Addition of Free Radicals to Unsaturated Systems. Part XX.[1] The Direction of Radical Addition of Heptafluoro-2-iodopropane to Vinyl Fluoride, Trifluoroethylene, and Hexafluoropropene

By **George L. Fleming, Robert N. Haszeldine,*** and **Anthony E. Tipping,** Chemistry Department, University of Manchester Institute of Science and Technology, Manchester M60 1QD

Heptafluoro-2-iodopropane reacts with vinyl fluoride under photochemical conditions to give a mixture of the 1:1 adducts 1,1,1,2,4-pentafluoro-4-iodo-2-trifluoromethylbutane and 1,1,1,2,3-pentafluoro-4-iodo-2-trifluoromethylbutane in high yield in the ratio 99:1; under thermal conditions the same adducts are formed in the ratio 97:3. Photochemical and thermal reaction with trifluoroethylene affords a mixture of the 1:1 adducts 1,1,1,2,3,4,4-heptafluoro-4-iodo-2-trifluoromethylbutane and 1,1,1,2,3,3,4-heptafluoro-4-iodo-2-trifluoromethylbutane in the ratios 96:4 and 85:15, respectively. In contrast, heptafluoro-2-iodopropane does not react smoothly with hexafluoropropene under comparable conditions.

TRIFLUOROIODOMETHANE has been observed to undergo bidirectional addition with various unsymmetrical olefins including vinyl fluoride,[2,3] trifluoroethylene,[4] and hexafluoropropene.[5] In order to extend the free-radical addition reactions, studied extensively in this department, to a new addend and to compare the results with those obtained previously with trifluoroiodomethane, the reactions under radical conditions of heptafluoro-2-iodo-propane with vinyl fluoride, trifluoroethylene, and hexafluoropropene have been studied. A qualitative study of the reaction of heptafluoro-2-iodopropane with 1,1-difluoroethylene has been reported, with only the 1:1 adduct $(CF_3)_2CF\cdot CH_2\cdot CF_2I$ detected,[6] and its reaction

[1] Part XIX, R. Gregory, R. N. Haszeldine, and A. E. Tipping *J. Chem. Soc.* (C), 1971, 1216.

[2] R. N. Haszeldine, D. W. Keen, and A. E. Tipping, *J. Chem. Soc.* (C), 1970, 414.

[3] R. Gregory, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc.* (C), 1970, 1750.
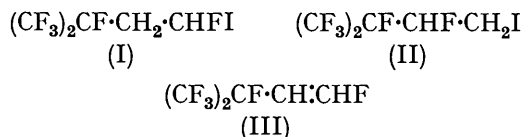
[4] R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 1957, 2800.

[5] J. Brown and R. N. Haszeldine, unpublished results.

[6] R. D. Chambers, J. Hutchinson, R. H. Mobbs, and W. K. R. Musgrave, *Tetrahedron*, 1964, **20**, 497.

with tetrafluoroethylene to afford compounds of the type $(CF_3)_2CF(CF_2 \cdot CF_2)_nI$ $(n = 1—16)$ has been described.[6-8]
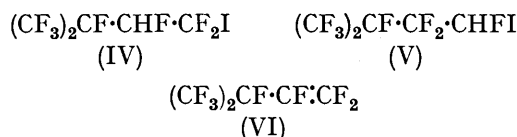
(a) *Vinyl Fluoride.*—Thermal reaction (200°; 16 h) of heptafluoro-2-iodopropane with vinyl fluoride (2·7 : 1·0 molar ratio) gave unchanged olefin (1%), unchanged iodoalkane (63%), and a mixture of the 1 : 1 adducts 1,1,1,2,4-pentafluoro-4-iodo-2-trifluoromethylbutane (I) (97%) and 1,1,1,2,3-pentafluoro-4-iodo-2-trifluoromethylbutane (II) (2%) in the ratio 97 : 3 as estimated by g.l.c. Reaction under photochemical conditions gave a mixture (98%) of the same adducts in the ratio 99 : 1.

$$(CF_3)_2CF \cdot CH_2 \cdot CHFI \qquad (CF_3)_2CF \cdot CHF \cdot CH_2I$$
$$\text{(I)} \qquad\qquad\qquad \text{(II)}$$
$$(CF_3)_2CF \cdot CH\text{:}CHF$$
$$\text{(III)}$$

