

Fluoro-olefin Chemistry. Part X.¹ Some Additions to 1-Fluoropropene under Ionic and Free-radical Conditions

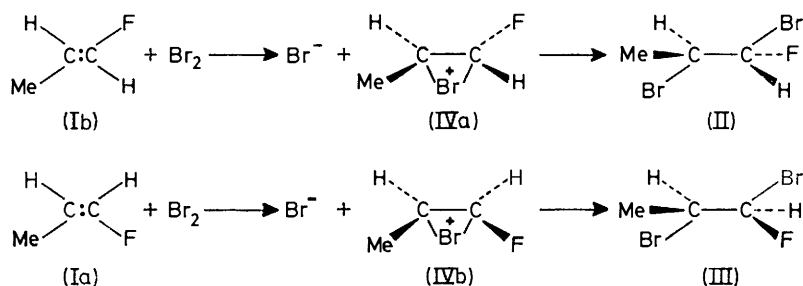
By Robert N. Haszeldine,* Ilyas-ud-D. Mir, and Anthony E. Tipping, Chemistry Department, University of Manchester Institute of Science and Technology, Manchester M60 1QD

The reactions of bromine with *cis*- or *trans*-1-fluoropropene under ionic conditions result in stereospecific *anti*-additions, and the addition of hydrogen bromide gives 1-bromo-1-fluoropropane exclusively. Photoreaction of hydrogen bromide with the olefin affords hydrogen, the 1 : 1 adducts, MeCH₂·CHFBr and MeCHBr·CH₂F, in the ratio 90 : 10, and the olefin dibromide. Similarly photoreaction of trifluoroiodomethane with the olefin also results in bidirectional addition and the adducts, CF₃·CHMe·CHI and MeCHI·CHF·CF₃, are formed in the ratio 49 : 51; under thermal conditions the adduct ratio is 46 : 54. The photoreaction of methanethiol with the olefin gives hydrogen, dimethyl disulphide, and 1,1-bis(methylthio)propane; 1 : 1 adducts were not detected in the products.

THE only reactions of 1-fluoropropene (I) carried out previously are the addition of dibromodifluoromethane under radical conditions² and the addition of *N*-bromobis(trifluoromethyl)amine under radical and ionic conditions.³ In the former reaction exclusive CF₂Br· radical addition to the terminal CHF group was reported, but the (CF₃)₂N· radical was observed to undergo bidirectional addition to the olefin and the adducts (CF₃)₂N·CHF·CHMeBr and (CF₃)₂N·CHMe·CHFBr were formed

dehydrobromination; the adduct (II) gave a mixture of (*E*)-1-bromo-1-fluoropropene (Va) (58%) and (*E*)-2-bromo-1-fluoropropene (VIa) (39%), and the adduct (III) afforded a mixture of the corresponding (*Z*)-isomers (Vb) (52%) and (VIb) (26%). The olefins observed are those expected on the basis of *E2 anti*-eliminations. In both dehydrobrominations major elimination involved the acidic proton in the CHFBr group.

The n.m.r. spectra of the adduct (II) showed a *gauche*



SCHEME 1

in a *ca.* 50 : 50 ratio. Under ionic conditions stereospecific *trans*-addition of (CF₃)₂NBr to the olefin was found and the adducts were formed in the ratio 89 : 11.

In the present work the reactions of the olefin (I) with bromine and hydrogen bromide under ionic conditions and with hydrogen bromide, trifluoroiodomethane, and methanethiol under free-radical conditions have been investigated.

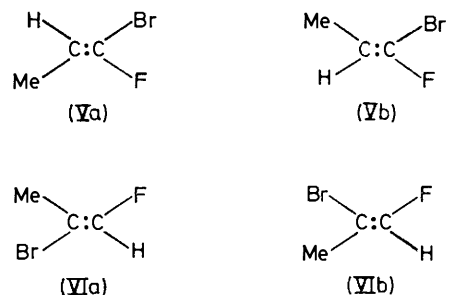
(a) *Ionic Additions*.—The reaction of bromine with the *trans*-olefin (Ib) at room temperature in the dark gave *erythro*(1*S*,2*S*)-1,2-dibromo-1-fluoropropane (II) (90%), and the corresponding reaction with the *cis*-olefin (Ia) gave a mixture (100%) of (II) and the *threo*(1*R*,2*S*)-isomer (III) in the ratio 3 : 97. Compounds (II) and (III) are the expected products of ionic *anti*-addition to the olefins (Ib) and (Ia), respectively (Scheme 1), and the minor amount of apparent *syn*-addition to the olefin (Ia) is probably the result of the presence of a small amount (3%) of the olefin (Ib) in the reactant alkene.

