# Addition of Free Radicals to Unsaturated Systems. Part XXI.[1] Reactions of 1*H*-Pentafluoropropene with Bromine, Hydrogen Bromide, and Trifluoroiodomethane under Free-radical Conditions

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1*H*-Pentafluoropropene, as a 95 : 5 mixture of *cis*- and *trans*-isomers, reacts with bromine in light to give a 75 : 25 mixture of the *threo*- and *erythro*-dibromides which on dehydrobromination affords a mixture of *cis*- and *trans*-1-bromo-1,2,3,3,3-pentafluoropropene. Photochemical reaction of the olefin with hydrogen bromide gives as the major products a mixture of *erythro*- and *threo*-1-bromo-1,2,3,3,3-pentafluoropropane and 2-bromo-1,1,1,2,3-pentafluoropropane in the ratio 70 : 16. The *threo*-adduct undergoes dehydrobromination to give a mixture of *cis*- and *trans*-1*H*-pentafluoropropene; the two other isomers afford the *cis*-olefin exclusively. Trifluoroiodomethane reacts with the olefin under photochemical or thermal conditions to give a mixture of *erythro*- and *threo*-1,1,1,2,3,4,4,4-octafluoro-2-iodobutane and 1,1,1,2,3-pentafluoro-3-iodo-2-trifluoromethylpropane in the ratios 56 : 40 : 4 and 50 : 43 : 7, respectively; dehydroiodination of the two former adducts separately yields *trans*-octafluorobut-2-ene and a 95 : 5 mixture of the *cis*- and *trans*-olefins, respectively.

FLUORO-OLEFINS react readily under free-radical conditions with bromine (photochemical initiation) and hydrogen bromide or trifluoroiodomethane (thermal or photochemical initiation), with the bromine atom or the trifluoromethyl radical as chain carrier.

The reactions of 1*H*-pentafluoropropene (I) with various nucleophiles [2,3] and with *N*-bromobistrifluoromethylamine under free radical conditions [3] have been studied, and reactions with bromine, hydrogen bromide, and trifluoroiodomethane under free-radical conditions are now reported. In all the reactions a 95 : 5 mixture of the *cis*- and *trans*-isomers of the olefin (I) was used.

After treatment of the olefin (I) with bromine (1·3 : 1·0 molar ratio) in artificial light 26% of the former was recovered and the 1 : 1 adduct 2,3-dibromo-1,1,1,2,3-pentafluoropropane (II) (93%) was obtained. The adduct

$CF_3{\cdot}CF{:}CHF$ (I) $\qquad$ $CF_3{\cdot}CFBr{\cdot}CHFBr$ (II)

was separated by g.l.c. into its two stereoisomers, present in the ratio 75 : 25 and identified on the basis of the reactions of the major isomer (IIa) and of a 71 : 29 mixture

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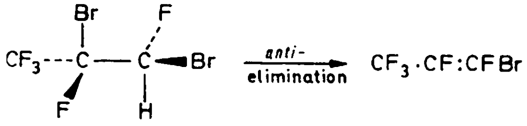
[1] Part XX, G. L. Fleming, R. N. Haszeldine, and A. E. Tipping, *J.C.S. Perkin I*, **1973**, 574.

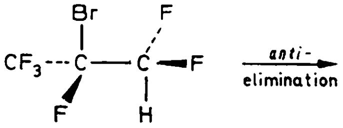
[2] R. Fontanelli, G. Paschetta, V. M. Tacchi, and D. Sianesi, *Ann. Chim.* (*Italy*), 1969, **59**, 211.

[3] R. N. Haszeldine, J. R. McAllister, and A. E. Tipping, unpublished results.

of the isomers (IIa and b) with potassium hydroxide. The major adduct (IIa) afforded 1-bromo-1,2,3,3,3-pentafluoropropene (79%) as an 8 : 92 mixture of *cis*- and *trans*-isomers (IIIa and b), whereas the mixture (IIa and b) gave a mixture (95%) of the same olefins (III) in the ratio 24 : 76. Thus the minor adduct isomer (IIb) must have given the olefins (IIIa and b) in the ratio 62 : 38. The olefins were identified on the basis of the magnitudes of their respective $J_{FF}$ values (*trans* 139·2; *cis* 18·4 Hz).