The structure of the major adduct (I) was established by (i) n.m.r. spectroscopy, which showed (on the basis of chemical shifts and relative intensities) the presence of two equivalent CF_3 groups, a tertiary $\geqslant CF$ group, a CHFI group, and a CH_2 group which appeared as an AB system, (ii) mass spectrometry, which showed the presence of a CHFI group (m/e 159), and (iii) dehydroiodination with powdered potassium hydroxide, which afforded the known[6] 1,3,4,4,4-pentafluoro-3-trifluoromethylbut-1-ene (III) (92%) as a mixture of *cis*- and *trans*-isomers in the ratio 88 : 12 as estimated by n.m.r. spectroscopy.

The structure of the minor adduct was established by its mass spectrum, which showed peaks at m/e 342 (0·1%, M^+), 201 [32%, $(CF_3)_2CF \cdot CHF^+$], and 141 (3%, CH_2I^+).

(b) *Trifluoroethylene.*—Thermal reaction (190°; 16 h) of the iodoalkane with trifluoroethylene (4 : 1 molar ratio), gave unchanged olefin (1%), unchanged iodoalkane (75%), and a mixture (99%) of the 1 : 1 adducts 1,1,1,2,3,4,4-heptafluoro-4-iodo-2-trifluoromethylbutane (IV) (85%) and 1,1,1,2,3,3,4-heptafluoro-4-iodo-2-trifluoromethylbutane (V) (14%) in the ratio 85 : 15 as estimated by g.l.c. and n.m.r. spectroscopy. Photochemical reaction gave the same adducts (98%) in the ratio 96 : 4.

$$(CF_3)_2CF \cdot CHF \cdot CF_2I \qquad (CF_3)_2CF \cdot CF_2 \cdot CHFI$$
$$\text{(IV)} \qquad\qquad\qquad \text{(V)}$$
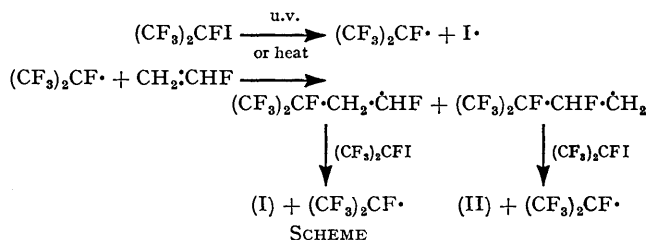$$(CF_3)_2CF \cdot CF\text{:}CF_2$$
$$\text{(VI)}$$

The structure of the major adduct (IV) was established by its n.m.r. and mass spectra and by dehydroiodination with potassium hydroxide to give heptafluoro-3-trifluoromethylbut-1-ene (VI) (96%). The n.m.r. spectra were extremely complex, because (i) the asymmetric carbon atom renders both the CF_3 groups and the fluorine atoms of the CF_2I group non-equivalent, although with the latter group the outer members of the

[7] B.P., 998,668/1965; Neth.P.Appl., 6,609,483/1967; Belg.P., 734,009/1969; B.P., 1,218,528/1971.

expected AB type multiplet were not apparent owing to only a small chemical shift difference, and (ii) few, if any, of the magnetic nuclei present in the molecule were not coupled. As a consequence it was not possible to analyse the band structure and obtain coupling constant data. The observed ^{19}F chemical shifts, however, were in the regions expected. The ^{1}H spectrum showed a single absorption at τ 4·83 which appeared as a complex distorted doublet [$J_{HF}(gem)$ 43·2 Hz]. The mass spectrum showed peaks at m/e 378 (0·1%, M^+) and 177 (16%, CF_2I^+).