It was of course not possible to determine whether bidirectional nucleophilic attack on the intermediate cyclic bromonium ions (IVa and b) had taken place.

The structures of the products were confirmed by

¹ Part IX, R. N. Haszeldine, R. Rowland, A. J. Mitchinson, and A. E. Tipping, *J.C.S. Perkin I*, 1976, 517.

vicinal H,F-coupling (9.1 Hz) and a *trans* vicinal H,H-coupling (6.6 Hz); the spectra of the adduct (III) showed a *trans* vicinal H,F-coupling (21.6 Hz) and a *gauche*



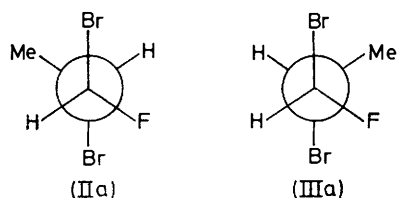
vicinal H,H-coupling (2.0 Hz), indicating that the favoured conformations of the adducts are (IIa) and (IIIa), respectively, in which the bulky bromine atoms are *trans*.

The reaction of the olefin (I) with hydrogen bromide at room temperature in the dark gave 1-bromo-1-fluoropropane (VII) (97%). Since a reaction carried out

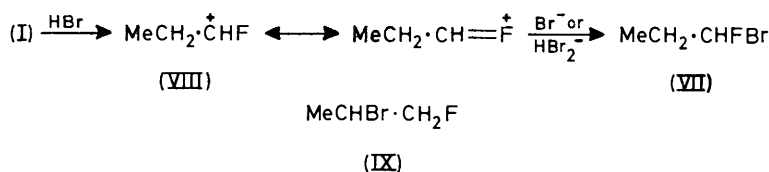
² P. Tarrant, A. M. Lovelace, and M. R. Lilyquist, *J. Amer. Chem. Soc.*, 1955, **77**, 2783.

³ R. N. Haszeldine, I-ud-D. Mir, and A. E. Tipping, *J.C.S. Perkin I*, 1976, 556.

under free-radical conditions gave a complex mixture of products (see later), the dark reaction probably involves



ionic intermediates; the carbocation (VIII) is thus more stable than the possible alternative carbocation $\text{MeCH}^+\text{CH}_2\text{F}$, and mesomeric stabilisation by fluorine of an adjacent positive charge is more effective than inductive stabilisation by methyl.



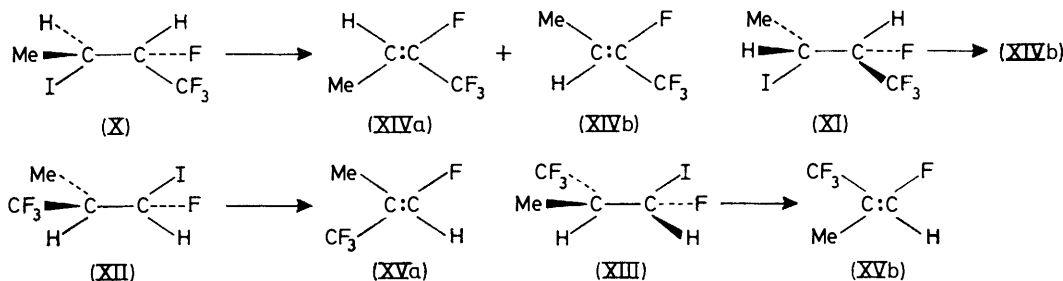
Ionic addition of hydrogen bromide to 1,1-difluoropropene similarly affords 1-bromo-1,1-difluoropropane and not 2-bromo-1,1-difluoropropane.⁴

The reactant olefin was a mixture of *cis*- (Ia) and *trans* (Ib) isomers in the ratio 38 : 62, whereas the recovered

mediate radicals, and it is possible that a certain proportion of the major adduct (VII) was formed *via* ionic addition of hydrogen bromide. Formation of hydrogen and the dibromides (II) and (III) indicates that bromine atom addition to the olefin is relatively slow.