Since the major adduct (IIa) yielded mainly the *trans*-olefin (IIIb) and the minor adduct (IIb) mainly the *cis*-olefin (IIIa) it is considered that adduct (IIa) is the *threo*-isomer and adduct (IIb) is the *erythro*-isomer. These assignments agree with the structures assigned to the dibromides from a consideration of n.m.r. coupling constants (Table 1).


(IIa) (IIIb) (*trans*)


(IIb) (IIIa) (*cis*)

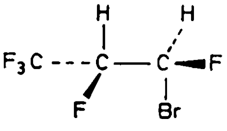
Since both dibromides gave mixtures of the olefins (IIIa and b), a certain proportion of dehydrobromination must occur either by a *syn*-elimination or by an *E*1cB mechanism involving the intermediate carbanion $\bar{C}FBr\cdot CFBr\cdot CF_3$.

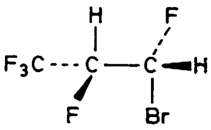
Separation of the products of photochemical reaction of hydrogen bromide with the olefin (I) (molar ratio *ca.* 4 : 1) gave unchanged hydrogen bromide (29%), hydrogen (39%), bromine, a mixture (83%) of three 1 : 1 adducts, and a mixture (14%) of the dibromides (IIa and b) in the ratio 5 : 2; reaction was not observed when a mixture of the reactants was kept at room temperature in the dark (7 days).

The 1 : 1 adducts were identified as 3-bromo-1,1,1,2,3-pentafluoropropane (IV) (68%) (two stereoisomers in the ratio 49 : 21) and 2-bromo-1,1,1,2,3-pentafluoropropane (V) (15%) by spectral evidence and by their reaction with potassium hydroxide. The n.m.r. and mass spectra of compound (V) are in complete agreement with the assignment. On dehydrobromination with potassium hydroxide the *cis*-isomer of olefin (I) (83%) was isolated as the exclusive product. The mass and n.m.r. spectra of the two isomers of structure (IV) are also in agreement with the proposed structure.

$CF_3\cdot CHF\cdot CHFBr$ (IV) $CF_3\cdot CFBr\cdot CH_2F$ (V)

Reaction of the major adduct of structure (IV) with potassium hydroxide gave exclusively the *cis*-isomer of the olefin (I) (88%), whereas the minor adduct gave a mixture (81%) of the *cis*- and *trans*-isomers of the olefin (I) in the ratio 38 : 62. An *E*2 *anti*-elimination of hydrogen bromide from the *erythro*-isomer of (IV) would give *cis*-1*H*-pentafluoropropene whereas a similar elimination from the *threo*-isomer would afford the corresponding *trans*-olefin. Thus the observed results suggest that the major isomer is the *erythro*-adduct (IVa) and the minor isomer is the *threo*-adduct (IVb). These assignments were confirmed by a detailed study of the n.m.r. coupling constants (Table 1).


(IVa)


(IVb)

The observation that the *threo*-isomer (IVb) on dehydrobromination affords a reasonable yield of the *cis*-isomer of olefin (I) as well as the expected *trans*-isomer implies that either an *E*2 *syn*-elimination or elimination *via* an intermediate carbanion is competing with the major *E*2 *anti*-elimination.

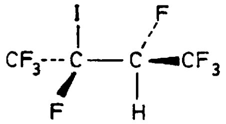
An *anti*-addition of hydrogen bromide to the 95 : 5 *cis* : *trans* mixture of olefin (I) *via* attack by a bromine atom on the terminal CHF group would give the *erythro*- (IVa) and *threo*- (IVb) adducts in the ratio 95 : 5. The observed ratio of 49 : 21 shows that *anti*-addition is preferred but is not exclusive.

Separation of the products of photochemical reaction of trifluoroiodomethane with the olefin (I) (*ca.* 3 : 1 molar ratio) gave hexafluoroethane (7%), contaminated with traces of trifluoromethane and silicon tetrafluoride, unchanged trifluoroiodomethane (73% recovered), unchanged olefin (I) (21% recovered), and a mixture consisting of three major components (ratio 4 : 56 : 40) and five minor components (*ca.* 4% of mixture). The three major components were identified as 1,1,1,2,3-pentafluoro-3-iodo-2-trifluoromethylpropane (VI) (3%) and 1,1,1,2,3,4,4,4-octafluoro-2-iodobutane (VII) (78%) (two stereoisomers).