The structure of the minor isomer (V) was established from its n.m.r. and mass spectra. The n.m.r. spectra were complex for the same reasons as discussed for the spectra of adduct (IV). The ^{19}F chemical shifts and relative intensities showed the presence of two equivalent CF_3 groups, a tertiary $\geqslant CF$ group, a CHFI group, and two non-equivalent fluorine nuclei in a $>CF_2$ group (J_{AB} *ca.* 290 Hz in the range expected for a $C-CF_2-C$ grouping[9]). The ^{1}H spectrum showed a single absorption at τ 2·81 in the region expected for a CHFI group, which appeared as a doublet [$J_{HF}(gem)$ 48 Hz] of overlapping triplets ($J_{HF_A} \simeq J_{HF_B}$ 21 Hz). The mass spectrum showed peaks at m/e 378 (43%, M^+) and 159 (9%, CHFI$^+$).

(c) *Hexafluoropropene.*—In contrast to the successful additions of the iodoalkane to vinyl fluoride and trifluoroethylene, heptafluoro-2-iodopropane and hexafluoropropene (2 : 1 molar ratio) did not react at 200° (24 h) or photochemically (24 h). A prolonged thermal reaction (200°; 120 h) gave a low conversion into a complex mixture of products as did a benzoyl peroxide-initiated reaction (2 mol %; 190°; 56 h). Successful reaction may therefore be possible under more forcing conditions of temperature and pressure.

Discussion.—The products formed from vinyl fluoride and trifluoroethylene may be explained on the basis of a free-radical chain mechanism involving the $(CF_3)_2CF \cdot$ radical as the chain carrier, *e.g.* as in the Scheme.

$$(CF_3)_2CFI \xrightarrow[\text{or heat}]{\text{u.v.}} (CF_3)_2CF \cdot + I \cdot$$
$$(CF_3)_2CF \cdot + CH_2\text{:}CHF \longrightarrow$$
$$(CF_3)_2CF \cdot CH_2 \cdot \dot{C}HF + (CF_3)_2CF \cdot CHF \cdot \dot{C}H_2$$
$$\downarrow {(CF_3)_2CFI} \qquad\qquad \downarrow {(CF_3)_2CFI}$$
$$\text{(I)} + (CF_3)_2CF \cdot \qquad \text{(II)} + (CF_3)_2CF \cdot$$
$$\text{SCHEME}$$

The high yields of 1 : 1 adducts obtained in the reactions indicate that the adduct ratios are meaningful and the ratios are compared in the Table with those previously obtained for reactions of the same olefins with trifluoroiodomethane.

Major attack of the $R_F \cdot$ radical [$(CF_3)_2CF \cdot$ or $CF_3 \cdot$] occurs on the CH_2 group of vinyl fluoride and on the CHF group of trifluoroethylene, as expected on the

[8] Belg.P., 721,892/1967.
[9] M. G. Barlow, unpublished results and unpublished correlations on data from this department and from the literature.

Isomer ratios and yields for reactions of iodoalkanes with vinyl fluoride and trifluoroethylene

	CH$_2$:CHF *		CHF:CF$_2$ †	
R$_F$I	U.v.	Thermal	U.v.	Thermal
(CF$_3$)$_2$CFI	99:1	97:3	96:4	85:15
	(98%)	(99%)	(98%)	(99%)
CF$_3$I	96:4	89:11	80:20	
	(90%) ^{a}	(96%) ^{b}	(85%) ^{c}	

* Major adduct of type R$_F$CH$_2$·CHFI. † Major adduct of type R$_F$CHF·CF$_2$I.

^{a} Ref. 3. ^{b} Ref. 2. ^{c} Ref. 4.

basis of intermediate radical stability, i.e. R$_F$·CH$_2$·ĊHF more stable than R$_F$CHF·ĊH$_2$ and R$_F$CHF·ĊF$_2$ more stable than R$_F$CF$_2$·ĊHF.

The radical (CF$_3$)$_2$CF· shows slightly greater specificity than CF$_3$· in attack at the least sterically hindered end of the double bond, and this can be attributed to a blend of factors: greater steric requirement for (CF$_3$)$_2$CF·, weaker carbon–iodine bond in (CF$_3$)$_2$CFI and hence a difference in energy of the secondary radical as generated relative to CF$_3$·, and difference in the electrophilicities of the radicals.

It is also interesting that the (CF$_3$)$_2$CF· radical formed by thermal decomposition of the iodoalkane is less specific (of higher energy) in its attack on the olefins than is the same radical formed by photochemical decomposition at ca. 30° (cf. CF$_3$I reactions with vinyl fluoride).

