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The reactions of hydrogen bromide, *N*-bromobistrifluoromethylamine, methanethiol, and trimethylsilane with perfluoro-3-methylbut-1-ene under free-radical conditions proceed by attack by Br·, $(CF_3)_2N$ ·, MeS·, and Me₃Si· exclusively at the terminal CF₂ group. Fluoride ion rearranges the olefin to perfluoro-2-methylbut-2-ene, and methoxide ion affords a complex mixture of products derived from both the reactant and rearranged olefins. Dimethylamine gives the unexpected 1:1 adduct, $(CF_3)_2CH$ ·CF₂·CF₂·NMe₂ and the corresponding arnide $(CF_3)_2CH$ ·CF₂·CO·NMe₂. Catalytic hydrogenation of the olefin proceeds normally to give 1*H*,2*H*-3-trifluoromethylheptafluorobutane.

The free-radical reactions of trifluoroiodomethane and iodine with perfluoro-3-methylbut-1-ene (1) give complex mixtures of products arising *via* trifluoromethyl radical or iodine atom attack on the terminal CF_2 group of the olefin.² Irradiation of olefin (1) gave mainly a mixture of dimers which were identified as open-chain alkenes.² Some further reactions of the olefin have now been studied.

Free-radical Additions.—The olefin and bromine, exposed to sunlight, gave 1,2-dibromo-1,1,2,3,4,4,4heptafluoro-3-trifluoromethylbutane (2) (84%), while irradiation of a mixture of the olefin and hydrogen bromide (1:3 molar ratio) afforded hydrogen (40%), bromine, the dibromide (2) (53%), and 1-bromo-1,1,2,3,-4,4,4-heptafluoro-3-trifluoromethylbutane (3) (46%). (CF₃)₂CF·CFICF₂ (CF₃)₂CF·CFBr·CF₂Br (CF₃)₂CF·CHF·CF₂Br (1) (2) (3)

The photochemical reaction with N-bromobistrifluoromethylamine gave a complex mixture of products from which only the hydrazine (4) (36%), the 1 : 1 adduct (5)

$$\begin{array}{ccc} (CF_3)_2 \mathbf{N} \cdot \mathbf{N} (CF_3)_2 & (CF_3)_2 CF \cdot CFBr \cdot CF_2 \cdot \mathbf{N} (CF_3)_2 \\ (4) & (5) \\ (CF_3)_2 CF \cdot CHF \cdot CF_2 \cdot SMe & (CF_3)_2 CF \cdot CHF \cdot CF_2 \cdot SiMe_3 \\ (6) & (7) \end{array}$$

(20% based on olefin, 17% based on amine), the dibromide (2) (18%), and perfluoro-2-azapropene (ca. 5%) Br., $(CF_3)_2N$, MeS, and Me₃Si radicals thus attack the terminal CF₂ group exclusively as did CF₃ and I.² Since these radicals all add bidirectionally to hexa-fluoropropene it would appear that the more bulky $(CF_3)_2CF$ group effectively prevents radical attack at the central carbon atom of (1).

Nucleophilic Additions.—Caesium fluoride in dry sulpholan at 85 °C converted (1) into perfluoro-2-methylbut-2-ene (8) (72%) and thence, via carbanion (9), 2H-2-trifluoromethyloctafluorobutane (10) (14%), while reaction in moist sulpholan gave (8) (6%) and (10)

$$\begin{array}{cccccc} (\mathrm{CF}_3)_2\mathrm{C}\overset{\circ}{\cdot}\mathrm{CF}_5\mathrm{CF}_3 & (\mathrm{CF}_3)_2\bar{\mathrm{C}}\overset{\circ}{\cdot}\mathrm{CF}_2\overset{\circ}{\cdot}\mathrm{CF}_3 & (\mathrm{CF}_3)_2\mathrm{CH}\overset{\circ}{\cdot}\mathrm{CF}_3 \\ (8) & (9) & (10) \\ & (\mathrm{CF}_3)_2\mathrm{CF}\overset{\circ}{\cdot}\mathrm{CHF}\overset{\circ}{\cdot}\mathrm{CF}_3 & (\mathrm{CF}_3)_2\mathrm{CF}\overset{\circ}{\cdot}\bar{\mathrm{CF}}\overset{\circ}{\cdot}\mathrm{CF}_3 \\ & (11) & (12) \end{array}$$

(73%). The absence of (11) suggests that the intermediate carbanion (12), if formed, is short lived and eliminates fluoride ion rather than abstracting a proton.