Photoreaction of trifluoriodomethane with the olefin (I) gave a mixture (96%) of the 1 : 1 adducts (*2R,3S*)-1,1,1,2-tetrafluoro-3-iodobutane (X) (23%), the corresponding (*2R,3R*)-isomer (XI) (26%), (*2R,3S*)-1,1,1,3-tetrafluoro-3-iodo-2-methylpropane (XII) (23%), and the corresponding (*2S,3S*)-isomer (XIII) (24%) as determined by n.m.r. spectroscopy and dehydroiodination. The adduct (X) on dehydroiodination with potassium hydroxide gave a mixture (45%) of (*E*)-1,1,1,2-tetrafluorobut-2-ene (XIVa) and the corresponding (*Z*)-isomer (XIVb) in the ratio 80 : 20; the adduct (XI) gave

the (*Z*)-isomer (XIVb) (90%) exclusively. Under similar conditions the adduct (XII) afforded (*E*)-1-fluoro-2-trifluoromethylpropene (XVa) (100%), and the adduct (XIII) gave the corresponding (*Z*)-isomer (XVb) (34%) (Scheme 2).



SCHEME 2

olefin consisted of the isomers in the ratio 57 : 43. This indicates either that the initial proton addition is reversible or that the *trans*-isomer (Ib) reacts faster than the *cis*-isomer (Ia).

(b) *Free-radical Additions*.—The photoreaction of an excess of hydrogen bromide with the olefin (I) gave hydrogen (61%), compounds (VII) (36%), (II) (33%), and (III) (26%), a minor component identified as 2-bromo-1-fluoropropane (IX) (4%) on the basis of its g.l.c. retention time and ¹⁹F n.m.r. spectrum [absorption at 144 p.p.m. to high field of reference $\text{CF}_3\cdot\text{CO}_2\text{H}$ (t, *J* 50.7 Hz) as expected for CH_2F], and an unidentified component (2%). Although the 1 : 1 adduct ratio [(VII) : (IX)] observed (90 : 10) indicates that major bromine atom attack occurs on the terminal CHF group of the olefin, the ratio has no quantitative significance because of the low yield of adducts obtained (40%). The dibromides (II) and (III) can be formed *via* both inter-

The olefins formed from the adducts (XI)—(XIII) and the major olefin formed from the adduct (X) are the expected products from *E2 anti*-eliminations of hydrogen iodide. The presence of the olefin (XIVb) in the products from the dehydroiodination of the adduct (X) indicates that with this adduct a minor amount of *syn*-elimination, possibly *via* an *Elcb* mechanism, is taking place; the olefin (XIVb), in which the bulky methyl and trifluoromethyl groups are *anti*, is expected to be more stable than the olefin (XIVa), in which these bulky groups are *syn*. The olefins (XIVa and b) were differentiated on the basis of the vicinal H,F-couplings (21.8 and 33.0 Hz, respectively); the olefins (XVa and b) were differentiated by their respective CF_3 ,F-couplings (7.0 and 22.0 Hz, respectively); the spectra of the olefins (XVa and b) also showed the expected large *geminal* H,F-couplings (*ca.* 80 Hz).

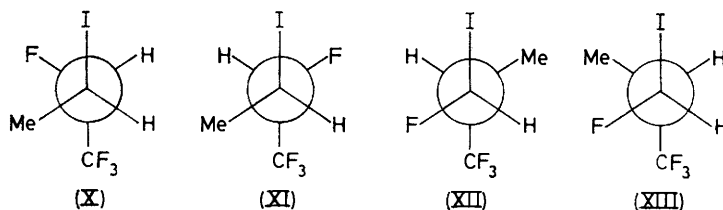
⁴ R. N. Haszeldine, *J. Chem. Soc.*, 1953, 3565.