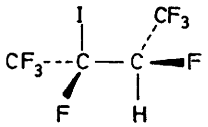
The products of a thermally initiated reaction of trifluoroiodomethane with the olefin (I) (molar ratio *ca.* 3·5 : 1) at 225° were unchanged trifluoroiodomethane (74% recovered), small amounts of hexafluoroethane, trifluoromethane, and silicon tetrafluoride, and a mixture of five minor components (*ca.* 4%), the 1 : 1 adduct (VI) (6%), and the two stereoisomers of adduct (VII) (77%), present in the ratio 42 : 35. The n.m.r. spectra of the adduct (VI), which showed an absence of coupling between the proton and a $CF_3$ group, the mass spectrum, which showed a peak at *m*/*e* 159 ($CHFI^+$), and the lack of reaction of the adduct with potassium hydroxide (no $>$CH–CI$<$ grouping) prove the assigned structure conclusively. The n.m.r. spectra of both isomers of the adduct (VII) showed vicinal $CF_3$–H coupling, the mass

$(CF_3)_2CF\cdot CHFI$ (VI) $CF_3\cdot CFI\cdot CHF\cdot CF_3$ (VII) spectra showed bands at *m/e* 227 ($CF_3\cdot CFI^+$) and 113 ($CF_3\cdot CHF^+$), and reaction of both isomers with potassium hydroxide afforded octafluorobut-2-ene. These observations verify the structure (VII).

The major isomer of the adduct (VII) on dehydroiodination gave *trans*-octafluorobut-2-ene (91%), as expected for an *E*2 *anti*-elimination from the *erythro*-isomer (VIIa). The minor adduct gave a mixture (99%) of *cis*- and *trans*-octafluorobut-2-ene in the ratio 95 : 5, which suggests strongly that it is the *threo*-isomer (VIIb). These assignments were confirmed by a consideration of n.m.r. coupling constants (see Table 1).



(VIIa)



(VIIb)

The adduct ratios [(VIIa) : (VIIb)] observed in these reactions (photochemical 1·4 : 1; thermal 1·2 : 1) show that *anti*-addition to the olefin (I), *via* trifluoromethyl radical attack on the terminal CHF group, is more preferred in the photochemical than in the thermal reaction.

Bidirectional radical attack on the olefin (I) by both the bromine atom and the trifluoromethyl radical is thus observed. The ratio found for bromine atom attack (82% on the CHF group and 18% on the $CF_3\cdot CF$ group) is not very meaningful because the olefin dibromide (II) (14%) is also formed and this product could result from attack on either vinylic group. If the dibromide (II) is formed exclusively by (i) attack of the bromine atom on the CHF group and (ii) attack on the $CF_3\cdot CF$ group, the ratios for bidirectional bromine atom attack on the olefin (I) are 85 : 15 and 70 : 30, respectively; thus a ratio of $78 \pm 8 : 22 \mp 8$ may be taken as representing bromine atom attack on the CHF and $CF\cdot CF_3$ groups.

The yields of the 1 : 1 adducts (VI) and (VII) obtained from the photochemical (82%) and thermal (83%) trifluoroiodomethane reactions were also lower than desirable, probably owing mainly to the formation of small amounts of non-volatile telomeric material and compounds derived from further reaction of the intermediate radicals $CF_3\cdot CFI\cdot\dot{C}F\cdot CF_3$ and $(CF_3)_2CF\cdot\dot{C}FI$, produced by trifluoromethyl radical abstraction of hydrogen from the adducts (VI) and (VII). With this limitation the ratio of trifluoromethyl radical attack on olefin (I) may be taken as occurring to the extent of *ca.* 94% on the CHF group and *ca.* 6% on the $CF_3\cdot CF$ group in both the photochemical and thermal reactions.

From the observed ratios of bromine atom and trifluoromethyl radical attack on each end of the double bonds in hexafluoropropene (Br·, *ca.* 60% on the $CF_2$ group;[4] $CF_3\cdot$, 80% on the $CF_2$ group[5]) and trifluoroethylene (Br·, *ca.* 60% on the CHF group;[6] $CF_3\cdot$, 80% on the CHF group[6]) the ratios of bromine atom and trifluoromethyl radical attack on the CHF and $CF_3\cdot CF$ groups in olefin (I) can be roughly predicted to be *ca.* 70 : 30 and *ca.* 94 : 6, respectively.