Sodium methoxide and (1) in sulpholan at 100 °C gave (8) (14%), (10) (40%), (11) (4%), 2-methoxy-1,1,1,4,4,4-hexafluoro-3-trifluoromethylbut-2-ene (13) (25%), and 2-methoxy-1,1,1,2,4,4,4-heptafluoro-3-trifluoromethylbutane (14) (7%) (Scheme 1); a number of minor unidentified products were also formed. Compound (14) is known to be formed (92%) by the reaction of olefin (8) with methanol at 100 °C.³

(1) + MeO⁻
$$\longrightarrow$$
 (CF₃)₂CF· $\bar{C}F$ ·CF₂·OMe $\xrightarrow{-F^-}$ (CF₃)₂C:CF·CF₂·OMe
(18)
(1) + F⁻ \longrightarrow (CF₃)₂CF· $\bar{C}F$ ·CF₃ $\xrightarrow{H^+}$ (CF₃)₂CF·CHF·CF₃
(11)
(CF₃)₂C:CF·CF₃ $\xrightarrow{F^-,H^+}$ (10)
(8) + MeO⁻ \longrightarrow (CF₃)₂ \bar{C} ·CF(CF)₃·OMe $\xrightarrow{H^+}$ (CF₃)₂CH·CF(CF₃)·OMe
(14)
(CF₃)₂C:C(CF₃)·OMe
(13)
SCHEME 1

were identified. In contrast, the photochemical reactions with methanethiol and trimethylsilane gave the 1:1 adducts (6) (96%) and (7) (87%), respectively. The The interesting features of the reaction are (i) the high yield (51%) of saturated products, (ii) the non-detection of olefin (18) an expected major product, (iii) the high

proportion (86%) of products arising from the rearranged olefin (8), and (iv) the formation of the hydrogen fluoride adduct (11). Both olefins (1) and (8) are thus more susceptible to fluoride ion attack than to methoxide ion attack under the conditions employed.

Methoxide ion in methanol gave (11) (24%), 2methoxy-1,1,1,3,4,4-heptafluoro-3-trifluoromethylbutane (15) (28%), an unidentified methyl ester (*ca*. was it the olefin $(CF_3)_2C:C(CF_3)\cdot NMe_2$ which could have arisen from (8).

Olefin (1) reacted with sodium methanethiolate in sulpholan at 90 °C to give unchanged (1) (66%), (10) (47%), (11) (3%), an unidentified saturated compound (ca. 13%), and a small amount of a mixture of higher boiling olefinic products [i.r. bands at 5.86, 6.03, and 6.13 μ m (C:C str.)]. The non-detection of compounds

$$(1) + \text{MeO}^{-} \longrightarrow (CF_3)_2 CF \cdot \bar{C}F \cdot CF_2 \cdot OMe \xrightarrow{\text{MeOH}} (CF_3)_2 CF \cdot CHF \cdot CF_2 \cdot OMe \xrightarrow{(16)} (16)$$

$$(F_3)_2 C \cdot CF \cdot CF_2 \cdot OMe \xrightarrow{(18)} (CF_3)_2 CH \cdot CF_2 \cdot CF_2 \cdot OMe \xrightarrow{(17)} (1) \longrightarrow (11), (8), (14), (13) \text{ as in Scheme 1} (CF_3)_2 CF \cdot CH(CF_3) \cdot OMe \xrightarrow{(15)} (CF_3)_2 CF \cdot \bar{C}(CF_3) \cdot OMe \xrightarrow{(15)} (15)$$

12%) [*m/e* 59 (100%, CO₂Me⁺), $\lambda_{\text{max.}}$ 5.50 μm (>C=O str.)], methyl formate (10%), (14) (14%), a mixture of 1methoxy-1,1,2,3,4,4,4-heptafluoro-3-trifluoromethylbutane (16) (5%) and unidentified components (6%), and 1-methoxy-1,1,2,2,4,4-heptafluoro-3-trifluoromethylbutane (17) (6%) (Scheme 2).

Major features of this reaction are (i) the detection of the methanol adduct (16), (ii) the isolation of the hydrogen fluoride adduct (11) in reasonably high yield, (iii) the absence of unsaturated compounds as major products, containing the SMe group and the formation of the rearranged hydrogen fluoride adduct (10) as the major product show that the olefin is more susceptible to fluoride ion attack than to thiolate ion attack under the conditions employed. The absence of the expected product $(CF_3)_2C:CF\cdot CF_2\cdot SMe$ is surprising since fluoroolefins generally react readily with alkanethiolate ion to afford the corresponding unsaturated sulphide.⁵

A mixture of olefin (1) and an excess of hydrogen passed over a palladium-alumina catalyst at room

$$(1) + Me_2NH \longrightarrow (CF_3)_2CF \cdot CHF \cdot CF_2 \cdot NMe_2 \xrightarrow{Me_2NH} (CF_3)_2C \cdot CF \cdot CF_2 \cdot NMe_2$$

$$(21) + F^- \longrightarrow (CF_3)_2 \overline{C} \cdot CF_2CF_2 \cdot NMe_2 \xrightarrow{Me_2NH} (CF_3)_2CH \cdot CF_2 \cdot CF_2 \cdot NMe_2$$

$$(19) \xrightarrow{hydrolysis} (CF_3)_2CH \cdot CF_2 \cdot CO \cdot NMe_2$$

$$(20)$$
Scheme 3

(iv) the isolation of the ether (17) showing the intermediacy of olefin (18), and (v) the direction of fluoride ion attack on olefin (13) indicating that the tertiary carbanion $(CF_3)_2CF\cdot\bar{C}(CF_3)\cdot OMe$ is more stable than the tertiary carbanion $(CF_3)_2\bar{C}\cdot CF(CF_3)\cdot OMe$. Formation of the adducts (16) and (11) and the absence of major olefinic products illustrates the ready proton abstraction from methanol by the intermediate carbanions.