The preferred conformations of the adducts (X)—(XIII) were established by the observed *vicinal* H,H- and H,F-couplings as shown in the Table. The CF₃F-

N.m.r. coupling constants and assignments

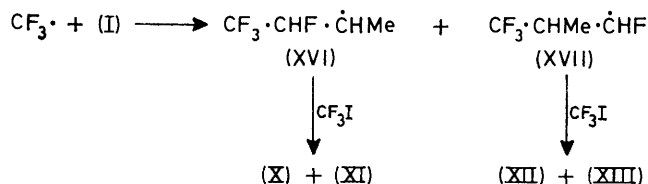
Adduct	$J_{H,H}/\text{Hz}$	Assignment	$J_{H,F}/\text{Hz}$	Assignment
(X)	3.9	<i>gauche</i>	23.4	<i>trans</i>
(XI)	7.0	<i>trans</i>	17.0	<i>gauche</i>
(XII)	6.6	<i>trans</i>	10.1	<i>gauche</i>
(XIII)	1.0	<i>gauche</i>	27.5	<i>trans</i>

couplings observed in the ¹⁹F spectra of the adducts (XII) and (XIII) (10.1 and 7.1 Hz, respectively) are of the magnitude expected for *gauche* couplings. In all cases the preferred conformations are those in which the bulky trifluoromethyl group and iodine atom are *anti*.



Stereospecific addition of trifluoroiodomethane to the reactant olefin [(Ia) : (Ib) 70 : 30] did not take place, since the adduct ratios obtained [(X) : (XI) and (XII) : (XIII)] were *ca.* 50 : 50; this result is consistent with those obtained from additions of trifluoroiodomethane to other olefins.

Since the adduct yield (96%) is high, the ratio of bidirectional CF₃• radical attack on the olefin (I) (51% on the CHF group and 49% on the CHMe group) is meaningful, and indicates that the intermediate radicals (XVI) and (XVII) are of similar stability.



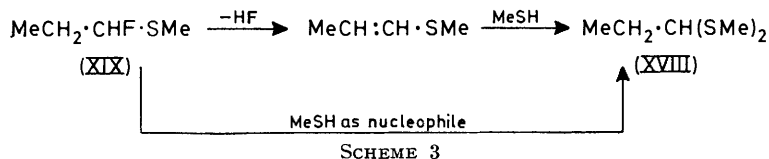
It has been observed previously that the photoreactions of trifluoroiodomethane with the olefins

suggested that the fluorine atom and the methyl group stabilised an adjacent lone electron to the same degree and that CF₃• radical attack on the olefin (I) would be bidirectional and in the ratio *ca.* 50 : 50 as found in the present work. Furthermore it has been observed that radical additions of the addends CF₃I and (CF₃)₂NX (X = Cl, Br, or I) to olefins invariably give almost identical 1 : 1 adduct ratios, *e.g.* photochemical additions to the olefins CH₂:CHF [attack on CH₂: 96% for CF₃•,⁵ 94% for (CF₃)₂N•⁷] and CHF:CF₂ [attack on CHF: 80% for CF₃•,⁸ 78% for (CF₃)₂N•⁹]. The only exception to this observed to date involved radical additions to hexafluoropropene [attack on CF₂: 80% for CF₃•¹⁰ and 96% for (CF₃)₂N•⁹] and it was suggested that central carbon attack by the

bulky (CF₃)₂N• radical was more hindered than attack by the less bulky CF₃• radical. Photochemical addition of *N*-bromobis(trifluoromethyl)amine to the olefin (I)³ involves initial (CF₃)₂N• radical attack to the extent of 46% on the CHF group and 54% on the CHMe group, which is similar to the ratio (59 : 41) found in the present work for CF₃• radical attack.

The thermal reaction of trifluoroiodomethane with the olefin (I) gave trifluoromethane (12%), the 1 : 1 adducts (X) (25%), (XI) (18%), (XII) (15%), and (XIII) (22%), and a non-volatile residue. The ratio of initial bidirectional CF₃• radical attack is thus 54 (CHF) : 46 (CHMe) and, although the adduct yield (80%) is lower than desirable, this ratio is considered to be reasonably accurate because the trifluoromethane and much of the telomeric material formed probably arises *via* CF₃• radical attack on an allylic hydrogen in the olefin (I).