The olefin (I) would be expected to be polarised as $CF_3\cdot\overset{\delta-}{C}F{:}\overset{\delta+}{C}HF$, and the observed higher proportion of bromine atom attack on the $CF_3\cdot CF$ group as compared with trifluoromethyl radical attack is in accord with the reported greater electrophilicity of the bromine atom.[7]

One interesting feature of the dehydrohalogenation reactions of the various 1 : 1 adducts was the apparent preference for the formation of *cis*-CF:CF systems from certain stereoisomeric pairs of adducts and for the formation of *trans*-CF:CF systems from other adduct pairs. It has been reported[8] that with the olefin CHF:CHF electronic factors afford particular stability to the *cis*-CF:CF grouping with respect to *trans*-CF:CF.

The present results suggest that the *cis*-isomer is preferred with the olefin $CF_3\cdot CF{:}CHF$ and the *trans*-isomers are preferred with the olefins $CF_3\cdot CF{:}CFBr$ and $CF_3\cdot CF{:}CF\cdot CF_3$. The preference for the *trans*-configuration is, however, probably not primarily associated with the presence of two other bulky groups in the olefin because the *cis*-isomers of the olefins $(CF_3)_2N\cdot CF{:}CF\cdot CF_3$ and $(CF_3)_2N\cdot CF{:}CF\cdot N(CF_3)_2$ are apparently preferred in dehydrohalogenation of the stereoisomers of the compounds $(CF_3)_2N\cdot CHF\cdot CFBr\cdot CF_3$[3] and $(CF_3)_2N\cdot CHF\cdot CFBr\cdot N(CF_3)_2$,[9] respectively.

*Nuclear Magnetic Resonance Spectra.*—The assignments of *erythro*- and *threo*-structures to the individual stereoisomers of the adducts (II), (IV), and (VII) were made on the basis of relevant n.m.r. coupling constants. These are shown in Table 1 together with reported n.m.r. data for a related compound. In this respect it is important to correct certain n.m.r. assignments for the two stereoisomers of formula $\overset{A}{CF_3}\cdot C\overset{B}{H}\overset{C}{F}\cdot C\overset{D}{H}I\cdot\overset{E}{CF_3}$ which we reported previously[10] as shown in Table 2. On the basis of these assignments the major isomer was considered to have the *erythro*-configuration and the minor isomer the *threo*-configuration. However we have been informed that recent mainly unreported work on the magnitudes of $CF_3,CF_3$ couplings in 1 2-di(bistrifluoromethyl) compounds has shown that the magnitudes of *gauche*- and *trans*-couplings are *ca.* 10 and *ca.* 2 Hz, respectively.[11] The observed AE couplings 0·9 and 2·1 Hz, are therefore *trans*-couplings and the CE coupling of 15·0 Hz observed in the spectrum of the minor isomer must be a *gauche*- and not a *trans*-coupling although it is twice as large as the *gauche* CE coupling in the spectrum of the major isomer. On this basis the conformations of the major and minor isomers are (VIIIa and b), respectively, with the major adduct being the *threo*-isomer

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[4] F. W. Stacey and J. F. Harris, *J. Org. Chem.*, 1962, **27**, 4089.

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

[6] R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 1957, 2800.

[7] P. I. Abell, *Trans. Faraday Soc.*, 1964, **60**, 2214.

[8] W. A. Sheppard and C. M. Sharts, 'Organic Fluorine Chemistry,' Benjamin, New York, 1969.

[9] G. L. Fleming, R. N. Haszeldine, and A. E. Tipping, *J.C.S. Perkin I*, 1972, 1877.

[10] R. Gregory, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc.* (*C*), 1970, 1750.

[11] F. J. Weigert (whom we thank), personal communication.