The reaction of dimethylamine with olefin (1) at room temperature gave unchanged (1) (45%), the rearranged 1 : 1 adduct (19) (55%), NN-dimethyl-2,2,4,4,4-penta-fluoro-3-trifluoromethylbutyramide (20) (10%), and an unidentified olefin (*ca.* 3%) (Scheme 3).

Amines of the type $R_FCF_2 \cdot NR_2$ are readily hydrolysed to the corresponding amides, e.g. $CHF_2 \cdot CF_2 \cdot NEt_2 \longrightarrow$ $CHF_2 \cdot CO \cdot NEt_2$.⁴ The unidentified olefin, of type $(CF_3)_2C:CFR$ or $(CF_3)_2C:C(CF_3)R \ [\lambda_{max}, 5.94 \ \mu m \ (C:C$ str.)], was not compound (21) since a CF_2 absorption in the ¹⁹F n.m.r. spectrum at *ca.* 20 p.p.m. was absent; nor temperature gave unchanged (1) (97% recovered) and the adduct (CF₃)₂CF·CHF·CHF₂ (94%).

EXPERIMENTAL

The techniques and instrumental methods were as described in earlier papers in this series. G.l.c. columns containing Silicone SE 30 oil, Kel-F 10 oil, trixylyl phosphate (TXP), or dinonyl phthalate (DNP) (20%) on Celite were used.

Perfluoro-3-methylbut-1-ene was prepared by the freeradical addition of 2-iodoheptafluoropropane to trifluoroethylene and dehydroiodination of the resultant major l: ladduct, $(CF_3)_2 CF \cdot CHF \cdot CF_2 I.^6$

Reactions of Perfluoro-3-methylbut-1-ene.—(a) With bromine. A mixture of the olefin (2.32 g, 9.29 mmol) and bromine (0.65 g, 4.07 mmol), sealed in vacuo in a Pyrex ampoule (ca. 100 cm³) and exposed to sunlight until the colour of the bromine had disappeared (6 h), gave unchanged olefin (1.32 g, 5.28 mmol, 57% recovered) and 1,2-dibromo-1,1,2,3,4,4-heptafluoro-3-trifluoromethylbutane (2) (1.38 g, 3.37 mmol, 84%) (Found: C, 14.7; F, 46.1%; M^+ , 410. C₅F₁₀Br₂ requires C, 14.7; F, 46.4%; M, 410), b.p. (Siwoloboff) 124 °C; m/e 412, 410, and 408 (2%, M^+), 331 and 329 [54, $(M - Br)^+$], 243, 241, and 239 {54, $[M - (CF_3)_2 CF]^+$ }, 181 (74, C₄F₇⁺), 131 and 129 (90, CF₂Br⁺), 93 (47, C₃F₃⁺), and 69 (100, CF₃⁺); ¹⁹F n.m.r. δ -7.5 [6 F, dm, (CF₃)₂CF, $J_{CF_3,F}$ 12.6 Hz], -22.0 (2 F, AB m, CF₂Br, J_{AB} 174 Hz), 49.0 (1 F, m, CFBr), and 93.0 [1 F, m, (CF₃)₂CF].

(b) With hydrogen bromide. A mixture of the olefin (4.63 g, 18.5 mmol) and hydrogen bromide (4.37 g, 54.0 mmol), irradiated (63 h) and the resultant material shaken with mercury in vacuo to remove bromine, gave (i) hydrogen (0.039 g, 19.5 mmol, 40%; M, 2.0), (ii) unchanged hydrogen bromide (0.48 g, 5.92 mmol, 11%) which was shown (i.r.) to be contaminated with a small amount of silicon tetrafluoride, and (iii) a mixture (6.73 g, 18.35 mmol) of two components in the ratio 46:54, which were separated by g.l.c. (4 m SE30 at 80 °C) and identified as 1-bromo-1,1,2,3,-4,4,4-heptafluoro-3-trifluoromethylbutane (3) (2.62 g, 8.45 mmol, 46%) (Found: C, 18.2; H, 0.5%; M^+ , 331. C₅-HF10Br requires C, 18.1; H, 0.3% M, 331), b.p. (isoteniscope) 79.7 \pm 0.5 °C; m/e 332 and 330 (0.3%, M⁺), 251 $[89, (M - Br)^+]$, 131 and 129 (16, CF_2Br^+), 113 (16, $C_3HF_4^+$), and 69 (100, CF_3^+), ¹H n.m.r. τ 4.92 [dq, CHF, $J_{F,H}$ 42.0, $J_{F,H}$ (vic) 10.2; J_{H,F_2} 10.2 Hz], ¹⁹F n.m.r. δ -17.6 (2 F, m, CF₂Br), -4.0 and -0.6 [6 F, m, (CF₃)₂-CF], 109.3 [1 F, m, (CF₃)₂CF], and 120.0 (1 F, dm, CHF), and the dibromide (2) (4.06 g, 9.90 mmol, 53%).