The photoreaction of methanethiol with the olefin (I) (2.9 : 1 molar ratio) gave unchanged methanethiol (3% recovered), hydrogen (57%), silicon tetrafluoride (61%), 1,1-bis(methylthio)propane (XVIII) (40% based on



CH₂:CHF⁵ and CH₂:CHMe⁶ gave identical adduct ratios resulting from initial bidirectional CF₃• attack (96% on CH₂ and 4% on CHR). From these observations it was

⁵ R. Gregory, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc. (C)*, 1970, 1750.

⁶ R. Gregory, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc. (C)*, 1971, 1216.

⁷ J. Freear and A. E. Tipping, *J. Chem. Soc. (C)*, 1969, 1955.

⁸ R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 1957, 2800; R. N. Haszeldine and B. Higginbottom, unpublished results.

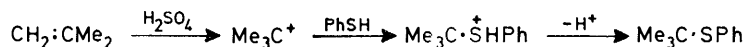
olefin, 28% based on methanethiol), dimethyl disulphide (65% based on thiol), five minor unidentified components (*ca.* 4%), and a non-volatile residue. Compound (XVIII) has been prepared in 60% yield by the reaction of methanethiol with propionaldehyde in the presence

⁹ G. L. Fleming, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc. (C)*, 1971, 3833.

¹⁰ R. N. Haszeldine, *J. Chem. Soc.*, 1953, 3559; J. Brown and R. N. Haszeldine, unpublished results.

of zinc chloride.¹¹ The hydrogen and dimethyl disulphide presumably arise *via* hydrogen atoms and methylthio-radicals, and the other products *via* (XIX), formed by radical or ionic addition of methanethiol to (I) (Scheme 3); (XIX) was not detected as a product, in contrast to other free-radical reactions of thiols with olefins which give 1:1 adducts in high yield.

Nucleophilic additions of thiols to fluoro-olefins often give the vinyl sulphides and not the saturated sulphides.¹² Acid-catalysed additions of thiols to electron-rich olefins are well documented, *e.g.*¹³ Scheme 4.



SCHEME 4

EXPERIMENTAL

Reactants and products were manipulated, where possible, in a conventional vacuum system to avoid contamination with air or moisture. Photochemical reactions were carried out with a Hanovia S500 medium-pressure u.v. lamp. Products were separated by repeated fractional distillation *in vacuo* or by preparative-scale g.l.c. [Perkin-Elmer F21 or Pye 104 machines using columns packed with trixylyl phosphate (TXP), Silicone SE 30 oil, and dodecyl phthalate (DDP) (20%) on Celite]. The identities of products were established 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 56.46 MHz for ¹⁹F and 60.0 MHz for ¹H or Varian HA 100 spectrometer operating at 94.1 MHz for ¹⁹F and 100.0 MHz for ¹H; external trifluoroacetic acid and internal tetramethylsilane as the respective references), and mass spectrometry (A.E.I. MS902 spectrometer). Spectral data for products marked with an asterisk are available as Supplementary Publication No. SUP 21793 (10 pp., 1 microfiche).*

1-Fluoropropene was prepared by fluorination of propanaldehyde with sulphur tetrafluoride followed by flow pyrolysis of the resultant 1,1-difluoropropane at 690 °C and 10 mm Hg over silica chips.³ The resultant olefin was a 70:30 mixture of the *cis*- and *trans*-isomers and was used as such unless stated to the contrary; pure samples of the individual isomers were obtained by g.l.c. [10 m fluorinated silicone oil (QF1) at -23 °C].

Reactions of 1-Fluoropropene.—(a) *trans*-1-Fluoropropene with bromine. A mixture of the olefin (0.31 g, 5.13 mmol) and bromine (0.82 g, 5.13 mmol), sealed *in vacuo* in a Pyrex tube (*ca.* 100 cm³) and maintained in the dark at room temperature (7 d), gave (1*S*,2*S*)-1,2-dibromo-1-fluoropropane (II) * (1.0 g, 4.55 mmol, 90%) (Found: C, 16.5; H, 2.4; F, 8.2%; *M*⁺, 220. C₃H₅Br₂F requires C, 16.4; H, 2.3; F, 8.6%; *M*, 220), b.p. (Siwoloboff) 163 °C.