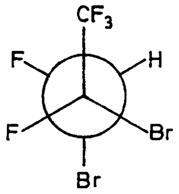
TABLE 1

N.m.r. coupling constants

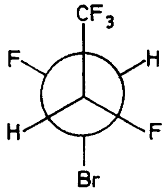
| Compound | Coupling | *erythro*-Isomer $J$/Hz | Inference | *threo*-Isomer $J$/Hz | Inference |
|---|---|---|---|---|---|
| A B CD<br>$CF_3\cdot CHBr\cdot CHFBr$ * | BC | 2·8 | *gauche* | 5·5 | *trans* |
| | BD | 19·8 | *trans* | 7·9 | *gauche* |
| | AD | 7·9 | *gauche* | 11·3 | *gauche* |
| A B C D<br>$CF_3\cdot CFBr\cdot CHFBr$<br>(II) | AD | 11·8 | *gauche* | 9·4 | *gauche* |
| | BC | 13·4 | *trans* | 2·2 | *gauche* |
| | BD | 22·0 | *gauche* | 37·8 | *trans* |
| A BC DE<br>$CF_3\cdot CHF\cdot CHFBr$<br>(IV) | AE | 9·8 | *gauche* | 8·7 | *gauche* |
| | BD | 5·5 | *trans* | 2·8 | *gauche* |
| | BE | 6·7 | *gauche* | 18·1 | *trans* |
| | CD | 8·4 | *gauche* | 17·2 | *trans* |
| | CE | 30·9 | *trans* | 13·9 | *gauche* |
| A BC D E<br>$CF_3\cdot CHF\cdot CFI\cdot CF_3$<br>(VII) | AD | 14·4 | *trans* | 10·9 | *gauche* |
| | AE | 2·2 | *trans* | 3·5 | *trans* |
| | BD | 4·6 | *gauche* | 17·5 | *trans* |
| | CD | 33·1 | *trans* | 20·5 | *gauche* |
| | CE | 7·6 | *gauche* | 13·8 | *gauche* |

* Ref. 11.

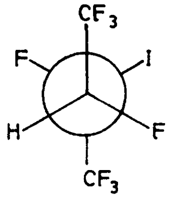
From these assignments the preferred conformations of the *erythro*-[(IIb), (IVa), (VIIa)] and *threo*-[(IIa), (IVb), (VIIb)] isomers are:



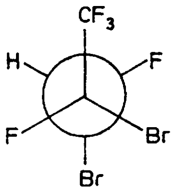
(IIb)



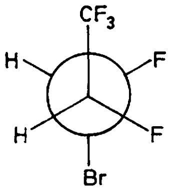
(IVa)



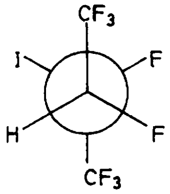
(VIIa)



(IIa)



(IVb)



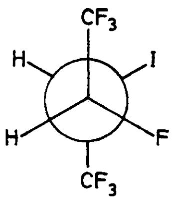
(VIIb)

TABLE 2

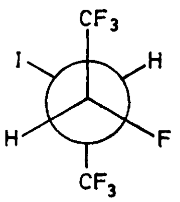
N.m.r. assignments for $CF_3\cdot CHF\cdot CHI\cdot CF_3$

| Coupling | Major isomer $J$/Hz | Inference | Minor isomer $J$/Hz | Inference |
|---|---|---|---|---|
| BD | 1·8 | *gauche* | 7·7 | *trans* |
| CD | 24·4 | *trans* | 13·3 | *gauche* |
| CE | 6·4 | *gauche* | 15·0 | *trans* |
| AE | 0·9 | | 2·1 | |

and the minor adduct the *erythro*-isomer, and not *vice versa* as reported previously.



(VIIIa)



(VIIIb)

## EXPERIMENTAL

Reactants and products were manipulated, where possible, in a vacuum system to avoid contamination with air or moisture.

Products were separated by fractional condensation *in vacuo* or by g.l.c. [Pye model 104 or Perkin-Elmer F21 machine; columns packed with Celite impregnated with dinonyl phthalate (DNP) (10% by weight)] and were identified by molecular weight determination (Regnault's method), elemental analysis, i.r. spectroscopy (Perkin-Elmer 257 spectrophotometer fitted with sodium chloride optics), n.m.r. spectroscopy (Perkin-Elmer R10 instrument operating at 60·0 MHz for $^1H$ and 56·46 MHz for $^{19}F$ or a Varian HA 100 instrument operating at 100·0 MHz for $^1H$ and 94·1 MHz for $^{19}F$ and using internal tetramethylsilane and external trifluoroacetic acid as the respective references), and mass spectrometry (A.E.I. MS902 machine). Spectroscopic data for compounds marked with an asterisk are available in Supplementary Publication No. SUP 20931 (10 pp.).†

Photochemical reactions were carried out in silica tubes (*ca.* 300 ml) at a distance of *ca.* 15 cm from a Hanovia S500 medium-pressure lamp.