(c) With N-bromobistrifluoromethylamine. A mixture of the olefin (2.74 g, 10.93 mmol) and the N-bromo-amine (2.02 g, 8.71 mmol), mixed in the vapour phase in a Pyrex bulb (ca. 5 dm³) and irradiated (70 h), gave (i) a mixture (0.24 g, 1.42 mmol) of perfluoro-2-azapropene (ca. 0.2 mmol, ca. 5%), NN-bistrifluoromethylamine (trace), unchanged N-bromo-amine (ca. 1.1 mmol, ca. 13% recovered), unchanged olefin (trace), and an unknown component (ca. 0.1 mmol) with an i.r. band at 4.40 μ m (C=N str.), (ii) a mixture (3.32 g, 12.75 mmol), which was shown by g.l.c. (4 m SE 30 at 50 °C) and i.r. and n.m.r. spectroscopy to consist of unchanged N-bromo-amine (0.74 g, 3.2 mmol, 37% recovered), unchanged olefin (1.75 g, 7.0 mmol, 64% recovered), tetrakistrifluoromethylhydrazine (4) (0.24 g, 0.80 mmol, 36%), and an unidentified component (0.59 g, 1.75 mmol) present in the ratio 25:55:6:14, (iii) a higher boiling fraction (0.77 g) which was separated by g.l.c. (4 m SE 30 at 125 °C) into its four components (ratio 14:40:37:8; a mixture (0.06 g, 0.24 mmol) of unchanged olefin (0.02 g, 0.07 mmol, 1% recovered) and an unidentified component (0.04 g, 0.17 mmol); 2-bromo-1,1,2,3,4,4,4heptafluoro-3-trifluoromethylbutyl-NN-bistrifluoromethyl-

amine (5) (0.36 g, 0.74 mmol, 20% based on olefin, 17% based on amine) (Found: N, 2.7; F, 62.8. $C_7F_{16}BrN$ requires N, 2.9; F, 63.0%), b.p. (Siwoloboff) 129 °C; m/e 383 $[1\%, (M - BrF)^+]$, 202 $[42, (CF_3)_2N \cdot CF_2^+]$, 181 (39, $C_4F_7^+$), 114 (38, $C_2F_4N^+$), and 69 (100, CF_3^+); ¹⁹F n.m.r. δ -24.6 [6 F, q, (CF_3)_2N, J_{CF_3,CF_2} 16.0, $J_{CF_3,F}$ 16.0 Hz], -7.1 [6 F, m, (CF₃)_2CF], 5.7 (2 F, AB m, CF_AF_B, J_{AB} 228 Hz), 55.7 (1 F, m, CFBr), and 94.7 [1 F, dm, (CF₃)_2CF, $J_{F,F}$ 38.0 Hz]; the dibromide (2) (0.28 g, 0.68 mmol, 18% on olefin, 15% on amine); and an unidentified compound (0.07 g, 0.12 mmol), ¹⁹F n.m.r. δ -20.4 [6 F, (CF₃)_2N], -4.8 (3 F, CF₃), -1.8 (3 F, CF₃), 33.9 (2 F, CF₂), 52.2 (1 F, CF), and 108 (1 F, CF), and (iv) a nonvolatile residue (*ca.* 0.4 g).

(d) With methanethiol. A mixture of the olefin (2.24 g, 8.90 mmol) and methanethiol (1.37 g, 28.6 mmol), irradiated

(18 h) with the tube shaken and the lower portion of the tube shielded from the u.v. radiation, gave (i) hydrogen (0.022 g, 11.0 mmol, 87%; M, 2.0), (ii) a mixture of unchanged olefin (1.55 g, 6.19 mmol, 69% recovered) and unchanged methanethiol (0.16 g, 3.31 mmol, 12% recovered)as shown by g.l.c. (4 m Kel-F 10 at 22 °C), and (iii) a mixture (1.39 g) which was separated by g.l.c. (SE 30 at 100 °C) into its two components (ratio 25:75) identified as methyl 1,1,2,3,4,4,4-heptafluoro-3-trifluoromethylbutyl sulphide (6) (0.80 g, 2.7 mmol, 96%) (Found: C, 24.4; H, 1.5%; M^+ , 298. C₆H₄F₁₀S requires, C, 24.2; H, 1.35%; M, 298), b.p. 117 °C; m/e 298 (28%, M^+), 181 (25, C₄F₇⁺), 110 (22, $C_3H_4F_2S^+$), 97 (87, $CF_2\cdot SMe^+$), 69 (100, CF_3^+), 59 (46, $C_2H_3S^+$), 47 (27, MeS⁺), and 32 (46, CHF⁺ and S⁺); ¹H n.m.r. τ 5.06 [1 H, ddt, CHF, $J_{\rm H,F}$ (gem) 42.0, $J_{\rm H,F}$ (vic) 12.0, $J_{\rm H.CF_2}$ 8.0 Hz] and 7.78 (3 H, s, SMe), ¹⁹F δ -4.4 (3 F, m, CF_3) , -0.74 (3 F, m, CF_3) , 10.1 (2 F, AB m, $\rm CF_AF_B,~J_{AB}~230~Hz),~109.0~[1~F,~m,~(\rm CF_3)_2\rm CF],$ and 125.3 (1 F, m, CHF); and dimethyl disulphide (0.59 g, 6.28 mmol, 50%).