(b) *cis*-1-Fluoropropene with bromine. A mixture of the olefin (0.135 g, 1.73 mmol) and bromine (0.40 g, 2.50 mmol), treated as in experiment (a), with the excess of bromine removed by treatment with mercury *in vacuo*, gave a mixture

(0.38 g, 1.73 mmol, 100%) of (1*R*,2*S*)- and (1*S*,2*S*)-1,2-dibromo-1-fluoropropane in the ratio 97:3, from which a sample of (1*R*,2*S*)-1,2-dibromo-1-fluoropropane (III) * (0.37 g, 1.68 mmol, 97%) (Found: C, 16.6; H, 2.3%) was isolated by g.l.c. (7.5 m TXP at 100 °C).

(c) *With hydrogen bromide in the dark.* A mixture of the olefin (0.28 g, 4.6 mmol) and hydrogen bromide (1.17 g, 14.4 mmol), treated as in experiment (a), gave (i) unchanged hydrogen bromide (0.89 g, 11.2 mmol, 76% recovered), (ii) unchanged 1-fluoropropene (0.083 g, 1.4 mmol, 30% recovered), and (iii) 1-bromo-1-fluoropropane (VII) * (0.44 g, 3.12 mmol, 97%) (Found: C, 25.4; H, 4.2%; *M*⁺, 141.

C₃H₆BrF requires C, 25.5; H, 4.2%; *M*, 141), b.p. (isoteniscope) 69.5 ± 0.5 °C.

(d) *With hydrogen bromide under photochemical conditions.* A mixture of hydrogen bromide (1.17 g, 14.5 mmol) and the olefin (0.33 g, 5.56 mmol), sealed in a silica ampoule (*ca.* 300 cm³) and irradiated (20 h) at 20 cm from the u.v. lamp, gave (i) hydrogen (0.007 g, 3.4 mmol, 61%), (ii) unchanged hydrogen bromide (0.28 g, 3.5 mmol, 24% recovered), and (iii) a higher boiling fraction (1.0 g) shown by g.l.c. (2 m SE30 at 58 °C) to contain four components in the ratio 35:5:2:58. The two major components (A and D) and a mixture of the two minor components (B and C) were separated by g.l.c. (4 m SE30 at 100 °C) and the two major components were identified as 1-bromo-1-fluoropropane (VII) (0.28 g, 1.98 mmol, 36%) and a mixture of the dibromides (II) (0.40 g, 1.83 mmol, 33%) and (III) (0.32 g, 1.45 mmol, 26%) in the ratio 56:44 as shown by n.m.r. spectroscopy. The mixture of the minor components showed an absorption at 144 p.p.m. (*t*, *J* 50.7 Hz) in its ¹⁹F n.m.r. spectrum.

(e) *With trifluoroiodomethane under photochemical conditions.* A mixture of the olefin (1.00 g, 16.8 mmol) and trifluoroiodomethane (8.03 g, 41.0 mmol) was sealed *in vacuo* in a silica tube (*ca.* 300 cm³), and the vapour phase was irradiated at *ca.* 15 cm from the u.v. lamp (65 h) to give, after treatment with mercury to remove traces of iodine, (i) a mixture (0.28 g, 3.01 mmol; *M*, 94) shown by i.r. spectroscopy to consist mainly of hexafluoroethane, together with smaller amounts of trifluoromethane, unchanged trifluoroiodomethane, and silicon tetrafluoride, (ii) unchanged trifluoroiodomethane (4.03 g, 21.0 mmol, 51% recovered), and (iii) a mixture (4.08 g) shown by g.l.c. (5 m DDP at 110 °C) to contain 5 minor components (5% of fraction) and four major components of longer retention time present in the ratio 24:25:24:27. The major components were separated by g.l.c. (as above) and identified as (2*R*,3*S*)-1,1,1,2-tetrafluoro-3-iodobutane (X) * (0.98 g, 3.83 mmol, 23%) (Found: C, 19.0; H, 2.1; F, 29.5%; *M*⁺, 256. C₄H₅F₄I requires C, 18.7; H, 2.0; F, 29.7%; *M*, 256), b.p. 107 °C; (2*S*,3*S*)-1,1,1,3-tetrafluoro-3-iodo-2-methylpropane (XIII) * (1.02 g, 3.98 mmol, 24%) (Found: C, 19.0; H, 2.2; F, 29.9%; *M*⁺, 256), b.p. 107 °C; (2*R*,3*S*)-1,1,1,3-tetrafluoro-3-