In contrast to the successful reactions of heptafluoro-2-iodopropane with vinyl fluoride and trifluoroethylene to give high yields of 1:1 adducts the iodoalkane was reluctant, presumably for steric reasons, to form a 1:1 adduct with hexafluoropropene under various conditions, although trifluoroiodomethane reacts successfully with this olefin.[5] It has been reported previously that heptafluoro-2-iodopropane reacts thermally with hexafluoropropene in the presence of 2-aminoethanol and copper(I) chloride or zirconium tetrachloride to give products of the type (CF$_3$)$_2$CF·[C$_3$F$_6$]$_n$I ($n = 1$ or 2) in low yield.[8,10]

EXPERIMENTAL

Techniques used were as described previously [1] except that i.r. spectra were recorded on a Perkin-Elmer 257 instrument with sodium chloride optics, mass spectra were recorded on an A.E.I. MS/2H or MS/902 instrument, and g.l.c. employed Perkin-Elmer Fraktometer models 154B or 451 with columns of silicone SE 30 oil (30%) or Kel-F 10 oil (30%) on Celite.

Heptafluoro-2-iodopropane was a gift from Pennwalt Corporation and was purified before use.

Reactions of Heptafluoro-2-iodopropane with Olefins.—
(a) With vinyl fluoride under thermal conditions. The iodoalkane (7·10 g, 24·0 mmol) and vinyl fluoride (0·42 g, 9·1 mmol), sealed in vacuo in a Pyrex ampoule (ca. 300 ml) and heated at 200° (16 h), gave (i) unchanged olefin (0·005 g, 0·1 mmol, 1% recovered), (ii) unchanged iodoalkane (4·49 g, 15·2 mmol, 63% recovered), and (iii) a higher-boiling 1:1 adduct fraction (3·00 g, 8·8 mmol, 99%) (Found: M, 340. Calc. for C$_5$H$_3$F$_8$I: M, 342) which was separated by g.l.c. (6 m Silicone at 80°) into its two components present in the ratio 97:3.

The major component was identified as 1,1,1,2,4-penta-fluoro-4-iodo-2-trifluoromethylbutane (2·91 g, 8·5 mmol,

97%) (Found: C, 17·6; H, 0·9%; M, 340. C$_5$H$_3$F$_8$I requires C, 17·9; H, 0·9%; M, 342), b.p. (Siwoloboff) 110°; λ$_{max.}$ 7·00w (C–H bend), 7·46m, 7·55m, 7·70vs, 8·06vs, 8·54s, 8·85m, 9·10m, 9·18s, 9·70m, 10·00m, 10·50m, 11·70w, 12·94w, 13·50w, and 14·60w μm; m/e 342 (0·5%, M$^+$), 215 [100, (CF$_3$)$_2$CF·CH$_2$·CHF$^+$], 196 (5·4, C$_5$H$_3$F$_7$$^+$), 176 (4·0, C$_5H_2F_6$$^+$), 159 (3·0, CHFI$^+$), 145 (27, C$_4H_2F_5$$^+$), 127 (11, I$^+$), 100 (7·5, C$_2F_4$$^+$), 95 (18, C$_3H_2F_3$$^+$), 77 (6·7, C$_3H_3F_2$$^+$), 75 (4·0, C$_3HF_2$$^+$), 69 (27, CF$_3$$^+$), 51 (35, CHF$_2$$^+$), and 46 (8·8, CH$_2$:CHF$^+$); ^{19}F n.m.r. δ −0·2 (6F, complex, CF$_3$), 62·3 (1F, complex, CHF), and 109·8 (1F, complex, >CF) p.p.m. relative to external trifluoroacetic acid, ^{1}H n.m.r. τ 6·8 (2H, complex AB system, CH$_2$) and 2·89 [1H, complex 8-line m, CHF, J$_{HF}$(gem) 50·3 Hz].