(e) With trimethylsilane. A mixture of the olefin (2.10 g. 8.40 mmol) and trimethylsilane (1.80 g, 24.4 mmol), sealed in a silica ampoule (ca. 100 cm³), with the lower portion of the tube covered, and irradiated (135 h), gave (i) hydrogen (0.002 g, 1.14 mmol, 27%), (ii) unchanged trimethylsilane (1.18 g, 16.0 mmol, 57% recovered), and (iii) a mixture (2.38 g), which was separated by g.l.c. (4 m SE 30 at 95 °C)into its two components (ratio 2:98), identified as hexamethyldisilane (0.02 g, 0.13 mmol, 0.1%) and 1,1,2,3,4,4,4heptafluoro-3-trifluoromethylbutyltrimethylsilane (7) (2.36 g, 7.3 mmol, 87%) (Found: C, 30.0; H, 3.4; F, 58.1. C8-H₁₀F₁₀Si requires C, 29.7; H, 3.1; F, 58.6%), b.p. (Siwoloboff) 142 °C; m/e 231 [2%, $(M - \text{SiMe}_3 - \text{HF})^+$], 163 $(11, C_4HF_6^+), 81 (23, C_2F_3^+), 77 (88, Me_2SiF^+), 73 (100,$ Me_3Si^+), 69 (44, CF_3^+), and 45 (30, $C_2H_2F^+$ and $MeSiH_2^+$); ¹H n.m.r. τ 1.80 (1 H, dm, CHF, $J_{\rm H,F}$ 43.8 Hz) and 6.55 (9 H, s, Me₃Si) p.p.m. to high field of external benzene, ¹⁹F δ -4.4 (3 F, m, CF₃), -1.0 (3 F, m, CF₃), 49.6 (2 F, AB m, CF_AF_B , J_{AB} 369 Hz), 113.2 [1 F, m, $(CF_3)_2CF$], and 131.6 (1 F, m, CHF).

(f) With caesium fluoride in sulpholan. A mixture of the olefin (0.535 g, 2.14 mmol), caesium fluoride (0.20 g, 1.30 mmol), and dry sulpholan (3 cm³), sealed in a Pyrex ampoule (100 cm³) in vacuo and the ampoule shaken at 85 °C (23 h), gave a mixture of perfluoro-2-methylbut-2-ene (8) (0.38 g, 1.53 mmol, 72%) and 2H-2-trifluoromethylocta-fluorobutane (10) (0.09 g, 0.29 mmol, 14%), in the ratio 84 : 16 as shown by n.m.r. spectroscopy.

(g) With caesium fluoride in moist sulpholan. A mixture of the olefin (1.06 g, 4.24 mmol), caesium fluoride (1.2 g, 7.9 mmol), and moist sulpholan (3 cm³), treated as in the previous experiment, gave a mixture (0.90 g, 3.36 mmol) which was shown by g.l.c. (4 m Kel-F 10 at 22 °C) to be a mixture of three major components (ratio 4:7:84) and four minor components (5%) of fraction); the three major components were separated by g.l.c. (as above) and identified as (i) unchanged perfluoro-3-methylbut-1-ene (0.03 g, 0.13 mmol, 3% recovered); (ii) perfluoro-2-methylbut-2ene (8) (0.06 g, 0.24 mmol, 6%); and (iii) 2H-2-trifluoromethyloctafluorobutane (10) (0.78 g, 2.9 mmol, 73%) (Found: C, 22.3; H, 0.5. C_5HF_{11} requires C, 22.2, H, 0.4%), b.p. (isoteniscope) 35.7 ± 0.5 °C; m/e 251 [21%, $(M - F)^+$], 201 [22, $(M - CF_3)^+$], 163 (22, $C_4HF_6^+$), 119 (24, $C_2F_5^+$), 113 (31, $C_3HF_4^+$), and 69 (100, CF_3^+); ¹H n.m.r. τ 6.68 [tseptet, $(CF_3)_2CH$, J_{H,CF_2} 12.7, $J_{H,(CF_3)_2C}$ 6.9 Hz],

¹⁹F δ – 14.6 [6 F, m, (CF₃)₂C], 8.5 [3 F, septet, $\int_{CF_3,(CF_3)_2C}$ 5.7 Hz], and 38.0 [2 F, octet, CF₂, $\int_{CF_3,(CF_3)_3C}$ 12.7 Hz].