¹² J. T. Barr, K. E. Rapp, R. L. Pruett, C. T. Bahner, J. D. Gibson, and R. F. Lafferty, *J. Amer. Chem. Soc.*, 1950, **72**, 3642; R. N. Haszeldine, J. R. McAllister, and A. E. Tipping, unpublished results.

¹³ V. N. Ipatieff, H. Pines, and B. S. Friedman, *J. Amer. Chem. Soc.*, 1938, **60**, 2731.

* For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1975, Index issue.

¹¹ H. J. Boonstra, L. Brandsma, A. M. Wiegman, and J. F. Arens, *Rec. Trav. chim.*, 1959, **78**, 252; H. J. Boonstra and C. L. Rinzema, *ibid.*, 1960, **79**, 962.

iodo-2-methylpropane (XII) * (0.98 g, 3.83 mmol, 23%) (Found: C, 19.0; H, 2.1; F, 29.3%; M^+ , 256), b.p. 108.5 °C; and (2R,3R)-1,1,1,2-tetrafluoro-3-iodobutane (XI) * (1.10 g, 4.30 mmol, 26%) (Found: C, 18.9; H, 2.0; F, 29.8%; M^+ , 256), b.p. 109 °C.

(f) *With trifluoroiodomethane under thermal conditions.* A mixture of the olefin (0.56 g, 9.37 mmol) and trifluoroiodomethane (4.87 g, 24.86 mmol) was sealed in a Pyrex tube (ca. 300 cm³) and all but the lower 8 cm of the tube was heated at 275 °C (18 h). This gave (i) trifluoromethane (0.08 g, 1.09 mmol, 12%), shown by i.r. spectroscopy to be contaminated with small amounts of hexafluoroethane and unchanged trifluoroiodomethane, (ii) unchanged trifluoroiodomethane (3.06 g, 15.60 mmol, 62% recovered), (iii) a mixture (1.92 g) shown by g.l.c. (5 m DDP at 110 °C) to contain the adducts (X) (0.60 g, 2.32 mmol, 25%), (XIII) (0.52 g, 2.02 mmol, 22%), (XII) (0.35 g, 1.35 mmol, 15%), and (XI) (0.44 g, 1.72 mmol, 18%), and several minor compounds with shorter g.l.c. retention times, and (iv) a non-volatile residue (ca. 0.3 g) which remained in the reaction tube and was not examined further.

(g) *With methanethiol.* A mixture of the olefin (0.57 g, 9.51 mmol) and methanethiol (1.33 g, 27.8 mmol) was sealed in a silica tube (300 cm³) and the vapour phase irradiated at ca. 15 cm from the u.v. lamp (17 h). This gave (i) hydrogen (0.015 g, 7.65 mmol, 57%), (ii) a mixture (0.156 g, 2.33 mmol; M , 83) of unchanged methanethiol (0.04 g, 0.87 mmol, 3% recovered) and silicon tetrafluoride (0.15 g, 1.46 mmol, 61%), and (iii) a mixture (1.37 g) shown by g.l.c. (10 m SE30 at 118 °C) to contain five minor components, together with two major components of longer retention time present in the ratio 4 : 21 : 75. The major components were separated by g.l.c. (as above) and identified as 1,1-bis(methylthio)propane (XVIII) * (0.52 g, 3.80 mmol, 40%) and dimethyl disulphide (0.82 g, 8.7 mmol, 65%). A non-volatile residue (ca. 0.4 g) was recovered from the reaction tube.