The minor component was identified as 1,1,1,2,3-penta-fluoro-4-iodo-2-trifluoromethylbutane (0·09 g, 0·3 mmol, 2%) (Found: M, 341); λ$_{max.}$ 7·00w (C–H bend), 7·45w, 7·63s, 7·75m, 7·95s, 8·10s, 8·30w, 8·50m, 8·70w, 9·20w, 10·02w, 10·48w, 13·50w, and 14·60w μm; m/e 342 (0·1%, M$^+$), 215 [16, (M − I)$^+$], 201 [32, (CF$_3$)$_2$CF·CHF$^+$], 145 (4·2, C$_4$H$_2$F$_5$$^+$), 141 (3·2, CH$_2I^+$), 131 (32, C$_3F_5$$^+$), 127 (3·2, I$^+$), 114 (29, C$_3H_2F_4$$^+$), 100 (4·2, C$_2F_4$$^+$), 69 (100, CF$_3$$^+$), 65 (13, C$_2H_3F_2$$^+$), 51 (6·4, CHF$_2$$^+$), 46 (3·2, CHF:CH$_2$$^+$), and 31 (11, CF$^+$).

(b) With vinyl fluoride under photochemical conditions. The iodoalkane (7·00 g, 23·7 mmol) and vinyl fluoride (0·42 g, 9·1 mmol) were sealed in vacuo in a silica tube (ca. 200 ml) and the vapour phase was irradiated at 15 cm from a Hanovia S500 u.v. lamp (16 h) to give (i) unchanged olefin (0·17 g, 3·7 mmol, 41% recovered), (ii) unchanged iodoalkane (5·42 g, 18·3 mmol, 77% recovered), and (iii) a mixture of 1:1 adducts (1·81 g, 5·3 mmol, 98%) (Found: M, 340) which was shown by g.l.c. (as before) to contain 1,1,1,2,4-pentafluoro-4-iodo-2-trifluoromethylbutane (1·79 g, 5·24 mmol, 97%) and 1,1,1,2,3-pentafluoro-4-iodo-2-trifluoromethylbutane (0·02 g, 0·06 mmol, 1%) in the ratio 99:1.

(c) With trifluoroethylene under thermal conditions. The iodoalkane (7·01 g, 23·7 mmol) and trifluoroethylene (0·50 g, 6·1 mmol), treated as in (a) at 190° (16 h), gave (i) unchanged olefin (0·01 g, 0·06 mmol, 1% recovered), (ii) unchanged iodoalkane (5·24 g, 17·7 mmol, 75% recovered), and (iii) a higher-boiling 1:1 adduct fraction (2·27 g, 6·0 mmol, 99%) (Found: M, 377. Calc. for C$_5$HF$_{10}$I: M, 378) which was separated by g.l.c. (7 m Kel-F at 90°) into its two components, present in the ratio 85:15.

The major component was 1,1,1,2,3,4,4-heptafluoro-4-iodo-2-trifluoromethylbutane (1·93 g, 5·1 mmol, 85%) (Found: C, 16·2; H, 0·4%; M, 378. C$_5$HF$_{10}$I requires C, 15·9; H, 0·3%; M, 378), b.p. (Siwoloboff) 98·5°; λ$_{max.}$ 3·42w (C–H str.), 7·20m, 7·40m, 7·65s, 7·85vs, 7·95vs, 8·27s, 8·45s, 8·60s, 8·85s, 9·05s, 9·20s, 9·60m, 9·90m, 10·32s, 10·59s, 12·38m, 12·60w, 13·01w, 13·60w, 14·30m (CF$_3$ def.), and 15·00w μm; m/e 378 (0·1%, M$^+$), 251 [88, (M − I)$^+$], 213 (13, C$_5$HF$_8$$^+$), 209 (6·3, CHF·CF$_2I^+$), 190 (3·8, C$_2HF_2I^+$), 181 (3·1, C$_4F_7$$^+$), 177 (16, CF$_2I^+$), 163 (19, C$_4HF_6$$^+$), 131 (6·3, C$_3F_5$$^+$), 127 (31, I$^+$), 119 (3·8, C$_2F_5$$^+$), 113 (23, C$_3HF_4$$^+$), 101 (9·3, C$_2HF_4$$^+$), 100 (3·1, C$_2F_4$$^+$), 93 (6·3, C$_3F_3$$^+$), 82 (21, CHF:CF$_2$$^+$), 75 (6·3, C$_3HF_2$$^+$), 69 (100, CF$_3$$^+$), 62 (3·8, C$_2F_2$$^+$), 51 (16, CHF$_2$$^+$), and 31 (8·1, CF$^+$); ^{19}F n.m.r. δ −4·8 and −1·0 (complex, 2 × CF$_3$), 24·0 (complex AB system, CF$_2$I), 110·8 (complex, >CF), and 115·5 (complex, CHF) p.p.m. relative to external trifluoroacetic acid, ^{1}H n.m.r. τ 4·83 [ddtq, CHF, J$_{HF}$(gem) 43·2 Hz].