(h) With sodium methoxide in sulpholan. A mixture of the olefin (2.31 g, 9.23 mmol), sodium methoxide (0.90 g, 16.0 mmol), and dry sulpholan (5 cm³), sealed in a Pyrex ampoule (ca. 40 cm^3) and the ampoule shaken and heated at 100 °C (85 h), gave (i) a mixture (1.41 g, 5.45 mmol) which was separated by g.l.c. (8 m T.X.P. at 22 °C) into its four components (ratio 39:6:2:53) identified as a mixture of unchanged perfluoro-3-methylbut-1-ene (0.25 g, 1.02 mmol, 11% recovered) and perfluoro-2-methylbut-2-ene (8) (0.27 g, 1.10 mmol, 14%) in the ratio 48:52 (n.m.r.); 3H-2trifluoromethyloctafluorobutane (11) (0.08 g, 0.33 mmol, 4%), m/e 251 [3%, $(M - F)^+$], 250 [8, $(M - HF)^+$], 181 $(46, C_4F_7^+)$, 131 (25, $C_3F_5^+$), 113 (13, $C_3HF_4^+$), and 69 (100, CF₃⁺), ¹H n.m.r. 7 5.29 [dquintet, CHF, J_{H.F} (gem) **43.5**, $J_{\rm H,F}$ (vic) 6.0, $J_{\rm H,CF_3}$ 6.0 Hz], ¹⁹F δ -3.6 [3 F, m, CF₃ in (CF₃)₂C], -1.4 [3 F, m, CF₃ in (CF₃)₂C], 0.5 (3 F, m, CF₃), 111.6 [1 F, m, (CF₃)₂CF], and 135.5 (1 F, dm, CHF); an unknown compound (0.03 g, 0.12 mmol); and 2H-2-trifluoromethyloctafluorobutane (10) (0.78 g, 2.88 mmol, 35%), and (ii) a higher boiling fraction (0.84 g, 3.30 mmol) which was shown by g.l.c. (4 m D.N.P. at 70 °C) to contain three major components (ratio 13:62:19) and four minor components of shorter g.l.c. retention times (5%)of fraction). The three major components were separated by g.l.c. (4 m D.N.P. at 70 °C) and identified as 2H-2trifluoromethyloctafluorobutane (10) (0.11 g, 0.42 mmol, 5%; 2-methoxy-3-trifluoromethylhexafluorobut-2-ene (13)(0.53 g, 2.02 mmol, 25%) (Found: C, 27.6; H, 1.3; F, 65.2%; M^+ , 262. $C_6H_3F_9O$ requires C, 27.5; H, 1.15; F, 65.3%; M, 262), b.p. (isoteniscope) 82.7 ± 0.5 °C, $\lambda_{\text{max.}}$ 6.03s, (C:C str.) μ m; m/e 262 (44%, M^+), 243 [46, $(\tilde{M} - F)^+$], 209 (40, C₅F₇O⁺), 193 (29, C₅H₃F₆O⁺), 184 $(38, C_6HF_5O^+), 178 (27, C_4F_6O^+), 159 (100, C_4F_5O^+), 131$ $(45, C_3H_3F_4O^+), 100 (29, C_2F_4^+), 93 (30, C_3F_3^+), 91 (23, C$ $C_3HF_2O^+$), 81 (25, $C_2F_3^+$), 78 (42, $C_2F_2O^+$), 69 (83, CF_3^+), 59 (28, C_2FO^+), and 31 (40, CF^+ and MeO^+); ¹H n.m.r. τ 6.45 (s, OMe), $^{19}{\rm F}$ δ -18.92 [3 F, qq, CF₃, $J_{\rm CF_3, CF_3}$ (cis) 14.4, J_{CF_3, CF_3} (gem) 10.0 Hz], -16.60 [3 F, q, CF₃, J_{CF_3, CF_3} (gem)], and -11.80 [3 F, q, =C(CF₃)·OMe]; and 2-methoxy-1,1,1,2,4,4,4-heptafluoro-3-trifluoromethylbutane (14) (0.17 g, 0.60 mmol, 7%) (Found: C, 25.4; H, 1.6. Calc. for $C_6H_4F_{10}O$: C, 25.5; H, 1.4%), which was identified by a comparison of its n.m.r. spectra with those reported.⁵