1*H*-Pentafluoropropene was prepared (84%) as a 95 : 5 mixture of *cis*- and *trans*-isomers by hydrogenation of hexafluoropropene over palladium–alumina and dehydrofluorination of the resultant adduct.[12]

*Reactions of* 1H-*Pentafluoropropene* (I).—(a) *With bromine.* A mixture of the olefin (1·92 g, 14·6 mmol) and bromine (1·86 g, 11·5 mmol), sealed in a Pyrex tube (*ca.* 300 ml) and irradiated (5 h) at 15 cm from a tungsten-filament lamp (300 W), gave unchanged olefin (0·50 g, 3·8 mmol, 26% recovered) and a higher-boiling fraction (2·96 g) which was separated by g.l.c. (6 m DNP at 100°) into its two components: (i) threo-2,3-*dibromo*-1,1,1,2,3-*pentafluoropropane* (IIa) * (2·22 g, 7·5 mmol, 70%) (Found: C, 12·5; H, 0·5%; *M*, 292. $C_3HBrF_5$ requires C, 12·3; H, 0·3%; *M*, 292), b.p. (Siwoloboff) 90°; and (ii) the erythro-*isomer* (IIb) * (0·74 g, 2·5 mmol, 23%) [Found: C, 12·6; H, 0·5%; *M* (mass spec.), 292].

In a second experiment the olefin (1·86 g, 14·1 mmol) and bromine (6·2 g, 38·0 mmol) sealed in a Pyrex tube (*ca.* 300 ml) were kept at room temperature in the dark (56 days). The products were treated with mercury to remove the excess of bromine and gave unchanged olefin (1·72 g, 13·0 mmol, 94% recovered) and a mixture (0·30 g, 1·03 mmol, 94%) of the *threo*- and *erythro*-dibromides in the ratio 76 : 24 as estimated by g.l.c. (2 m DNP at 70°).

In a third experiment a mixture of the olefin (1·43 g, 10·7 mmol), bromine (5·9 g, 37·0 mmol), and aluminium bromide (0·25 g) sealed in a Pyrex tube (*ca.* 300 ml) was kept at room temperature in the dark (32 days). The products were worked up as in the previous experiment to give unchanged olefin (1·25 g, 9·6 mmol, 89% recovered) and a mixture (0·34 g, 1·17 mmol, 98%) of the *threo*- and *erythro*-dibromides in the ratio 73 : 27 as estimated by g.l.c. (as before).

(b) *With hydrogen bromide.* A mixture of the olefin (1·99 g, 15·1 mmol) and hydrogen bromide (3·53 g, 58·0 mmol) sealed in a silica tube (*ca.* 300 ml) was irradiated (48 h). The products were treated with mercury to remove the bromine formed in the reaction to give hydrogen (0·015 g, 7·5 mmol, 39% based on HBr consumed), unchanged hydrogen bromide (1·28 g, 15·7 mmol, 29% recovered), and a mixture (3·31 g) which was separated by

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† For details of Supplementary Publications see Notice to Authors No. 7 (*J.C.S. Perkin I*, 1973, Index Issue.)

[12] D. Sianesi and R. Fontanelli, *Ann. Chim.* (*Italy*), 1965, **55**, 850.

g.l.c. (6 m DNP at 100°) into its five components, present in the ratio 16 : 49 : 21 : 10 : 4 and identified as (i) 2-*bromo*-1,1,1,2,3-*pentafluoropropane* (V) * (0·52 g, 2·3 mmol, 15%) (Found: C, 17·1; H, 1·0%; *M*, 212. $C_3H_2BrF_5$ requires C, 16·9; H, 0·9%; *M*, 213), b.p. (Siwoloboff) 50°; (ii) erythro-3-*bromo*-1,1,1,2,3-*pentafluoropropane* (IVa) * (1·51 g, 7·1 mmol, 47%) (Found: C, 17·2; H, 1·0%; *M*, 213), b.p. (isoteniscope) 52·4°; (iii) threo-3-*bromo*-1,1,1,2,3-*pentafluoropropane* (IVb) * (0·66 g, 3·1 mmol, 21%) (Found: C, 17·2; H, 1·2%; *M*, 213), b.p. (isoteniscope) 57·4°; (iv) *threo*-2,3-dibromo-1,1,1,2,3-pentafluoropropane (IIa) (0·44 g, 1·5 mmol, 10%), and (v) *erythro*-2,3-dibromo-1,1,1,2,3-pentafluoropropane (IIb) (0·18 g, 0·6 mmol, 4%).