Dehydrobromination of 1,2-Dibromo-1-fluoropropane.—(a) (1R,2S)-*Isomer.* The dibromide (III) (0.33 g, 1.50 mmol) was condensed *in vacuo* onto powdered potassium hydroxide (ca. 7 g) and the mixture heated to 40 °C (30 min) to give unchanged dibromide (0.13 g, 0.60 mmol, 40% recovered) and a lower-boiling fraction (0.097 g, 0.81 mmol, 78%) (Found: F, 13.6%; M , 140. Calc. for C₃H₄BrF: F, 13.6%; M , 139), λ_{\max} 5.98 μm (C:C str.), shown by n.m.r. spectroscopy to be a mixture of (Z)-1-bromo-1-fluoropropane (Vb) *

(0.076 g, 0.55 mmol, 52%), and (Z)-2-bromo-1-fluoropropane (VIb) * (0.021 g, 0.26 mmol, 26%) in the ratio 66 : 34.

(b) (1S,2S)-*Isomer.* A mixture of the dibromide (II) (0.29 g, 1.32 mmol) and powdered potassium hydroxide (5 g), heated at 50 °C (30 min), gave a mixture (0.18 g, 1.27 mmol, 97%) (Found: C, 26.2; H, 3.2; F, 13.8%; M , 139. Calc. for C₃H₄BrF: C, 25.9; H, 2.9; F, 13.7%; M , 139), λ_{\max} 5.99s μm (C:C str.), shown by n.m.r. spectroscopy to consist of (E)-1-bromo-1-fluoropropane (Va) * (0.167 g, 0.76 mmol, 58%), and (E)-2-bromo-1-fluoropropane (VIa) * (0.113 g, 0.51 mmol, 39%) in the ratio 60 : 40.

Dehydroiodination of the 1 : 1 Adducts of 1-Fluoropropane and Trifluoroiodomethane.—(a) (2R,3S)-1,1,1,2-Tetrafluoro-3-iodobutane (X). A mixture of the iodide (0.092 g, 0.36 mmol) and powdered potassium hydroxide (5 g), heated *in vacuo* at 45 °C (30 min), gave 1,1,1,2-tetrafluorobut-2-ene (0.02 g, 0.16 mmol, 45%) (Found: C, 37.8; H, 3.4%; M^+ , 128. Calc. for C₄H₄F₄: C, 37.5; H, 3.1%; M , 128), λ_{\max} 5.81m μm (C:C str.), shown by n.m.r. spectroscopy to be a mixture of the (E)-isomer (XIVa) * (0.016 g, 0.13 mmol, 36%) and the (Z)-isomer (XIVb) (0.04 g, 0.03 mmol, 9%) in the ratio 80 : 20.

(b) (2R,3R)-1,1,1,2-Tetrafluoro-3-iodobutane (XI). A mixture of the iodoalkane (0.32 g, 1.25 mmol) and powdered potassium hydroxide (5 g), heated *in vacuo* at 40 °C (30 min), gave unchanged iodoalkane (0.01 g, 0.04 mmol, 3% recovered) and (Z)-1,1,1,2-tetrafluorobut-2-ene (XIVb) * (0.14 g, 1.08 mmol, 90%) (Found: C, 37.2; H, 3.2%; M , 128), λ_{\max} 5.78m μm (C:C str.).

(c) (2S,3S)-1,1,1,3-Tetrafluoro-3-iodo-2-methylpropane (XIII). A mixture of the iodoalkane (0.15 g, 0.58 mmol) and powdered potassium hydroxide (5 g), heated *in vacuo* at 40 °C (30 min), gave (Z)-1-fluoro-2-trifluoromethylpropene (XVb) * (0.025 g, 0.20 mmol, 34%) (Found: F, 59.0%; M^+ , 128. C₄H₄F₄ requires F, 59.4%; M , 128), λ_{\max} 5.88m μm (C:C str.).

(d) (2R,3S)-1,1,1,3-Tetrafluoro-3-iodo-2-methylpropane (XII). A mixture of the iodoalkane (0.08 g, 0.30 mmol) and powdered potassium hydroxide (5 g), heated *in vacuo* at 40 °C (45 min), gave (E)-1-fluoro-2-trifluoromethylpropene (XV) * (0.04 g, 0.30 mmol, 100%) (Found: C, 37.3; H, 3.2; F, 59.2%; M^+ , 128. C₄H₄F₄ requires C, 37.5; H, 3.1; F, 59.4%; M , 128), λ_{\max} 5.87s μm (C:C str.).

[5/1973 Received, 9th October, 1975]