (2) (0.005 g, 0.030 mmol, 1% on alkane), (3) (0.021 g, 0.12 mmol, 3%), (4) (trace), (5) (0.096 g, 0.53 mmol, 12%), (6) (0.017 g, 0.094 mmol, 2%), (7) (0.025 g, 0.128 mmol, 3%), (8) (0.031 g, 0.160 mmol, 4%), and unchanged adducts (9)—(12) (1.073 g, 5.16 mmol, 54% recovered); (iv) a higher-boiling fraction (0.63 g) shown by g.l.c. (8-m TXP at 120 °C) to be a mixture of 2 : 1 adducts containing mainly compounds (13) (0.11 g, 0.32 mmol, 7% on alkane, 12% on C<sub>3</sub>F<sub>6</sub>), (14) (0.50 g, 1.42 mmol, 33% on alkane, 55% on C<sub>3</sub>F<sub>6</sub>), and (15) (0.01 g, 0.02 mmol, 0.5% on alkane, 1% on C<sub>3</sub>F<sub>6</sub>); and (v) a tarry residue which was not examined further.

In a second experiment a mixture of 1,1,1,2,3,3-hexafluoro-4-methylhexane (12) (0.45 g, 2.17 mmol) and hexafluoropropene (0.12 g, 0.80 mmol), heated in a Pyrex tube (ca. 30 cm<sup>3</sup>) at 300 °C (72 h), gave unchanged hexafluoropropene (0.09 g, 0.57 mmol, 71% recovered), unchanged 1 : 1 adduct (12) (0.35 g, 1.69 mmol, 78% recovered), and the products shown in Table 2.

A third experiment with a mixture of 1,1,1,2,3,3-hexafluoroheptane (11) (0.48 g, 2.31 mmol) and hexafluoropropene (0.12 g, 0.80 mmol), heated in a Pyrex tube (ca. 30 cm<sup>3</sup>) at 300 °C (72 h), gave unchanged hexafluoropropene (0.075 g, 0.50 mmol, 63% recovered), unchanged 1 : 1 adduct (11) (0.35 g, 1.71 mmol, 74% recovered), and the products shown in Table 2.

*Pyrolysis of the n-Butane-Hexafluoropropene 1 : 1 Adduct Mixture.*—A mixture (1.12 g, 6.40 mmol) of adducts (9)—(12) (ratio 1.4 : 1 : 4.2 : 22.3), heated in a Pyrex tube (ca. 30 cm<sup>3</sup>) at 320 °C (120 h), gave only unchanged adducts (100% recovered).

*Dehydrofluorination of 1,1,1,2,3,3-Hexafluoro-4-methylhexane (12).*—The 1 : 1 adduct (12) (0.413 g, 2.0 mmol) and an excess of dry potassium hydroxide (5 g), heated under reduced pressure in a flask (ca. 100 cm<sup>3</sup>) at 60—70 °C (1 h), gave a fraction (0.25 g) which was separated by g.l.c. (8-m TXP at 55 °C) into its two components (ratio 1 : 18), identified as unchanged (12) (0.02 g, 0.1 mmol, 5% recovered) and 1,1,1,2,3-pentafluoro-4-methylhex-2-ene (20) (0.23 g, 1.22 mmol, 64%) (Found: C, 45.0; H, 4.6; F, 50.2%; *M*, 188. C<sub>7</sub>H<sub>9</sub>F<sub>5</sub> requires C, 44.7; H, 4.8; F, 50.5%; *M*, 188); b.p. 74 °C; λ<sub>max</sub> 5.78 μm (C=C str.); *m/e* 188 (17%, *M*<sup>+</sup>), 159 (40, C<sub>5</sub>H<sub>4</sub>F<sub>5</sub><sup>+</sup>), 95 (41, C<sub>3</sub>H<sub>2</sub>F<sub>3</sub><sup>+</sup>), 69 (55, CF<sub>3</sub><sup>+</sup>), 56 (100, C<sub>4</sub>H<sub>8</sub><sup>+</sup>), and 42 (42, C<sub>3</sub>H<sub>6</sub><sup>+</sup>); <sup>19</sup>F n.m.r. spectroscopy showed that the olefin was a mixture of the (*E*)- and (*Z*)-isomers in the ratio 15 : 85:(*E*)-isomer [CH<sub>3</sub><sup>a</sup>CH<sub>2</sub><sup>b</sup>CH<sup>c</sup>(CH<sub>3</sub>)<sup>d</sup>CF<sup>e</sup>=CF<sup>f</sup>CF<sub>3</sub><sup>g</sup>], δ<sub>F</sub> + 8.0 p.p.m. (dd, F<sub>a</sub>, J<sub>ab</sub> 22.0, J<sub>fg</sub> 11.0 Hz); (*Z*)-isomer, δ<sub>F</sub> + 10.6 (3 F, dd, F<sub>a</sub>, J<sub>fg</sub> 11.0, J<sub>eg</sub> 9.5 Hz), -57.3 (1 F, dqd, F<sub>e</sub>, J<sub>ce</sub> 33, J<sub>fe</sub> 2.4 Hz), and -83.8 p.p.m. (1 F, qd, F<sub>f</sub>); δ<sub>H</sub>, 0.77 (3 H, t, H<sub>a</sub>, J<sub>ba</sub> 7.2 Hz), 1.05 (3 H, d, H<sub>d</sub>, J<sub>cd</sub> 7.2 Hz), 1.20 (2 H, m, H<sub>b</sub>), and 2.54 (1 H, dsex., H<sub>c</sub>, J<sub>bc</sub> 7.2 Hz).