(c) *With trifluoroiodomethane under photochemical conditions.* A mixture of trifluoroiodomethane (6·46 g, 33·0 mmol) and the olefin (1·33 g, 10·1 mmol) sealed in a silica tube (*ca.* 300 ml) was irradiated (115 h) with the lower portion (5 cm) of the tube shielded. The volatile products were shaken with mercury to remove iodine to give (i) hexafluoroethane (0·15 g, 1·1 mmol, 7%) [shown (i.r.) to be contaminated with traces of silicon tetrafluoride, trifluoromethane, and trifluoroiodomethane], (ii) a mixture (4·98 g, 26·1 mmol) shown by g.l.c. (8 m QF1 at 20°) to contain unchanged trifluoroiodomethane (4·70 g, 24·0 mmol, 73% recovered) and unchanged 1*H*-pentafluoropropene (0·28 g, 2·1 mmol, 21% recovered), and (iii) a higher-boiling fraction (2·22 g, *ca.* 6·8 mmol) shown by g.l.c. (6 m DNP at 100°) to contain three major components in the ratio 4 : 56 : 40 and five minor components (*ca.* 4% of the fraction). The major components were separated by g.l.c. (as above) and identified as (i) 1,1,1,2,3-*pentafluoro*-3-*iodo*-2-*trifluoromethylpropane* (VI) * (0·09 g, 0·3 mmol, 3%) [Found: C, 14·7; H, 0·4%; *M* (mass spec.), 328. $C_4HF_8I$ requires C, 14·6; H, 0·3%; *M*, 328]; (ii) erythro-1,1,1,2,3,4,4,4-*octafluoro*-2-*iodobutane* (VIIa) * (1·19 g, 3·6 mmol, 45%) (Found: C, 14·9; H, 0·4%; *M*, 328), b.p. (Siwoloboff) 68°; and (iii) threo-1,1,1,2,3,4,4,4-*octafluoro*-2-*iodobutane* (VIIb) * (0·86 g, 2·6 mmol, 33%) (Found: C, 14·8; H, 0·3%; *M*, 330), b.p. (isoteniscope) 72°.

A small unidentified residue remained in the reaction tube.

(d) *With trifluoroiodomethane under thermal conditions.* A mixture of trifluoroiodomethane (4·23 g, 21·6 mmol) and the olefin (0·84 g, 6·3 mmol) sealed in a Pyrex tube (*ca.* 300 ml) was heated at 225° (120 h). The products were worked up as in the previous experiment to give (i) unchanged trifluoroiodomethane (3·11 g, 15·9 mmol, 74% recovered) [shown (i.r.) to be contaminated with small amounts of hexafluoroethane, trifluoromethane, and silicon tetrafluoride], and (ii) a mixture (1·76 g) shown by g.l.c. (2 m DNP at 60°) to contain 1,1,1,2,3-pentafluoro-3-iodo-2-trifluoromethylpropane (VI) (0·13 g, 0·4 mmol, 6%), *erythro*-1,1,1,2,3,4,4,4-octafluoro-2-iodobutane (VIIa) (0·86 g, 2·6 mmol, 42%), *threo*-1,1,1,2,3,4,4,4-octafluoro-2-iodobutane (VIIb) (0·71 g, 2·2 mmol, 35%), and several minor components (*ca.* 4% of the mixture).

A small amount of unidentified material remained in the reaction tube.

*Reaction of* 2,3-*Dibromo*-1,1,1,2,3-*pentafluoropropane* (II) *with Potassium Hydroxide.*—(a) threo-*Isomer* (IIa). The dibromide (0·33 g, 1·1 mmol) was condensed *in vacuo* onto an excess of dry powdered potassium hydroxide (5 g) and heated at 40° (30 min). Separation of the products gave unchanged dibromide (0·06 g, 0·2 mmol, 18% recovered) and 1-*bromo*-1,2,3,3,3-*pentafluoropropene* (III) * (0·15 g, 0·71 mmol, 79%) [Found: C, 17·2%; *M* (mass spec.), 211. $C_3F_5Br$ requires C, 17·1%; *M*, 211]. The product was shown by n.m.r. spectroscopy to be a 93 : 7 mixture of the *trans*-isomer (IIIb) * (0·14 g, 0·66 mmol, 73%) and the *cis*-isomer (IIIa) * (0·01 g, 0·05 mmol, 6%).