(j) With sodium methoxide in methanol. A mixture of the olefin (2.27 g, 9.10 mmol), sodium methoxide (0.90 g, 16.0 mmol), and methanol (5 cm³), sealed in a Pyrex ampoule (ca. 40 cm³) and the ampoule shaken and heated at 100 $^{\circ}$ C (70 h), gave a mixture (1.40 g, 6.75 mmol), which was shown by g.l.c. (8 m T.X.P. at 22 °C) to contain five components (A-E) in the ratio 52:12:20:9:7, and a higher boiling mixture, which was treated with phosphorus pentaoxide at room temperature (1 h) to remove methanol, and the resultant material (0.79 g, 2.10 mmol) was shown by g.l.c. (4 m D.N.P. at 62 °C) to contain seven components (A, B, D—H) in the ratio 27: 12: 2: 6: 24: 19: 10. Components A-E were separated from the first fraction by g.l.c. (8 m T.X.P. at 22 °C) and components E-H were separated from the higher boiling fraction by g.l.c. (4 m D.N.P. at 62 °C) and were identified as: (i) unchanged perfluoro-3-methylbut-1-ene (1.07 g, 4.29 mmol, 47% recovered); (ii) 3H-2trifluoromethyloctafluorobutane (11) (0.31 g, 1.15 mmol, 24%); (iii) a compound tentatively identified as 2-methoxy-1,1,1,3,4,4,4-heptafluoro-3-trifluoromethylbutane (15) (0.38

g, 1.35 mmol, 28%), m/e 281 [10%, $(M - H)^+$], 251 [3, $(M - OMe)^+$], 181 (21, C₄F₇⁺), 113 (14, CF₃·CH·OMe⁺), 69 (100, CF_3^+), and 31 (18, MeO⁺); ¹H n.m.r. τ 6.84 (m, \rightarrow CH and OMe), ¹⁹F δ -2.9 (3 F, m, CF₃), -2.0 (3 F, m, (CF_3) , -0.5 (3 F, m, CF_3), and 112.0 [1 F, m, $(CF_3)_2 CF$]; (iv) an unidentified methyl ester (0.6 mmol, ca. 12%), m/e 159 $(5\%, C_2F_4 \cdot CO_2Me^+)$, 131 (7, $C_3F_5^+$), 81 (10, $C_2F_3^+$), 69 (99, (CF_3^+) , 59 (100, CO_2Me^+), 50 (11, CF_2^+), and 31 (31, MeO^+); ¹H n.m.r. τ 4.35 (1 H, m), 6.53 (3 H, m, OMe), and 7.08 $(2 \text{ H}, \text{m}), {}^{19}\text{F} \delta - 0.4 (6 \text{ F}, 2\text{CF}_3) \text{ and } 0.5 (1 \text{ F}); (v) \text{ methyl}$ formate (0.03 g, 0.47 mmol, 10%), which was identified by a comparison of its i.r. spectrum with that of a known pure sample; (vi) 2-methoxy-1,1,1,2,4,4,4-heptafluoro-3-trifluoromethylbutane (14) (0.19 g, 0.70 mmol, 14%); (vii) a mixture (0.16 g, 0.57 mmol, 11%) containing 1-methoxy-1,1,2,3,4,4,4-heptafluoro-3-trifluoromethylbutane (16) (5%) as shown by n.m.r. spectroscopy, $\lambda_{max.}$ 5.60 and 5.68w (C:C or C:O str.) µm, ¹H n.m.r. τ 6.60 (11 H) and 5.30 [1 H, dtd, CHF, $J_{\rm H,F}$ (gem) 42.6, $J_{\rm H,CF_2}$ 8.0, $J_{\rm H,F}$ 4.0 Hz], ¹⁹F $\delta = 14.7$ (ca. 3 F), -3.5 (3 F), -0.9 (3F), 7.3 (2F), 9.3 (ca. 1F), 37.9 and 38.9 (ca. 4F), 109 (1F, CF), and 132.9 (1F, dm, CHF), m/e 263 (12%, C₅HF₉OMe⁺), 229 (7, C₆HF₈O⁺), 213 (6, $C_4HF_7OMe^+$), 131 (8, $C_3F_5^+$), 113 (19, $C_2HF_3\cdot OMe^+$), 81 (100, CF_2 ·OMe⁺), 69 (63, CF_3^+), and 31 (10, OMe⁺); and 1-methoxy-1,1,2,2,4,4,4-heptafluoro-3-trifluoromethyl-(viii) butane (17) (0.08 g, 0.29 mmol, 6%) (Found: C, 26.0; H, 1.4. C₆H₄F₁₀O requires C, 25.6; H, 1.5%), m/e 263 [30%, $(M - F)^+$], 201 (33, C₄HF₈⁺), 181 (17, C₄F₇⁺), 131 (27, $C_2F_4OMe^+$), 113 (48, $C_3HF_4^+$), 81 (100, $CF_2 \cdot OMe^+$), 69 (65, (CF_3^+) , 47 (19, CFO⁺), and 31 (13, MeO⁺); ¹H n.m.r. τ 6.48 (1 H, m, \rightarrow CH) and 6.62 (3 H, s, OMe), ¹⁹F δ -13.15 [6 F, tdt, $(CF_3)_2C$, J_{CF_3, CF_4} 11.8, $J_{CF_3, H}$ 7.5, J_{CF_3, CF_2} 5.5 Hz], 16.9 (2 F, m, CF₂ OMe), and 38.5 (2 F, m, CF₂).