^{10} Belg.P., 744,646/1969.

The minor component was 1,1,1,2,3,3,4-*heptafluoro*-4-*iodo*-2-*trifluoromethylbutane* (0·34 g, 0·9 mmol, 14%) (Found: C, 16·2; H, 0·4%; M, 378), b.p. (Siwoloboff) 103°; $\lambda_{max.}$ 7·20w, 7·45m, 7·68s, 7·88vs, 7·96vs, 8·45s, 8·50s, 9·04w, 9·20m, 10·13s, 10·58w, 12·41w, 12·60w, 13·02w, 13·60w, 14·43w, 14·57w, 15·00m, and 15·60w μm; m/e 378 (43%, M^+), 251 [32, $(M - I)^+$], 213 (11, $C_5HF_8^+$), 209 (9, $CF_2 \cdot CHFI^+$), 190 (5·1, $C_2HF_2I^+$), 177 (4·1, CF_2I^+), 163 (15, $C_4HF_6^+$), 159 (9, $CHFI^+$), 131 (4·0, $C_3F_5^+$), 127 (25, I^+), 113 (11, $C_3HF_4^+$), 101 (22, $C_2HF_4^+$), 82 (18, $CF_2 \cdot CHF^+$), 75 (5·2, $C_3HF_2^+$), 69 (100, CF_3^+), 51 (18, CHF_2^+), and 31 (9, CF^+); ^{19}F n.m.r. δ −4·4 (complex, 2 × CF_3), 31·8 (complex AB system, CF_2, J_{AB} 290 Hz), 88·2 (complex, CHF), and 110·8 (complex, $\gtrsim$CF) p.p.m. relative to external trifluoroacetic acid, ^{1}H n.m.r. τ 2·81 [d overlapping t, CHF, $J_{HF}(gem)$ 48 Hz, $J_{HA} \simeq J_{HB}$ 21 Hz].

(d) *With trifluoroethylene under photochemical conditions.*
The iodoalkane (11·01 g, 38·5 mmol) and trifluoroethylene (0·70 g, 8·5 mmol), treated as in (b) (96 h), gave (i) unchanged olefin (0·34 g, 4·2 mmol, 49% recovered), (ii) unchanged iodoalkane (9·78 g, 34·2 mmol, 89% recovered), and (iii) a higher-boiling 1 : 1 adduct fraction (1·60 g, 4·20 mmol, 98%) shown by g.l.c. [as in (c)] to contain 1,1,1,2,3,4,4-heptafluoro-4-iodo-2-trifluoromethylbutane (1·52 g, 4·03 mmol, 94%) and 1,1,1,2,3,3,4-heptafluoro-4-iodo-2-trifluoromethylbutane (0·08 g, 0·17 mmol, 4%), present in the ratio 96 : 4.

(e) *With hexafluoropropene under thermal conditions.* The iodoalkane (6·73 g, 22·7 mmol) and hexafluoropropene (4·50 g, 30·0 mmol), treated as in (a) at 200° (120 h), gave (i) unchanged olefin (4·23 g, 28·2 mmol, 94% recovered), (ii) unchanged iodoalkane (5·84 g, 19·7 mmol, 87% recovered), and (iii) a higher-boiling fraction (1·12 g, 97%) which was shown by g.l.c. (2 m Silicone at 90°) to contain at least six components and was not examined further. A reaction at the same temperature for a shorter time (24 h) gave only unchanged reactants, as did a photochemical reaction carried out as in (b) (24 h).