(b) *Mixture of* erythro-(IIa) *and* threo-(IIb) *isomers.* The dibromide (0·64 g, 2·2 mmol), as a 71 : 29 mixture of *threo*- and *erythro*-isomers, was treated with potassium hydroxide as in the previous experiment. Separation of the products gave unchanged dibromide (0·03 g, 0·1 mmol, 5% recovered) as a 70 : 30 mixture of the isomers, and 1-bromo-1,2,3,3,3-pentafluoropropene (III) (0·42 g, 2·0 mmol, 95%) (Found: *M*, 210), shown by n.m.r. spectroscopy to be a 76 : 24 mixture of the *trans*-(IIIb) (0·31 g, 1·5 mmol, 71%) and *cis*-(IIIa) (0·11 g, 0·5 mmol, 24%) isomers.

*Reaction of* 2-*Bromo*-1,1,1,2,3-*pentafluoropropane* (V) *with Potassium Hydroxide.*—The adduct (0·32 g, 1·5 mmol) was condensed *in vacuo* onto dry powdered potassium hydroxide (5 g) and kept at room temperature (30 min). Separation of the products gave unchanged adduct (0·07 g, 0·3 mmol, 20% recovered) and *cis*-1*H*-pentafluoropropene (I) (0·13 g, 1·0 mmol, 83%) (Found: *M*, 132. Calc. for $C_3HF_5$: *M*, 132), as determined by i.r. and n.m.r. spectroscopy.

*Reaction of* 3-*Bromo*-1,1,1,2,3-*pentafluoropropane* (IV) *with Potassium Hydroxide.*—(a) erythro-*Isomer* (IVa). The adduct (0·95 g, 4·5 mmol) was condensed onto dry powdered potassium hydroxide (10 g) and kept at room temperature (20 min). Separation of the products gave unchanged adduct (0·08 g, 0·4 mmol, 9% recovered) and *cis*-1*H*-pentafluoropropene (I) (0·48 g, 3·6 mmol, 88%) (Found: *M*, 132), as determined by i.r. and n.m.r. spectroscopy.

(b) threo-*Isomer* (IVb). The adduct (0·38 g, 1·8 mmol) was treated with potassium hydroxide (5 g) at room temperature (30 min) *in vacuo*. Separation of the products gave unchanged *threo*-adduct (0·05 g, 0·2 mmol, 11% recovered) and 1*H*-pentafluoropropene (I) (0·17 g, 1·3 mmol, 81%) (Found: *M*, 132), shown by n.m.r. spectroscopy to be a mixture of the *cis*- (0·06 g, 0·5 mmol, 31%) and *trans*- * (0·11 g, 0·8 mmol, 50%) isomers.

*Reaction of* 1,1,1,2,3,4,4,4-*Octafluoro*-2-*iodobutane* (VII) *with Potassium Hydroxide.*—(a) erythro-*Isomer* (VIIa). The iodo-compound (0·39 g, 1·2 mmol) was condensed *in vacuo* onto dry powdered potassium hydroxide (5 g) and the mixture was heated at 45° (30 min). Separation of the products gave unchanged iodide (0·02 g, 0·1 mmol, 8% recovered) and *trans*-octafluorobut-2-ene (0·20 g, 1·0 mmol, 91%) (Found: *M*, 201. Calc. for $C_4F_8$: *M*, 200), as determined by i.r. and n.m.r. spectroscopy.

(b) threo-*Isomer*. The iodide (0·33 g, 1·0 mmol), treated with dry powdered potassium hydroxide (5 g) *in vacuo* at 40° (20 min), gave unchanged iodide (0·05 g, 0·2 mmol, 20% recovered) and octafluorobut-2-ene (0·16 g, 0·8 mmol, 99%) (Found: *M*, 210), which was shown by $^{19}$F n.m.r. spectroscopy to be a 95 : 5 mixture of the *cis*- (0·15 g, 0·75 mmol, 92%) and *trans*- (0·01 g, 0·05 mmol, 7%) isomers.

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