(k) With dimethylamine. A mixture of the olefin (1.31 g, 5.24 mmol) and dimethylamine (0.31 g, 6.9 mmol), sealed in vacuo in a Pyrex ampoule and shaken at room temperature (10 m) gave (i) unchanged olefin (0.59 g, 2.34 mmol, 45% recovered), (ii) unchanged dimethylamine (ca. 0.04 g, ca. 0.9 mmol, 13% recovered), (iii) a higher boiling fraction (0.56 g), $\lambda_{max.}$ 5.62m (C=O str.) and 5.94m (C:C str.) $\mu m,$ which was shown by n.m.r. spectroscopy to be a mixture of NN-dimethyl-3-trifluoromethyl-1,1,2,2,4,4,4-heptafluorobutylamine (19) (0.46 g, 1.57 mmol, 55%), ¹H n.m.r. -2.73 (1 H, tseptet, CH, $J_{\rm H, CF_2}$ 11.7, $J_{\rm H, CF_3}$ 8.2 Hz) and 4.22 (6 H, m, Me₂N) p.p.m. to high field of external benzene, ¹⁹F δ –15.6 [6 F, tdt, (CF₃)₂C, J_{CF_3,CF_3} (vic) 11.7, J_{CF_3,CF_4} 6.8 Hz], 24.6 (2 F, m, CF₂N), and 33.2 (2 F, octet, C⁻CF₂⁻ 2,2,4,4,4-pentafluoro-NN-dimethyl-3-trifluoromethyl-C). butyramide (20) (0.08 g, 0.29 mmol, 10%), ¹H n.m.r. 1.80 (1 H, tseptet, CH, $J_{\text{H.CF}_2}$ 11.0, $J_{\text{H.CF}_3}$ 8.2 Hz] and 3.60 (6 H, s, Me₂N) p.p.m. to high field of external benzene, ¹⁹F δ -14.6 [6 F, td, (CF₃)₂C, $J_{\text{CF}_3,\text{CF}_2}$ 11.0 Hz] and 29.6 (2 F, octet, CF_2), and an unidentified olefin (ca. 0.02 g) present in the ratio 80:15:5, and (iv) an involatile residue (ca. 0.4 g) which was soluble in water and gave a positive test for fluoride ion.

(1) With sodium methanethiolate. A mixture of the olefin (2.30 g, 9.20 mmol), sodium methanethiolate (1.06 g, 15.2 mmol), and sulpholan (10 cm³), sealed *in vacuo* in a Pyrex ampoule (ca. 40 cm³) and the ampoule shaken and heated at 90 °C (68 h), gave (i) a mixture (2.09 g, 8.04 mmol) which was separated by g.l.c. (8 m T.X.P. at 22 °C) into its four components (ratio 76:1:18:5); unchanged olefin (1.53 g, 6.11 mmol, 66% recovered), 3H-2-trifluoromethyloctafluorobutane (11) (0.02 g, 0.08 mmol, 3%),

2H-2-trifluoromethyloctafluorobutane (10) (0.39 g, 1.44 mmol, 47%), and an unidentified saturated compound (0.15 g, 0.41 mmol, 13%), (ii) a higher boiling olefinic fraction (0.07 g), λ_{max} 5.86m and 6.03w (C:C str.) μm , (iii) dimethyl disulphide (0.06 g, 0.6 mmol), and (iv) a nonvolatile residue.

(m) Hydrogenation. The olefin (2.26 g, 9.05 mmol), slowly passed admixed with an excess of hydrogen through a Pyrex tube (50 m, 1.5 cm i.d.) containing a catalyst of palladium on alumina at room temperature (30 m), gave unchanged olefin (2.19 g, 8.74 mmol, 97% recovered) and 1H,2H-heptafluoro-3-trifluoromethylbutane (0.07 g, 0.29 mmol, 94%) (Found: C, 24.0; H, 1.1. C₅H₂F₁₀ requires C, 23.8; H, 0.8%), m/e 233 [1%, $(M - F)^+$], 182 [14, $(M - CHF_3)^+$], 113 (38, $C_3HF_4^+$), 95 (19, $C_3H_2F_3^+$), 83 (81, $CHF\cdot CHF_2^+$), 69 (91, CF₃⁺), 51 (100, CHF₂), and 32 (40, CHF⁺), ¹H n.m.r. τ 4.40 [1 H, tt, CHF₂, $J_{\rm H,F_{4}}$ (gem) 54.0, $J_{\rm H,F}$ (vic) 5.0, $J_{\rm H,H}$ (vic) 5.0 Hz] and 5.52 [1 H, dm, CHF, $J_{\rm H,F}$ (gem) 44.0 Hz], ¹⁹F δ -2.5 (3 F, m, CF₃), 0.1 (3F, m, CF₃), 51.8 (2 F, dm, CHF₂), 111.5 (1 F, dm, CHF), and 112.5 (1 F, m, CF).

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