*N.m.r. Spectra.*—(a) <sup>19</sup>F Spectra. The products were of the type CF<sub>3</sub>CHF<sub>2</sub>CF<sub>2</sub>R or CF<sub>3</sub>CFRCHF<sub>2</sub> and were readily dis-

tinguished by their  $^{19}\text{F}$  spectra. Compounds of type  $\text{CF}_3\text{-CH}^{\text{a}}\text{F}^{\text{c}}\text{CF}^{\text{a}}\text{F}^{\text{b}}\text{R}$  showed absorptions in their spectra at  $\delta_{\text{F}} + 2.0 \pm 1.5$  ( $\text{CF}_3$ ),  $-136 \pm 2.3$  ( $\text{CHF}$ ), and  $-21.6$  to  $-44.0$  p.p.m. ( $\text{AB}$ ,  $\text{CF}_2$ ) with the typical H-F geminal coupling (b-c) of *ca.* 44 Hz; other couplings observed were  $a\text{-c} \simeq a\text{-A} \simeq a\text{-B} \simeq c\text{-AB} \simeq 11$ ,  $a\text{-b}$  *ca.* 6,  $b\text{-A}$  7--12,  $b\text{-B}$  *ca.* 6, and  $\text{A-B}$   $270 \pm 10$  Hz.

In contrast the spectra of compounds of type  $\text{CF}_3\text{-CF}^{\text{b}}\text{RCH}^{\text{c}}\text{-F}^{\text{a}}\text{F}^{\text{b}}$  showed absorptions at  $\delta_{\text{F}} + 1.7 \pm 2.8$  ( $\text{CF}_3$ ),  $-106.5 \pm 4$  ( $\text{CF}$ ), and  $-5.42$  to  $-57.8$  p.p.m. ( $\text{AB}$ ,  $\text{CHF}_2$ ) with the typical H-F<sub>2</sub> geminal coupling (c-AB) of *ca.* 54 Hz; other couplings observed were  $a\text{-c} \simeq a\text{-A} \simeq a\text{-B} \simeq b\text{-AB} \simeq 8$ , and  $b\text{-c}$  *ca.* 4 Hz.

(b)  $^1\text{H}$  Spectra. These showed doublet absorptions at  $\delta$   $4.35 \pm 0.2$ , typical of the  $\text{CHF}$  group, or triplet absorptions at  $5.54 \pm 0.2$  p.p.m., typical of the  $\text{CHF}_2$  group. In addition methyl, methylene and methine absorptions of the alkyl groups were observed at  $\delta_{\text{H}}$  *ca.* 0.65 ( $\text{CHMe}$  or  $\text{CH}_2\text{Me}$ ,  $J$  *ca.* 7 Hz), *ca.* 1.15 ( $\text{CFMe}$  or  $\text{CF}_2\text{Me}$ ,  $J$  *ca.* 20 Hz), 1.2-1.4 ( $\text{CH}_2$ ), *ca.* 1.8 ( $\text{CFCH}_2$  or  $\text{CF}_2\text{CH}_2$ ), and *ca.* 2.4 ( $\text{CF}_2\text{CH}$ ).

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