(f) *With hexafluoropropene in the presence of benzoyl peroxide.* The iodoalkane (8·50 g, 28·7 mmol), hexafluoropropene (2·13 g, 14·2 mmol), and benzoyl peroxide (0·26 g, 1·0 mmol), heated as in (a) at 190° (56 h), gave (i) unchanged olefin (2·00 g, 13·3 mmol, 94% recovered), (ii) unchanged iodoalkane (7·82 g, 26·4 mmol, 92% recovered), and (iii) a higher-boiling fraction (0·21 g) which was shown

by g.l.c. [as in (e)] to contain at least five components and was not examined further.

Reaction of 1,1,1,2,4-*Pentafluoro*-4-*iodo*-2-*trifluoromethylbutane* (I) *with Potassium Hydroxide.*—The adduct (3·04 g, 8·9 mmol), condensed *in vacuo* onto an excess of dry, powdered potassium hydroxide (*ca.* 10 g) and left at room temperature (1 h), gave 1,3,4,4,4-pentafluoro-3-trifluoromethylbut-1-ene (III) (1·75 g, 8·2 mmol, 92%) (Found: C, 28·1; H, 0·9%; M, 214. Calc. for $C_5H_2F_8$: C, 28·0; H, 1·0%; M, 214), b.p. (Siwoloboff) 49°; m/e 214 (29%, M^+), 195 [14, $(M - F)^+$], 176 (25, $C_5H_2F_6^+$), 145 (100, $CF_3 \cdot CF \cdot CH \cdot CHF^+$), 126 (4·4, $C_4H_2F_4^+$), 100 (2·3, $C_2F_4^+$), 95 (93, $C_3H_2F_3^+$), 75 (17, $C_3HF_2^+$), 69 (40, CF_3^+), 51 (4·7, CHF_2^+), and 31 (6·7, CF^+). The ^{1}H and ^{19}F n.m.r. spectra were in agreement with those reported [6] and showed the presence of the *cis*- and *trans*-olefin isomers in the ratio 88 : 12.

Reaction of 1,1,1,2,3,4,4-*Heptafluoro*-4-*iodo*-2-*trifluoromethylbutane* (IV) *with Potassium Hydroxide.*—The adduct (2·32 g, 6·1 mmol), treated with potassium hydroxide as in the previous experiment, gave unchanged adduct (0·49 g, 1·3 mmol, 21% recovered) and *heptafluoro*-3-*trifluoromethylbut*-1-*ene* (VI) (1·20 g, 4·6 mmol, 96%) (Found: C, 23·7%; M, 250. C_5F_{10} requires C, 24·0%; M, 250), b.p. (isoteniscope) 27·0°; $\lambda_{max.}$ 3·68m, 4·08m, 4·13m, 5·58vs (C:C str.), 7·35vs, 7·56vs, 7·70vs, 7·82vs, 8·03vs, 8·50s, 8·70s, 8·92s, 10·20vs, 10·40s, 10·85s, 11·10s, 13·30s, 13·82s, 14·20s, and 15·23s μm; m/e 250 (98%, M^+), 231 [23, $(M - F)^+$], 181 [77, $(M - CF_3)^+$], 169 [23, $(CF_3)_2CF^+$], 162 [14, $(M - CF_4)^+$], 150 (17, $C_3F_6^+$), 131 (55, $C_3F_5^+$), 119 (9, $C_2F_5^+$), 112 (13, $C_3F_4^+$), 100 (36, $C_2F_4^+$), 93 (68, $C_3F_3^+$), 74 (14, $C_3F_2^+$), 69, (100, CF_3^+), 50 (8, CF_2^+), and 31 (41, CF^+); ^{19}F n.m.r. δ 0·4 (dddd, F_a, J_{ad} 8·3, J_{ab} 7·6, J_{ac} 3·7, J_{ae} 0·9 Hz), 14·2
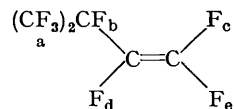
(dddsept, F_e, J_{ec} 58·5, J_{ed} 39·5, J_{eb} 3·1 Hz), 32·1 (dddsept, F_c, J_{cd} 118·2, J_{cb} 43·4 Hz), and 134·2 (complex, F_b and F_d, J_{bd} 12·8 Hz) p.p.m. relative to external trifluoroacetic acid.